



# **Technical Report on the Development of a Geochemical Atlas of Cyprus**

## **Volume 1 – Text**

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## EXECUTIVE SUMMARY

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Large-scale geochemical mapping programs have been implemented in many parts of the world. Regional geochemical mapping and resulting geochemical atlases were originally intended for mineral exploration but have subsequently been applied to environmental monitoring and other resource management objectives.

The Geochemical Atlas of Cyprus has been designed on the basis of the principles and protocols established under IGCP Projects 259/360 and the FOREGS Geochemical Atlas of Europe. Compared with previous national soil geochemical atlases, the mapping of Cyprus has been conducted at the high sampling density of one site per  $\sim 1 \text{ km}^2$ .

Based on a grid-cell sampling model, project teams collected the  $< 2 \text{ mm}$  fraction of top soil (0–25 cm) and sub soil (50–75 cm) from 5,516 sites, along with detailed field data and photographic records. This work was completed in 280 crew-days over the period May 2006 to December 2009. Sample archives have been established in Cyprus and at UNSW. Samples were analysed for over 60 elements by aqua regia ICP-MS and INAA at Actlabs, Australia and Canada. Major elements were analysed by XRF and CS-analyser, and soluble ions by ion chromatography at the GSD laboratories, Lefkosia. A detailed program of sample processing and analytical quality control was implemented. Detailed physical, mineralogical and geochemical analyses were conducted on selected samples representing two orientation lines that cross the island, a series of vertical profiles through regolith in various locations and a suite of samples from six mine areas. The geochemical data have been integrated with other spatial data provided by the GSD in ArcGIS. Field and other training was provided to GSD staff in Cyprus and Australia.

In addition to this report, the results have been presented in the associated Geochemical Atlas of Cyprus.

The key results of the project are:

- Major, minor and trace element geochemistry patterns in soils across Cyprus are overwhelmingly dominated by the parent lithology from which the soils are derived. Various combinations of elements permit mapping of even subtle differences between rock types and regolith-landform variations at the kilometre scale.
- In urban and industrial areas there are elevated levels for some metals, including Pb, Sn and Cu, at a number of sites. Mining activities have also contributed to increased element concentrations in soil related to the mineral deposits themselves and associated mining and mineral processing operations. In agricultural areas there are indications of increased soil concentrations of elements that may be linked to fertiliser use or groundwater irrigation.
- Along the coast, there is physical reworking and concentration of heavy minerals shedding from Troodos and possibly the Keryneia Terrane, along with component elements such as Cr and Ni. Higher contents of mobile elements, such as Na, Br and B, reflect either seawater influences or hydromorphic dispersion of elements from the mountains.
- Linear geochemical anomalies defined by various rare elements such as Hg and Re appear to reflect deep geological structures that transect the island.
- A combination of elements – Ag, As, Cu, Zn and In – offers stronger soil geochemical indications of significant sulfide mineralisation than the commodity elements alone (e.g. Cu).
- The soil geochemistry indicates four main environmental concerns: (i) metals contamination in the vicinity of the (mostly-abandoned) sulfide mines, (ii) elevated Pb and other heavy metals in the top soil of urban areas (iii) slightly elevated Na, Cd and other elements in the main agricultural areas and (iv) a large area with anomalous Hg values in the sub soil of the northern Polis Valley. Soil contamination for the mines does not extend far beyond the mine leases, but is more extensive in the stream sediments draining the mine sites.

- The sheeted dykes on the western side of Troodos should be considered for more detailed follow-up sulfide mineral exploration based on the soil geochemical patterns, as well as areas with thin carbonate rock cover displaying elevations in a number of the transition elements in the soil.
- It is clear from the data that, for most elements, there is no single set of “background” levels that can be set to differentiate natural element concentrations from potential contamination. The atlas data can, however, guide the setting of lithology-specific and terrane-specific indicatory levels for natural element abundances against which the results of any subsequent detailed geochemical surveys or environmental studies can be compared.
- Significant loss of detail in the geochemical patterns would have occurred if the sampling density had been reduced below 25% of the original density.
- Biogeochemistry has provided distinct indications of mineralisation (and contamination) based on elements such as Re.

A number of follow-up studies and extensions to the current Atlas project are recommended.

## Report Structure

Volume 1 (this volume):	Text and references.
Volume 2:	General figures and tables.
Volume 3:	Atlas maps and some processed data maps.
Volume 4:	Appendix figures relating to the analytical quality control.



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## Acronyms and abbreviations

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<i>ar-</i>	Aqua regia acid extraction
CEC	Cation exchange capacity
CS	Carbon-sulfur analyser
CTSS	Circum-Troodos Sedimentary Sequence
DL	Detection limit
DQO	Data quality objective
EC	Electrical conductivity
FAO	UN Food and Agricultural Organisation
Fmn	Formation (geological)
FOREGS	Forum of European Geological Surveys (now EuroGeoSurveys)
Gp	Group (geological)
GPS	Global positioning system
GRM	Geological reference material
GSD	Geological Survey Department of Cyprus, Ministry of Agriculture
HFSE	High field strength elements
ICP-MS	Inductively-coupled plasma – mass spectrometry
ICP-OES	Inductively-coupled plasma – optical emission spectrometry
INAA	Instrumental neutron activation analysis
LOI	Loss-on-ignition
Ma	Mega annum (million of years)
MOA	Cyprus Ministry of Agriculture
MOR	Mid-ocean ridge
NASGLP	North American Soil Geochemical Landscape Project
QAQC	Quality assurance – quality control
REE	Rare earth element(s) (H- heavy, L- light)
RSD	Relative standard déviation
SOC	Soil organic carbon
TOC	Troodos Ophiolite Complex
<i>tot-</i>	Total analysis
<i>tot-C</i>	Total carbon
<i>tot-S</i>	Total sulfur
UTM	Universal Transverse Mercator (projection)
WGS84	World grid system, 1984 datum
XRD	X-ray diffractometry
XRF	X-ray fluorescent spectrometry

## The Periodic Table of elements

<i>Symbol</i>	<i>Element</i>	<i>Atomic number</i>	<i>Atomic mass (g)</i>	<i>Typical oxidation state(s)</i>	<i>Average crustal abundance (mg/kg)</i>
Ac	Actinium	89	227.0	+3	Trace
Ag	Silver	47	107.9	+1	0.08
Al	Aluminum	13	26.7	+3	82,000
Ar	Argon	18	40.0	0	3.5
As	Arsenic	33	74.9	±3 +5	2
At	Astatine	85	210.0	+1	Not determined
Au	Gold	79	197.0	+3 +1	0.003
B	Boron	5	10.8	+3	10
Ba	Barium	56	137.3	+2	425
Be	Beryllium	4	9.0	+2	3
Bi	Bismuth	83	209.0	+3 +5	0.01
Br	Bromine	35	79.9	±1 +5	2.5
C	Carbon	6	12.0	±4	200
Ca	Calcium	20	40.1	+2	41,500
Cd	Cadmium	48	112.4	+2	0.2
Ce	Cerium	58	140.1	+3 +4	67
Cl	Chlorine	17	35.5	-1	145
Co	Cobalt	27	58.9	+2 +3	25
Cr	Chromium	24	52.0	+3 +2 +6	100
Cs	Caesium	55	132.9	+1	3
Cu	Copper	29	63.6	+2 +1	60
Dy	Dysprosium	66	162.5	+3	5
Er	Erbium	68	167.3	+3	4
Eu	Europium	63	152.0	+3 +2	2
F	Fluorine	9	19.0	-1	585
Fe	Iron	26	55.9	+3 +2	56,300
Fr	Francium	87	223.0	+1	Not determined
Ga	Gallium	31	69.7	+3	20
Gd	Gadolinium	64	157.3	+3	6
Ge	Germanium	32	72.6	+4 +2	2
H	Hydrogen	1	1.0	±1	1,400
He	Helium	2	4.0	0	0.01
Hf	Hafnium	72	178.5	+4	3
Hg	Mercury	80	200.6	+2 +1	0.09
Ho	Holmium	67	164.9	+3	1.5
I	Iodine	53	126.9	-1 +5 +7	0.5
In	Indium	49	114.8	+3	0.3
Ir	Iridium	77	192.2	+4 +3 +6	0.001
K	Potassium	19	39.1	+1	21,000
Kr	Krypton	36	83.8	0	0.000 1
La	Lanthanum	57	138.9	+3	40
Li	Lithium	3	6.9	+1	20
Lu	Lutetium	71	175.0	+3	01
Mg	Magnesium	12	24.3	+2	23,300

Mn	Manganese	25	54.9	+2 +3 +4 +6 +7	950
Mo	Molybdenum	42	95.9	+6 +3 +5	1.5
N	Nitrogen	7	14.0	-3	19
Na	Sodium	11	23.0	+1	23,600
Nb	Niobium	41	92.9	+5 +3	20
Nd	Neodymium	60	144.2	+3	42
Ne	Neon	10	20.2	0	0.005
Ni	Nickel	28	58.7	+2 +3	84
O	Oxygen	8	16.0	-2	460,000
Os	Osmium	76	190.2	+4 +6 +8	0.001 5
P	Phosphorus	15	31.0	-3	1,000
Pa	Protactinium	91	231.0	+5 +4	0.000 002
Pb	Lead	82	207.2	+2 +4	0.15
Pd	Palladium	46	106.4	+2 +4	0.02
Pm	Promethium	61	145.0	+3	Unstable
Po	Polonium	84	209.0	+4 +2	Trace
Pr	Praseodymium	59	140.9	+3 +4	9
Pt	Platinum	78	195.1	+4 +2	0.005
Ra	Radium	88	226.0	+2	0.000 001
Rb	Rubidium	37	85.5	+1	90
Re	Rhenium	75	186.2	+7 +4 +6	0.000 7
Rh	Rhodium	45	102.9	+3 +4 +6	0.001
Rn	Radon	86	222.0	0	Trace
Ru	Ruthenium	44	101.1	+4 +3 +6 +8	0.001
S	Sulfur	16	32.1	-2	350
Sb	Antimony	51	121.8	+3 +5	0.2
Sc	Scandium	21	45.0	+3	22
Se	Selenium	34	79.0	+4 -2 +6	0.05
Si	Silicon	14	28.1	±4	280,000
Sm	Samarium	62	150.4	+3 +2	7
Sn	Tin	50	118.7	+4 +2	2.5
Sr	Strontium	38	87.6	+2	370
Ta	Tantalum	73	180.9	+5	2
Tb	Terbium	65	158.9	+3 +4	1
Tc	Technetium	43	98.0	+7 +4 +6	Unstable
Te	Tellurium	52	127.6	+4 +6 -2	0.001
Th	Thorium	90	232.0	+4	10
Ti	Titanium	22	47.9	+4 +3 +2	5,600
Tl	Thallium	81	204.4	+1 +3	0.9
Tm	Thulium	69	168.9	+3 +2	0.5
U	Uranium	92	238.0	+6 +3 +4 +5	2.5
V	Vanadium	23	50.9	+5 +2 +3 +4	120
W	Tungsten	74	183.8	+6 +4	1.3
Xe	Xenon	54	131.3	0	0.000 03
Y	Yttrium	39	88.9	+3	33
Yb	Ytterbium	70	173.0	+3 +2	3
Zn	Zinc	30	65.4	+2	70
Zr	Zirconium	40	91.2	+4	165



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# 1 INTRODUCTION

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## 1.1 REGIONAL GEOCHEMICAL SURVEYS AND ATLASES

### 1.1.1 Historical background

A major application of applied geochemistry in recent years has been the implementation of large-scale geochemical mapping programs and the generation of geochemical atlases for a variety of purposes. Geochemical atlases represent “snap shots” of the distribution and abundance of specific chemical components in the environment at the time of sampling. Atlas coverage ranges from regional to continental scales and mapping has been conducted at sampling densities as low as one site per 5,000 km<sup>2</sup>. Providing sampling, analytical and other factors are internally consistent over the survey area, a geochemical atlas can be used as a reference against which spatial and temporal changes in the geochemistry of the natural environment can be measured.

Geochemical mapping originated in the Soviet Union in the 1930s as a tool in mineral exploration (Garrett *et al.* 2008). By the 1960s geochemical mapping had been conducted at prospect to regional scales in parts of Europe, North America and Africa, incorporating a range of sampling media. An early example involved exploration for Cu in Zambia (Armour-Brown and Nichol 1970). The development of large scale, systematic, regional reconnaissance and baseline geochemical surveys commenced with projects such as that led by Shacklette *et al.* (1971) which examined the relationship between soil and plant chemistry across much of the USA, as well as the subsequent National Uranium Resource Evaluation / Reconnaissance Program in North America (Garrett *et al.* 1980; Shacklette and Boergen 1984; Gustavsson *et al.* 2001). Another early atlas was the Wolfson Geochemical Atlas of the England and Wales (Nichol *et al.* 1966; McGrath and Loveland 1992). Regional scale, multielement, geochemical surveys atlases were subsequently implemented in many parts of North America, Russia, China, southern Africa and Australia to locate mineral resources. Regional geochemical mapping and follow-up studies have been credited with the discovery of a large number of major deposits, spanning nearly every mineral commodity.

In post-mining and industrialised areas, regional geochemical mapping is now targeted at environmental purposes, including the differentiation of natural and anthropogenic sources of metals and organics to assist in contaminant detection, environmental management and regulation (Plant *et al.* 2003; Plant *et al.* 2000; Albanese *et al.* 2007). Geochemical atlases of various types can also be used in assessing of the suitability of soils for growing crops or stock grazing and highlight excess or deficiencies in crop fertilizers and trace elements, determining ground water quality for urban or industrial use or irrigation, identifying areas potentially harmful to public health (deficiencies or excesses of trace metals, radiogenic elements or harmful organic components) and providing indicative geochemical base levels to which areas that are contaminated might be expected to be returned after remediation.

The 1986 Chernobyl nuclear disaster provided further momentum to regional geochemical mapping in Europe. The need to determine the extent and impact of the radioactive cloud from this event provided momentum for governments to support widely-spaced environmental sampling and mapping programs across Scandinavia, Finland and north western Russia (e.g. the Barents Project). Many atlases have focussed on soil geochemistry, including the new EuroGeoSurveys GEMAS project, due to the vital role of soil in food supply and water quality and its potential as a vector for transfer of contaminants from the environment to humans (Plumlee and Zieger 2003; Plumlee *et al.* 2006; NGU 2008; Smith 2009). Agricultural applications commonly relate to the distribution of nutrients.

In many respects, environmental geochemical atlases perform the same essential functions as mineral exploration geochemical atlases. The approach to design and data interpretation of environmental geochemical atlases has been largely derived from mineral exploration methods. Mineral exploration surveys, however, typically optimize or bias the sampling and analytical strategies to detect and enhance geochemical dispersion patterns for key elements related to base or precious metal mineral deposits. Where soil or sediment profiles are undisturbed, core samples may be added to generate a 3D

or 4D geochemical model, allowing the effects of environmental change and anthropogenic inputs over time to be estimated (Gasparon *et al.* 2007).

In terms of environmental applications, properly designed geochemical atlases can quantify the expected range of elements and some controlling factors encouraging change from “absolute” regulations to one of more complex evidence-based risk analysis. In essence this is a move away from single geochemical values representing the upper limit to background to variable limits. Some regulatory authorities, however, demonstrate a lack of awareness of the significant natural geochemical variation and its causes, which must be taken into account when implementing policies. There are examples of regulatory action limits for soil metal contents in industrial sites that are lower than typical natural concentrations (Tarvainen 1996; Plant *et al.* 1997). Naturally high trace element values may still constitute a health risk to humans; hence there may be a valid basis for regulatory limits being lower than some local natural background ranges.

Prior to the 1990s, most existing geochemical data were not commonly in a form readily applicable to baseline determinations (Plant *et al.* 1997). Various governments therefore sponsored generation of new geochemical atlases with a particular focus on defining regulatory limits for contaminants in soils and other media. It is now a requirement that European Union members develop a national geochemical database to assist in assessment of the state of the environment.

Regional geochemical mapping for environmental purposes has culminated in the global geochemical atlas under development by the IUGS, through projects IGCP 259 and 360 (Darnley *et al.* 1995; Darnley 1997; IUGS 2004) and associated national and international projects. The overall objective of IGCP 360 is to generate a digital and visual database that will:

*“document the concentration and distribution of chemical elements and species in the Earth’s near surface environment” and “create a geochemical baseline against which future human-induced or natural changes to the chemistry of the land surface may be recognised and measured.”*

The Geochemical Atlas of Cyprus has been developed within this broad initiative.

### 1.1.2 Atlas design

In the natural environment, similar geological substrates generally give rise to similar major and trace element concentration ranges, provided there is no overprint from local anthropogenic contamination or atypical geological features such as mineralisation. This produces the coherent patterns of distribution of geochemical components in the natural environment typically observed in regional geochemical surveys.

Unlike some geophysical characteristics of rocks and soils geochemical samples are intrinsically “point values”. A sample collected at an individual site and the sub-sample ultimately analysed may not necessarily represent the typical or expected geochemistry of the wider environment around the site. Irrespective of attempts to obtain representative analytical sub-samples of a given location/site/sample, and the most stringent quality control protocols, the geochemical results from the few grams of sub-sample analysed in the laboratory are unique to that sub-sample. Geochemical variability at all sampling scales reflects the fundamental character of the natural environment – in itself a chaotic system that affects sampling strategies (Neuerberg 1985).

The natural concentration of elements in soils varies by orders of magnitude depending on the parent material and the subsequent processes that have led to the formation and characteristics of the soil (Tarvainen and Kallio 2002). For example, in the detailed stream sediment geochemical survey of the Campania region of Italy, the relative standard deviation was in the order of 100% for most elements (de Vivo *et al.* 2003). Factors other than sample preparation and analytical methodology also influence analytical outcomes. These largely reflect inherent sample inhomogeneity and include:

- the scale or sample spacing,
- the sample media,
- the uniformity of sample media across a survey area,

- the basis on which the sample sites are selected (the bias toward a selected sample type or setting) and position of a sample in the landscape,
- the materials actually collected in the field; whether fresh or weathered, *in situ* or transported, and
- the time period over which the sample collection was undertaken (e.g. seasonal variations or effects of moisture).

Changes in these factors over a survey region may cause analytical differences between otherwise visually similar field sites or actual samples, creating an inference of analytical error. In terrains with highly variable substrates, particularly at the scale of sampling, even adjacent samples are likely to show dissimilar geochemical values for a number of elements.

For soil sampling, the key attributes that require definition in the design of a survey are the primary geology and its local variability and the character of the regolith-landform. These factors determine the characteristics of a given “*geochemical landscape*” (Fersman 1934; Perel'man 1955; Fortescue 1992). In turn, the geochemical landscape will dictate the sampling parameters required to generate sampling of a consistent and uniform media. Adjustment to sampling parameters, such as site spacing and location or sample depth, will be required across a region to accommodate changes in landscape elevation, geology, erosion and deposition and other parameters such as media availability.

To provide internal consistency, the basic prerequisites for regional or global geochemical databases of permanent value are:

- a commonly available representative sample media, collected in a standardised manner,
- continuity of data across different types of landscape,
- adequate quantities of the designed sample media for future reference and research requirements,
- analytical data for all elements of environmental or economic significance and parameters which exert major influence on sample geochemistry,
- the lowest possible detection limits for all elements; and
- adequate quality control at every stage of the process.

### 1.1.3 Scale

The sampling scale, both areal coverage and density of samples, and sampling media has a major influence on the scale of geochemical patterns that can be measured. Geochemical data display fractal properties at scales from regional maps down to mineral grains (Bølviken *et al.* 1992; Xie and Yin 1993; Shen and Cohen 2005).

Low density regional soil sampling, in the order of one sample per 100 km<sup>2</sup>, has traditionally been viewed as offering a low probability of detecting small zones of mineralisation or contamination as the “influence” of a given point may only extend a few hundred metres (Smith and Reimann 2008). Yet, some studies have shown that even lower density sampling can deliver a high rate of detection of known mineralisation (Reimann *et al.* 2007), especially stream sediments which theoretically represent an integration of regolith<sup>1</sup> within the local catchment.

Changes to sampling scale are common in mineral exploration. Most regional programs commence with low density stream sediment surveys and progressing to high density stream sediments or soil surveys in areas identified as potentially mineralised.

Densities used for geochemical surveys have ranged from high (~1 stream sediment sample per 1 km<sup>2</sup>) in Austria (Thalman *et al.* 1989) to ‘ultra low’ (~one site per 1,000 to 5,000 km<sup>2</sup>) adopted in most of the surveys in Europe (Plant *et al.* 2003; Reimann *et al.* 2003), the USA (Gustavsson *et al.* 2001) and China (Li and Wu 1999). The NRAC stream sediment survey was linked to the maximum size of catchments containing near-uniform lithology, yielding one site per 15 to 50 km<sup>2</sup> over a 35,000 km<sup>2</sup> area (Cohen *et al.* 1995, 1998) as was the Greenland survey at one per 25 km<sup>2</sup> over ~150,000 km<sup>2</sup>

<sup>1</sup> *Regolith* is the general term applied to the mantle of weathered or partially weathered material at the Earth’s surface and includes material that is defined as “soil”.

(Steenfeld 2001). The Barents Survey was undertaken using humus and soils at one site per 100 km<sup>2</sup> to 300 km<sup>2</sup> over an 188,000 km<sup>2</sup> area, whereas the till geochemical survey of Finland involved ~82,000 samples at one site per 4 km<sup>2</sup> (Salminen *et al.* 1995, 2004; Salminen and Tarvainen 1995). The Geological Survey of Ireland's regional soil geochemical mapping was conducted at a density of one site per 50 km<sup>2</sup> (McGrath and McCormack 1998). The western Yilgarn regolith geochemical survey covered 400,000 km<sup>2</sup> at one site per 60–100 km<sup>2</sup> (Cornelius *et al.* 2007, 2008).

To ensure spatial continuity of an atlas and to measure geochemical gradients, a degree of spatial correlation between samples is desirable (as may be determined using variography). Very high spatial correlations between geochemical values in non-neighbouring sample pairs indicates some degree of data redundancy and an excessively high sampling density in relation to the homogeneity of the substrate.

Further to the question of sample density is the one of sample geometry, for which there are various options:

- regular grid arrays (rectilinear, radial, polygonal or similar),
- grid-cell arrays, where individual samples are collected at a variable spacing but from within defined cells,
- random walks or irregular traverses (roads, tracks, trails, ridge and spurs), or
- site locations controlled by features of the environment such as geology, land use, soil type, water catchment, geomorphological features, property or political boundaries, depending upon survey objective.

#### 1.1.4 Sampling media

Studies on regolith evolution and regolith-landform relationships, and the implication for the identification and selection of sampling media, have been conducted in environments ranging from those displaying modern or relict deep weathering and duricrust formation (Butt and Zeegers 1992) to glaciated terrains (Kauranne *et al.* 1992; McClenaghan *et al.* 2001). Regional geochemical surveys have used a wide variety of sampling media, from the more conventional rocks, soils, glacial materials, stream sediments, floodplain sediments and waters, to the less conventional plants (Dunn 2007; Cohen *et al.* 1999) and soil gas (Klusman 1993, 2009). The selection of media should reflect the nature of the “target”, which could range from point sources of contamination or mineralisation to regional ambient concentrations and distributions of elements and chemical species. Further discussion of media selection is provided in Section 2.

Recognising that different sampling media will have widely different mineralogical composition, element forms and pathways to element accumulation, there are inherent problems in generating a set of samples whose geochemistry can be directly compared. It is strongly emphasised that minor variations in the composition and origin of sampling media collected may have very significant effects on trace element geochemistry at all scales (Salminen and Tarvainen 1997). The two general alternatives to reduce this problem are:

- restrict sampling to very specific horizons and/or regolith materials; or
- measure sufficient “control” variables to be able to normalise element contents against those controls.

Both approaches have limitations. The former presents the problem of regolith identification and consistent coverage of such media or horizons in regional mapping. For example, the A<sub>0</sub> horizon is generally present in central Troodos, but generally absent in calcreted areas in the Kokkinokhoria region. In the pilot NASGLP study, of the 265 sites where the 0–5 cm depth sample was collected, an O-horizon sample could only be collected at 38 sites whereas the A-horizon soils were sampled at 244 sites (Woodruff *et al.* 2009).

Regional soil or sediment geochemical mapping projects have varied substantially between those that target specific soil (or regolith) horizons and those that simply maintain a constant sampling depth. The Barents Survey targeted specific horizons (including O, A<sub>0</sub>, B and C horizons), the NASGLP project covers both depth and horizon-controls, and the NRAC project maintained a constant media (active

channel sediments). Conversely the FOREGS and WAGS Yilgarn regolith surveys (Morris and Saunders 2001) maintained generally constant sampling depths but with the nature of the material and regolith-landform setting recorded.

In the Mexican NASGLP orientation traverse there was high correlation between A and C-horizon geochemistry for a range of elements (Chipre *et al.* 2009). Smith *et al.* (2009) concluded that the O- and A-horizons represent a combination of human and geologic influence, and the C-horizon represents primarily geologic influence on soil geochemistry. Yet, work by Eberl and Smith (2009), comparing top soil (A-horizon) and deeper samples (B+C-horizon), indicated very close correlation between mineralogy of the two depths with slightly higher carbonates and silica at depth.

Studies in Fennoscandia (Ottesen *et al.* 1989; Eden and Bjorklund 1994) and China (Xie *et al.* 1993; Xie and Cheng 1997) demonstrated the close correlation between till and stream geochemistry and low-density overbank or floodplain deposits. One potential consideration is the temporal stability of a sampling media if it contains highly mobile components. There may be seasonal variations in trace element concentrations as shown for soils in the regions in Arctic areas near existing major smelters, and which is controlled largely by changes in soil organic matter (Niskavaara *et al.* 1997).

### 1.1.5 Geochemical and physical analysis

There is a wide variety of options for the physical and chemical characterisation of media such as soils and sediments. The options include the physical fraction analysed (bulk sample, specific size fraction, heavy mineral concentrates, magnetic fraction) and the chemical components (total contents, partial or selective extraction, volatile components).

Many regional geochemical studies have commenced with orientation surveys designed to test different analytical and sampling options. For example, the Barents and other northern European surveys provided a guide to the subsequent FOREGS Geochemical Atlas of Europe.

Elements in soils associate with or tend to be contained within various specific mineral species or forms. Elements may constitute major structural components of minerals (e.g. Fe in goethite or Ca in carbonates), trace substitution (e.g. Zn for Ca in carbonates) and non-specific forms (Cu adsorbed to Fe-oxides or U adsorbed to organics). Interpretation of the distribution of trace elements is, therefore, also dependent on the abundance of the host minerals. Mineral abundances are commonly difficult to determine directly, therefore proxy variables are used such as major cations for their host minerals or SOC for organics.

Other parameters are also important to measure. pH is considered a “master variable” in soils (McBride 1994) and strongly influences the form, solubility, mobility, adsorption potential and availability of most elements. This parameter has a major impact on soil chemistry and the distribution of elements within regolith profiles and their association with various secondary mineral phases.

Whereas grain size has been identified as a factor in the distribution of elements, it is not the particle size *per se* that exerts control but the association of different minerals with different grain sizes. In most soils and sediments the clay size fraction is typically dominated by clay minerals, Fe+Mn oxides and organics, whereas the coarse fractions contain quartz and lithic fragments. Analysis of proxies for the major minerals controlling trace element geochemistry – Al for clays, Mn and Fe for Fe-Mn oxyhydroxides, Ca and Mg for carbonates and LOI or *tot*-OC for organics – is typically of more use than undertaking grain size analysis.

Further consideration of analytical options is provided in Section 2.

### 1.1.6 Data processing and visualisation

Geochemical atlas data may be subjected to a range of deterministic and stochastic statistical analysis methods. In doing so, the processing of geochemical atlas data can be divided into three components (Grunsky 2007):

- *Data visualisation*, designed to present individual variables or variable combinations in a form that allows visual interpretation.

- *Exploratory data analysis*, to examine parametric and spatial characteristics of each variable and bivariate relationship. This stage may also include methods for determining background characteristics.
- *Data modelling*, designed to examine or explain parametric or spatial multivariate patterns of correlation, clustering and anomalous groups within datasets.

One of the most fundamental questions relates to the characterisation of “background” data populations from which “anomalous” value ranges can be set. This approach has been traditionally used in exploration geochemistry to define values with a high probability of being related to mineralisation, and in environmental geochemistry to detect contamination and to assist in setting regulatory limits or investigation trigger values. Various definitions of “background” values or ranges have been presented (Hawkes and Webb 1962, Garrett 1991) and mostly converge on the concept of the range of element values that would be expected in the absence of mineralisation (exploration) or contamination (environmental).

As emphasised by Reimann and Garrett (2005) and others, in most geological terrains there is generally no single background distribution (values and statistical population characteristics) for any given element in soils or sediment. Rather, there exists a complex series of overlapping distributions related to the effects of a wide variety of processes and phenomena – from parent lithology to soil-forming processes. They also point out that regions with a long history of human activity may have regional background values that are above the pre-human background values.

Further to this, Darnley *et al.* (1995) and Garrett (2003) emphasise that “baseline” geochemical surveys should not imply there is a single “baseline”, but rather map and attempt to quantify the factors, both natural and anthropogenic, that affect variations and levels of elements. Cohen *et al.* (2010) have advocated abandoning the concept of “background” and “anomaly” when treating selective extraction geochemical data in favour of recognising that the multielement geochemical characteristics of soils and sediments represent the summation of a series of signals, some of which may be influenced by the effects of mineralisation or contamination. The problem then is to recognise and isolate the signals of interest.

In exploration geochemistry, anomalies are conventionally defined in terms of variation from statistical trends in data (parametric and spatial) rather than simple high or low values within single variables or Euclidian distances from multivariate means (Austria and Chork 1976; Garrett 1989; Chork and Rousseeuw 1992; Grunsky 2007). Parametric methods are commonly dependent on assumptions such as normality and log-normality or transformations of data to normality (Box and Cox 1964; Mancey and Howarth 1980), though most geochemical datasets do not fit preconceived notions of distribution type (Reimann and Garrett 2005; Reimann and Filzmoser 2000). Instead, non-parametric and non-linear multivariate methods may be used (Kohonen 1995; Clare and Cohen 2002)

Various approaches have been used to isolate multielement patterns in soils and sediments. These include dimension reduction techniques such as classical and robust principal components analysis (PCA) and factor analysis (FA) (Gnanadesikan and Kettenring 1972; Reimann *et al.* 2002; Filzmoser *et al.*, 2009), alternative PCA approaches that take into account spatial variations in the structure of multivariate data, various forms of clustering from simple k-means to neural networks (MacQueen 1967; Clare and Cohen 2002), multifractals (Cheng *et al.* 1994) and other covariance/correlation matrix decomposition methods. Defining common groups (or clusters) that relate to regional scale geological processes and isolating anomalous samples is a fundamental task of geochemical analysis (Cheng *et al.* 1996).

Effective visual presentation of data is crucial for geochemical atlases, with various considerations relating to the current project discussed in Section 4. In an example of data presentation from the Barents survey (Fig 1.1) the random positioning of sample points is illustrated in the left hand symbol plot and the coherent distribution pattern displayed following processing shown in the grided data on the right (Reimann *et al.* 1998). The low relative estimation error in the kriged data is indicative of the spatial continuity of the geochemistry of the regolith samples collected at one site per 50 km<sup>2</sup>.

### 1.1.7 Examples

A list of previous and ongoing large-scale geochemical atlases is provided in Table 1.1.

#### *China*

Four major national geochemical surveys have been conducted in China (Wang *et al.* 2007), including:

- The regional geochemistry-national reconnaissance project (RGNR), involving stream sediment sampling of upland areas at a density of one sample per 1 km<sup>2</sup> over a massive 6 million km<sup>2</sup>,
- The follow-up 76 geochemical element mapping project (76 GEM) using stream sediments and focussing on targets generated by the RGNR project,
- The deep-penetrating geochemical mapping project (DEEPMAP) in areas of sedimentary basin cover of basement rocks in which soils collected at a density of one sample per 100 km<sup>2</sup> over 800,000 km<sup>2</sup>, and
- The multi-purpose eco-geochemical mapping project involving soils in Quaternary plain areas for environmental and agricultural applications (containing a similar design to the current Cyprus project).

Within DEEPMAP, the <125 µm soil fraction was analysed by various partial extractions to measure mobile metals. This has revealed new zones of buried sandstone-hosted U-Mo mineralisation under transported cover in the Turpan-Hami Basin of NW China (Fig 1.2). The studies have also shown that stream sediments and floodplain sediments contain similar source area to element concentration relationships, confirming the mass balance models developed by Hawkes (1976).

Another application of mapping in China has been medical geochemistry. One study has shown the close spatial correlation between regions with depleted Se values in the soil and endemic Keshan and Kashin-Beck disease (Fig 1.3) which is caused by nutritional deficiencies in Se (Tan 1989; Li and Wu 1999). This emphasises that some environmental problems relate to deficiencies of elements in the environment rather than excesses.

#### *FOREGS Geochemical Atlas of Europe*

This environmental geochemical survey was completed by a consortium of 25 national geological surveys (FOREGS, now EuroGeoSurveys), to provide high quality environmental geochemical baseline data for Europe using standardised sampling and analytical methods (Salminen *et al.* 2005; de Vos *et al.* 2006). The survey collected stream water, stream sediment, floodplain sediment, soil and humus across Europe at a low density. This project has provided the basis for the design of the Cyprus project.

Even from this very low density sampling program, large-scale and highly coherent regional patterns are observed (Figs 1.4 and 1.5). The data visualisation, incorporating the raw data with sample locations and element concentration represented by concentration-size proportional dots and smoothed data derived from variography and kriging. Patterns for Ni and Cu are similar, with elevated values in areas dominated by volcanics and mafic lithologies and low values in the glaciated regions of Northern Europe (apart from some areas with exposed basement). Neither sampling media strongly reflects the location of known Ni or Cu deposits (although the deposits mostly occur in terranes with generally elevated base metal values) or major Ni smelters. Lanthanum values are elevated in a belt running across the Variscan and most of the Alpine Orogen, whereas Sr is most elevated in the weakly weathered glacial sediments of Scandinavia and at various locations along the southern coast of Europe (indicative of climatic controls).

An environmental risk assessment, based on regulatory limits in various EU countries and the atlas data has been undertaken by Rapant *et al.* (2008). Noting the significant differences between regulatory limits for residential sites (France is an order of magnitude above Italy for some elements), the mean top soil values for Europe are above the regulatory values for As, Ba, Cr, Ni and V in some countries (Table 1.2).

In a very detailed follow-up study of the stream sediment geochemistry in the Campagna region of Italy 2,389 stream sediments were collected from 13,600 km<sup>2</sup> area. The maps display contiguous geochemical patterns (Fig 1.6), with Pb values highest around the major industrial and urban areas.

### ***Other studies in northern Europe***

The Finnish geological survey (GTK) carried out regional geochemical mapping between 1982 and 1994 (Salminen 1995; Salminen and Tarvainen 1995), including a multi-sampling media survey at one sample per 300 km<sup>2</sup> and a more detailed till sampling at one sample per 4 km<sup>2</sup> (82,062 sites). In the low density samples there were substantial differences in patterns between different media, such as Zn in till versus stream waters. A subsequent study, using just 90 samples, compared aqua regia extractable with “bioavailable” elements based on an ammonium acetate-EDTA extraction (Fig 1.7). There was a moderate correlation between the two although bioavailable Zn and V were typically <5% of total contents. It is interesting to note that the sub-set delivered very similar median values to the original survey for the elements reported (Table 1.3).

In a study of soil and rock geochemistry in a 120 km N-S traverse across Norway neither geology nor anthropogenic inputs were observed to be the overall dominant factor in the accumulation of elements in the O-horizon (organics), but a combination of weathering and possible biogenic effects (Reimann *et al.* 2007b). Most elements, other than group I and II, displayed significant enrichment in the B- and C-horizons relative to the adjacent rocks (Fig 1.8). The element contents of the O-, C- and rocks displayed similar spatial trends in enrichment and depletion. Peak transition metal contents were mainly associated with black shales (a natural source), which is commonly observed in other surveys. Gold and Pt were elevated in the Oslo city area.

The geochemical survey of the Central Barents region (the Kola Ecogeochemistry Project) involved a range of media, including moss and various soil horizons. Again, the question of the balance between natural and anthropogenic influences on regolith geochemistry was examined (Reimann *et al.* 1998; Reimann and Caritat 2005). An examination of the Bi content of the organics (A<sub>o</sub>) horizon from an east-west traverse that intersected the long-running and highly polluting Monchegorsk Ni smelter, shows the influence of the smelter extends for about 25 km around the site (slightly further to the west) but otherwise the regional trend is a gradual decrease in Bi from west to east, probably related to underlying geological changes (Fig 1.9).

### ***The North American Soil Geochemical Landscapes Project (NASGLP) and related projects***

This project was initiated in 2001 and is designed at one site per 1,600 km<sup>2</sup> or 13,500 sites covering Canada, the USA and Mexico (Smith *et al.* 2005, 2009). Some analysis of samples derived from the former NURE and related geochemical mapping projects have been completed. While there are some data quality issues, the low-density stream sediment map indicates consistently high Cu values along the Cordillera, moderate to high values in the Rocky Mountains and northern prairies and the Mississippi Valley, but low values in the south-eastern USA (Fig 1.10). An east-west traverse conducted as part of the pilot studies for the NASGLP project indicates the effect of rainfall on the Ca (mainly as secondary carbonates) in the soil Fig (1.11)

### ***Stream sediment survey of northeastern NSW***

A stream sediment geochemical survey of the NE region of NSW was conducted by Cohen *et al.* (1995) as part of a systematic and comprehensive audit of all the values of public lands and natural resources of New South Wales on a regional basis. Data from the 1,677 individual sites demonstrates the dominant effect of catchment geology on the regolith geochemistry, including the presence of mineral deposits. The distribution of As is largely controlled by the distribution of Palaeozoic metasedimentary rocks (Fig 1.12), whereas the distribution of Cr is controlled by both the distribution of mafic and ultramafic rocks (geological control) and the edge of the Clarence-Moreton Basin where detrital Cr-bearing minerals (e.g. chromite) have accumulated as streams flowing down from the adjacent Palaeozoic-Mesozoic uplands slow on entry to the basin.

## 1.2 THE CYPRUS SETTING

Cyprus lies in the northeastern corner of the Mediterranean Sea and covers an area of 9,251 km<sup>2</sup> rising to 1,951m at Mount Olympus. Cyprus is the third largest island of the Mediterranean Sea, after Sicily and Sardinia.

### 1.2.1 Geology

Cyprus is situated within a chain of Tethyan ophiolites, cropping out around the eastern Mediterranean Sea. These represent the last vestiges of the Tethyan Ocean which dominated the Crust during the Mesozoic. The general tectonic setting of Cyprus is indicated in Fig 1.13, with Cyprus situated at the African-Eurasian plate boundaries. The geological formation of Cyprus is the result of a series of complex geological events that has delivered a unique geology, including the Troodos Ophiolite Complex (TOC) and the famous Cyprus-type Cu deposits. The main geological terranes are shown in Fig 1.14 and a more detailed geological map in Fig 1.15.

#### *The tectonic evolution of Cyprus*

The development of Cyprus was initiated by a series of tectonic events, commencing in the Upper Cretaceous at ~90 Ma and culminating in the obduction of the Troodos Ophiolite onto the margin of the African Plate during subduction of the African Plate under the Eurasian Plate (Mukasa and Ludden 1987; Robinson and Malpas 1990). There are various models for the tectonic evolution, with the main differences being in the origin of the Mamonia Terrane and the nature of the continental crust underpinning Cyprus after initial formation of the TOC (Figs 1.16 and 1.17). Most authors support a model based on subduction of the African Plate beneath the Eurasian Plate.

A basic sequence of events and the deposition of the main geological units are presented in Fig 1.18. In the initial stage of formation of Cyprus, back-arc spreading and magma up-welling generated a vertical sequence of ultramafic cumulates (“the Mantle Sequence”), mafic cumulates and mafic dykes, and pillow basalts within the a supra-subduction zone in Tethys oceanic crust (Morris *et al.* 1998). This sequence would form the core to the subsequently obducted TOC. Others reject the classic subduction-rifting model in favour of a strike-slip tectonics model (Harrison *et al.* 2004), supported by geophysical evidence of a thick continental crust underpinning to Cyprus (Papazachos and Papaioannou 1999).

Subsequent tectonic activity resulted in detachment and rotation of the newly formed island by 90° and the attachment to its southern and western part of older rocks forming the Mamonia Terrane which ranges in age from 230 to 75 million years. There remains some dispute over the origins of the Mamonia Terrane (Spray and Roddick 1981) partly due to the nature of metamorphic rocks in the sequence.

Reconvergence of the surrounding plates obducted the TOC in the mid Miocene. The stratigraphic completeness of the ophiolite – from Mantle Sequence through to ocean-floor volcanics – makes it unique and the most studied ophiolite in the world.

During the period of low tectonic activity that followed obduction, carbonate-dominated sedimentation occurred with subsequent gradual shallowing of the sedimentary basin giving rise to the Lefkara and Pakhna Formations, which form the two main units of the Circum-Troodos Sedimentary Succession (CTSS). A stratigraphic section through the CTSS and Quaternary units is provided in Fig 1.20. During the second and last tectonic episode (10–15 Ma) the placement of the Pentadaktylos Range north of Troodos occurred, with uplift of the area. At the end of the Miocene (6 Ma) a series of allochthonous limestones were emplaced over the northern flanks of the TOC-CTSS sequences. East of Cyprus the Tethys Sea closed at the Straits of Gibraltar forming the Mediterranean Sea.

Marine sedimentation and relative tectonic inactivity dominated south of the area following the accretion of Mamonia Terrane to the TOC. At the same time, periodic and abrupt uplift (diapiric rising) of Troodos extended into the Pleistocene (2.6 Ma).

The reconnection of the Mediterranean Sea with the Atlantic Ocean with the opening of the Straits of Gibraltar and rising sea level resulted in the deposition the marls and calcarenites of the Nicosia Formation (including the Athalassa Member). An abrupt uplift of the area occurred during the Pleistocene at ~2 Ma (the last tectonic episode). Combined with heavy rainfall, this uplift resulted in extensive erosion of the ranges, particularly on Troodos, with the transportation of large quantities of

erosion material. These clastic sediments were deposited in valleys and across the Mesaoria region, forming the Pleistocene Fanglomerates.

Block faulting that uplifted Troodos to its present position typifies the overall tectonic pattern of the island. This is preserved in both inactive and active faults due to the on-going seismic activity. The main structural features of Cyprus are the Arakapas Transform Zone and Yerasa Fault on the SW side of Troodos, the Polis Basin graben (which houses the Polemi Basin) and a series of other faults running either NW or NNE, some of which correspond with the major valleys incised in a radial pattern around Troodos.

Cyprus may be divided into five tectono-lithological terranes (Fig 1.19):

- (a) the Troodos Ophiolite Complex,
- (b) the Arakapas Transform Zone (which may be included with the TOC),
- (c) the Mamonia Terrane, and
- (d) the Pentadaktylos (Keryneia) Terrane,
- (e) the Circum-Troodos Sedimentary Succession and younger autochthonous sediments.

### ***Troodos Ophiolite Complex***

The rocks of the TOC dominate the central part of the island (3,200 km<sup>2</sup>) and constitute the geological core of Cyprus. TOC rocks crop out in two areas; (i) the elongated domal structure carrying the main mass in the Troodos mountain range and (ii) the Limassol and Akapnou Forests south of the range which is termed the Arakapas Transform Zone due to the extent of structural deformation. There are minor outcrops of TOC in the Akamas Peninsula and the Troulloi area in the east. The TOC consists of four stratigraphic units which are, in ascending order: plutonics (mantle sequence and cumulates), intrusives, volcanics and chemical sediments. The stratigraphy of the TOC is topographically inverted, with the mantle sequence outcropping in the highest points of the range and the basaltic volcanics forming the flanks of the ophiolite. This apparent inversion is related to the way the ophiolite was uplifted (diapirically) and to its differential erosion.

The Mantle Sequence is considered to be the residual from partial melting of the upper mantle and the formation of basaltic magma, from which the remaining rocks of the TOC have been derived. It is mainly composed of harzburgite and dunite, plus irregular lherzolite intrusives within the harzburgite. In the Mantle Sequence 50–80% of the original minerals were altered to serpentine, and serpentinites (some containing chrysotile asbestos) occur where the alteration was almost complete. The overlying mafic cumulate rocks are the products of crystallisation and concentration of the crystals at the floor of the magma chamber beneath the zones of sea floor spreading. The main cumulate rocks are observed in small discontinuous occurrences and include dunite (with podiform chromite in areas), wehrlite, pyroxenite, gabbro and plagiogranites (Georgiou 1987; Parson *et al.* 1992).

The harzburgites are commonly deformed and foliated due to high temperature plastic flow of the mantle. Regionally the trend of this foliation is NNW–SE, with the steep dip revealing a mantle upflow beneath a spreading centre. The steep dip may be related also with the serpentinite diapirism which uplifted Troodos. The harzburgite is composed of ~80% olivine, 20% orthopyroxene and up to ~1% accessory chromite. The minerals tend to be Mg-rich with the olivines 90–91% forsterite (the Mg-rich component) and the pyroxenes 88–89% enstatite. Where the clinopyroxene percentage is high the rock is classified as lherzolite. The chemical composition of chromite in the harzburgites is 42–52% Cr<sub>2</sub>O<sub>3</sub>, 18–27% Al<sub>2</sub>O<sub>3</sub>, 2–9% Fe<sub>2</sub>O<sub>3</sub>, 12–18% FeO, 12–18% MgO, 0.1–0.5 MnO and 0.1–0.3% TiO<sub>2</sub>.

The dunites are almost entirely olivine (95–99%) with minor amounts of chromite (0.5–5%) and some clinopyroxene. They occur within the Mantle Sequence in the form of pockets or lenses, mainly in the western sector of the harzburgite zone where the transition from the mantle to the cumulates (Crustal Sequence) is developed. The chemical composition of the olivines is 90.5–93.5% forsterite and the remainder mainly clinopyroxene (diopside as a solid solution with 47–48% enstatite, 47–48% wollastonite and 4–5% ferrosilite). The chromites in the cumulate dunite are more Cr-rich than in the Mantle Sequence, averaging 53.0% Cr<sub>2</sub>O<sub>3</sub>. The wehrlites are mainly composed of olivine, clinopyroxene and accessory chromite. In some sub-types minor plagioclase and orthopyroxene are present. The modal composition is 43–75% olivine, 25–55% clinopyroxene, 0–5% orthopyroxene (enstatite) and 0–5% plagioclase (anorthite).

The chromite in the cumulate dunite is more Cr-rich than in the Mantle Sequence. The dunite chromite average composition is 53.0% Cr<sub>2</sub>O<sub>3</sub>, 13.5% Al<sub>2</sub>O<sub>3</sub>, 5.2% Fe<sub>2</sub>O<sub>3</sub>, 16.9% FeO, 11.3% MgO, 0.2% MnO and 0.2% TiO<sub>2</sub>.

The wehrlites are composed mainly of olivine and clinopyroxene and accessory chromite. In some subtypes minor plagioclase and orthopyroxene are present. The modal composition is 43-75% olivine, 25-55% clinopyroxene, 0-5% orthopyroxene and 0-5% plagioclase (anorthite). The typical poikilitic texture is well-developed in the various types of wehrlites.

The pyroxenites are usually massive, though there is some rare layering, and composed mainly of clinopyroxenes with minor orthopyroxene, anorthositic plagioclase and olivine. The clinopyroxene content varies from 80-95% (diopside), whereas the orthopyroxene is mainly enstatite.

The gabbros within the cumulate sequence have varying composition with 9–30% olivine, 31–38% clinopyroxenes and 32–59% plagioclase, with plagioclase becoming more dominant higher up in this part of the mafic series. The isotropic gabbros have granular xenomorphic or hypidiomorphic textures and a modal composition of 40–65% plagioclase (labradorite), 30–50% clinopyroxene (diopside or augite), 3–8% orthopyroxene (hypersthene), 0.5% ilmenite-magnetite and 0.5% epidote.

Small zones of plagiogranites crop out stratigraphically above the isotropic gabbros. They have a granophyric texture and consist of quartz, strongly zoned plagioclase with Ca cores and Na rims, hornblende with Mn alteration, augite, actionolite and epidote. This mineral composition is partly a product of low-grade metamorphisms that is probably related to high-heat flow spreading centres.

The Sheeted Dyke Complex has a basaltic to doleritic composition and was formed by the solidification of the magma in the channels through which it intruded from the magma chambers at the bottom of the oceanic crust feeding the sea-floor basalts. The Sheeted Dyke Complex is followed by a suite of volcanic rocks that consist of two series of pillow lavas and lava flows, mainly of basaltic composition. The pillow lavas have a characteristic spherical to ellipsoidal pillow shape, 30–70 cm in diameter, which were formed as a result of submarine volcanic activity. Between the intrusive rocks and the pillow lavas is a transitional zone known as the Basal Group. Dykes dominate the Basal Group whereas pillows are less common.

The Perapedhi Formation is composed of amber (chemical sediment), radiolarites and radiolarite shales. These were the first sediments deposited over the ophiolite rocks as a result of hydrothermal activity (hot solutions rich in Fe and Mn) and sedimentation on the sea floor.

This Troodos type material underlining Mesaoria plain ends abruptly along an east-west trending line, known as Kythrea or Ovgos Fault Zone, which separates the Troodos Zone from the Pentadakylos Zone. In the south-western part of the island it covers rocks from the Mamonia Zone.

### ***Mamonia Terrane (or Complex)***

This contains a diverse and structurally complex assemblage of igneous, sedimentary and metamorphic rocks, ranging in age from Middle Triassic to Upper Cretaceous (230–75 Ma). These rocks are regarded as allochthonous in relation to the overlying autochthonous carbonate successions and the Troodos ophiolite rocks and were placed over and adjacent the Troodos ophiolite during the Maastrichtian. They occur only on the southern part of Cyprus with extensive outcrop only in the Pafos region. The stratigraphic classification of the Mamonia Terrane units is problematic; however, three main groups can be recognized:

- Volcanics (lavas) and sedimentary rocks (recrystallised limestones) of the Dhiarizos Group. The volcanics are considered tholeiitic and possibly N-MORB by Malpas *et al.* (1992, 1993), having previously been considered as alkalic basalts (Swarbrick and Robertson 1980).
- Pelagic sedimentary rocks (limestones, mudstones and quartzose sandstones) of the Ayios Photios Group.
- Metamorphic rocks (schists and marbles) of the Ayia Varvara Formation. These rocks were partly derived from the metamorphism of sedimentary rocks derived from the underlying Dhiarizos Group.

Overlying the Mamonia Terrane rocks is the allochthonous sedimentary Kathikas Formation (formerly Melange), which is directly related to the emplacement of the Mamonia Terrane. The overlying Kannaviou Formation contains the earliest sedimentary cover over the Mamonia Terrane basement.

### ***The Pentadaktylos (Keryneia) Zone***

This is the northern-most geological terrane in Cyprus and is considered to be the southern portion of the Tauro-Diraride Alpine Zone. It forms a narrow, steep-sided chain of mountains (3–7 km wide) that rise abruptly from the surrounding lowlands. It extends from Cape Kormakitis in the west to Cape Andreas in the east. The peaks vary between 800 and 1024 m in elevation along the range. To the north this very rugged range is separated from the sea by a narrow and terraced coastal plain <5 km wide. In contrast, it is flanked to the south by the broad lowlands of the Mesaoria Plain.

The Pentadaktylos Zone is a structurally complex assemblage of Permian to Recent sedimentary and subordinate metamorphic and igneous rocks. The three main geological formations are the allochthonous Dhikomo, Sykhari and Hilarion Formations, which form the main carbonate masses of the Pentadaktylos Range. All are Triassic-Lower Cretaceous (250–135 Ma). The Dhikomo Formation consists of deformed, thinly-bedded limestones with layers of grey and green phyllites. The Sykhari Formation is composed of massive to thickly-bedded dolomitic limestones. The Hilarion Formation consists of medium-bedded to massive limestones, which were subjected to a low degree of metamorphism. Continuous outcrops of limestones occur in the central part of the range, whereas in the eastern part occur in the form of olistholiths referred to as the Kantara Formation (Permo-Carboniferous, 350–250 Ma). These allochthonous formations were thrust southward over the younger autochthonous marine sediments, including conglomerate, siltstone, sandstone, marl, greywacke, chalk and gypsum of the Lapithos, Kalogrea-Ardana and Kythrea Formations.

The oldest autochthonous unit in the Pentadaktylos Range is the Lapithos Formation of Campanian to Eocene age (85–40 Ma) and consists of pelagic marls and chalks, limestones, and cherts which occur as faulted and schistose beds containing contemporaneous lava horizons of basaltic and rhyolitic composition. The Lapithos Formation is overlain by the Upper Eocene (35 Ma) Kalogrea-Ardana Flysch, which is then uncomformably overlain by the Kythrea Formation (or Kythrea Flysch) that crops out along both sides of the Pentadaktylos Range as a thick and strongly folded sequence of sandstones, siltstones and marls of mid-Miocene age (15 Ma). On the south side of the range, the Kythrea Flysch interfingers with the Pakhna Formation.

### ***The Circum-Troodos Sedimentary Succession***

The geological history of Cyprus from the Upper Cretaceous (67 Ma) is characterised by marine sedimentation in progressively more shallow environments. A stratigraphic column for southwestern Cyprus is provided in Fig 1.20, based on Malpas *et al.* (1992).

Sedimentation began with the deposition of the Maastrichtian Kannaviou Formation containing (grey to pink) bentonitic clays, volcanoclastics and Mn-rich siltstones, followed by the deposition of the deep marine Moni and overlying the Kathikas Formation. The Moni Formation contains grey bentonitic clays and blocks of sedimentary and volcanic rocks derived from the Mamonia Terrane and include sheets of serpentinite emplaced in a clay matrix. The Kathikas Formation contains clasts of Mamonia Terrane rocks in a clay-sand matrix and lies on the suture zone between Troodos and Mamonia and it is tectonically undisturbed (Swarbrick and Naylor 1980).

Carbonate sedimentation begins from the Palaeocene (65 Ma) with the deposition of the Lefkara Formation, which includes pelagic marls and chalks with a characteristic white colour, with or without cherts. The maximum thickness of the Lefkara Formation is 750 m and it may be subdivided stratigraphically into four members: Lower Marls, Chalks (with chert layers), Massive Chalks and Upper Marls.

The Lefkara Formation is followed by the Pakhna Formation (Miocene, 22 Ma), which mainly consists of yellowish marls and chalks. The colour of the rocks, the presence of calcarenitic layers and the sporadic development of conglomerates are characteristics that differentiate the Pakhna from the Lefkara Formation. Sedimentation in the Pakhna Formation began and terminated in shallow-water environment with the development of reefal limestones (Terra Member at the base and Koronia Member at the top), in basins created due to the Troodos uplift. Hemi-pelagic sediments (chalks and marls) were formed in the central part of the basins and occasionally conglomerates were deposited at the margins. The maximum thickness of the Pakhna Formation is 800 m. The carbonates are nearly pure calcite.

The deposition of the Kalavassos Formation evaporites followed in the Upper Miocene (Messinian, 6 Ma) as a result of the closure of the Mediterranean Sea from the Atlantic Ocean and the evaporation of its waters. The Kalavassos Formation is composed of gypsum and gypsiferous marls. Sediment composition reflects cyclical rise and fall of sea level. Gypsum occurs in four types: sugary crystalline), laminated ('marble'), selenite (transparent with large twin crystals) and alabaster (massive semi-transparent gypsum).

Following reconnection of the Mediterranean Sea with the Atlantic Ocean, a new cycle of sedimentation began (Pliocene, 5 Ma). The Nicosia Formation was deposited first and contains siltstones (grey and yellow) and layers of calcarenites and marls, followed by the Athalassa Member (Plio-Pleistocene, 2.6 Ma) consisting of calcarenites interlayered with sandy marls and finally the Pleistocene Fanglomerates (gravels, sand and silt). The Fanglomerate surfaces are indurated.

### ***Younger autochthonous sediments***

Younger autochthonous sediments cover the area between the Pentadaktylos Zone and TOC on the Mesaoria Plain, the southern coast of the island and major river valleys. They are partly the result of the rapid uplifting of Troodos in the beginning of Pleistocene and the erosion of sedimentary and igneous rocks, gives rise to the formation of extensive deposits of undifferentiated gravels, sands and silts. Most deposition was as a series of extensive fanglomerate deposits (Fig 1.21). They are very well developed in the Mesaoria Plain, south and southwest of Lefkosia. The indurated palaeo-surfaces of the fanglomerates and associated alluvials are being dissected in the current cycle of erosion.

### ***Mineral deposits and mining***

Directly associated with the TOC are the massive sulfides, chromite and asbestos mineral deposits. These ore deposits were formed in different stratigraphic units of the ophiolite (lavas, dunite and harzburgite, respectively) and came to the surface as a result of uplift. The exposure of the ore bodies to the surface, and especially that of massive sulfides, resulted in the discovery and exploitation of Cu in ancient times. The location of the mineral deposits of Cyprus is indicated in Figs 1.22 to 1.24.

At least two types of Cu deposits are hosted in the basaltic units of the Troodos Ophiolite: (a) the famous "Cyprus-type" massive sulfide ore deposits and (b) the disseminated sulfide deposits. Both are associated with hydrothermal alteration of the basalts by seawater. The latter are characterised by low Cu content, do not contain the massive ore part of the Cyprus-type deposits, lack stockwork, and do not contain primary Cu minerals such as chalcopyrite ( $\text{CuFeS}_2$ ), but rather they contain secondary Cu minerals such as chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ). The Cyprus-type Cu deposits are at the Cu-rich end of the spectrum of volcanic-hosted massive sulfides and are dominated by pyrite-chalcopyrite and a close association with pillow lavas (Fig 1.25). There are areas with elevated Zn and Au, but these elements are generally sub-economic. The lack of Pb and other large ion lithophile elements such as Ba and spatial association with plagiogranites is highlighted by Sawkins (1990).

The Cu deposits display vertical zoning of massive sulfides at the top, underlain by an extensive stockwork zone with intensive wall-rock alteration. The ore-mineral paragenesis of massive and stockwork zones is relatively monotonous with predominating pyrite, intergrown with chalcopyrite and minor amounts of sphalerite (Friedrich *et al.* 1984). The deposits contain 0.5 to ~4.5% Cu and irregular zones of Zn enrichment (up to 10%), but these are typically uneconomic.

High-Mg lavas are known to be associated with some massive sulfide deposits, the Cyprus deposits being an example (Keays 1987). Immiscible magmatic sulfides are strongly enriched in the ore-forming metals which may then be liberated from the sulfides under the effects of the sea-floor hydrothermal alteration stage and subsequently redeposited as high level stockwork and volcanogenic massive sulfide deposits.

The pillow basalts have umbers and ochres associated with them, especially in areas containing hydrothermal alteration (Constantinou and Govett 1972). These units carry elevated trace element siderophile and chalcophile concentrations (Robertson and Hudson 1973).

Examples of the mineralized sequence and associated footwall and hanging-wall units are provided for Kalavassos, Agrokippia-Mitsero and Mathiatis from the AMIRA Data Metallogenic project (Figs 1.26 to 1.28).

The TOC contains podiform chromite deposits in the lower part of its ultramafic suite. The largest and economically important deposits are confined to the transition (contact) zone between the Mantle Sequence, composed of harzburgite and dunite pockets within the harzburgite, particularly in dunite apophases and lenses within the upper part of the harzburgite. Each chromite-enriched zone is enveloped by dunite. The exploitable deposits range from  $10^5$ – $10^6$ t and appear in variously shaped layers, lenses and pods. The main deposits are Kokkinorotsos, Kannoures and Hadjipavlou. The chromite deposits are adjacent to Europe's largest (now abandoned) asbestos mine, Amiantos (Fig 1.29).

The transition-zone chromite occurrences are dominated by massive granular chromite and very rarely by nodular chromite. In the chromite concentrations of the main dunite a variety of additional textures are present, such as ocluded silicate, chromite net, skeletal and orbicular chromite. Common inclusions in chromite are silicates, oxides, sulfides, Ni-Fe and Cu-Zn alloys, native Cu and a variety of platinumoids, particularly the solid solution series  $\text{RuS}_2$ - $\text{OsS}_2$ - $\text{IrS}_2$ .

The geochemistry of the chromites shows a wide variation. The  $\text{Cr}_2\text{O}_3$  content of the massive ore ranges between 45% and 51%, with a Cr/Fe ratio around 3. The Cr-Al values are characterized by a reciprocal relationship (Fig 1.30). The orebodies in the dunite bodies within the harzburgite are richer in Al and poorer in Cr, whereas those in the main dunite mass are poorer in Al and richer in Cr. The orebodies, after their formation in sub-vertical channels in the transition zone between harzburgite and dunite, have been plastically deformed at high temperatures along with their host rock.

A range of industrial minerals and other geological materials are quarried in Cyprus, including carbonate-rich units for production of cement and building stone (Fig 1.31). The sedimentary rocks are the main sources of the industrial minerals of the island. The main industrial minerals include gypsum (used in the cement production), brick clays, umber, ochre and terra verte (natural pigments), marls and chalks (cement production), bentonitic clays (various industrial uses), building stone, celestite and magnesite.

### 1.2.2 Landform and regolith

#### *Topography*

The topography of Cyprus is controlled by the geology and is dominated by the Troodos Mountains in the south, the Keryneia Mountain Range along the northern coast and the intervening Mesaoria Plain (Figs 1.32 and 1.33). The highest point, Mt Olympus, sits within the ultramafic core to the TOC.

The land slope in the vicinity of each sample site, recoded in the field logs, is typically flat along the coastal strip, steep over central Troodos and some of the deeply incised valleys that have cut through the CTSS into the TOC or Mamonia Terrane basement, and moderate elsewhere on the Troodos Mountain flanks (Fig 1.34).

Troodos is deeply dissected with a radial pattern of both modern and ancient streams. The surrounding carbonate-dominated CTSS formations that onlap the TOC are also heavily dissected, exposing underlying TOC and Mamonia Terrane units in the valley floors. The TOC and Mamonia Terrane are split on the western side of the island by the Polis Valley.

The original CTSS deposits and indurated fanglomerate and palaeog gravel units lap onto and dip away from Troodos. Some of these surfaces have been tilted during subsequent tectonic activity. Recent stream activity has resulted in the incising of these surfaces with mesa-style outliers of CTSS on the north and eastern flanks of Troodos. This is shown in the view south towards Troodos from Tseri (Fig 1.35). The Mesaoria Plain and discontinuous coastal floodplains occupy the areas of low elevation.

#### *Regolith*

The design of sampling protocols and interpretation of geochemical maps must be based on a detailed understanding of regolith evolution and stratigraphy in a region, and the relationship between regolith type and landforms. Various criteria to describe regolith materials, schemes to classify regolith types and approaches to assembling regolith sequences have been developed (Anand and Paine 2002). Such schemes may be extended to the Cyprus setting.

The regolith development in Cyprus reflects the young age of the terrane (exposure from Mid Miocene) and rapid tectonic uplift, which has limited the development and preservation of deep

weathering profiles. In western Cyprus  $^{14}\text{C}$  dating of shoreline samples indicates an uplift of 12 m in sporadic events over the last 32,000 years (Vita-Finzi 1993). The large volume of erosional products has been rapidly transported by gravitation and fluvial processes, and deposited to form the Pliocene–Recent valley-fill sediments. There is evidence of repeated peneplanation and valley fill deposition in river sections. Erosionally resistant gravel beds with extensive calcrete cementation, cap many ridges and give rise to inverted topographic expressions of older valley systems.

A consequence of the rapid erosion is the development of extensive outwash fluvial and colluvial deposits away from the elevated regions into the fringing valley systems often leaving the ridge lines without regolith cover. There are rare occurrences of palaeo-soil horizons that have been preserved from erosion by capping of younger colluvial or alluvial materials, but these have not normally been sampled in this geochemical program as they are only exposed in erosional gullies and deep road cuttings.

There are periodic dust storm events sourced from Africa that deposit aeolian dust across the landscape. Most of this would wash into drainage lines in the higher landscape or settle into the soil in the flatter agricultural lands. Over several thousand years this may have provided a measurable percentage of the very fine fraction sediments.

Though a detailed regolith-landform study has not been completed across Cyprus, for geochemical purposes the regolith-landform of the Republic of Cyprus can be divided into five main groups:

- (i) *Central Troodos* where the steep relief and historical deforestation have resulted in limited preservation of residual weathering profiles on ridge tops, pockets of colluvium or alluvium in small depressions or stream bed and either skeletal or on regolith cover elsewhere;
- (ii) *Troodos flanks* where the depth of colluvial cover progressively increases towards the coast but with sporadic outcrops of Troodos complex rocks and dissected Mesozoic-Cainozoic sedimentary on-lap units, and a number of sulfide mineral deposits contained within the basaltic pillow lavas;
- (iv) *The Mesaoria Plain* which is dominated by sheet wash colluvium and deltaic deposits, palaeo-river gravels and capped by recent alluvium that is commonly carbonate-cemented;
- (v) *Recent broad coastal valley* systems that ring the central uplands and are incised into the coastal peneplains, filled with coarse flood, landslide and sheet wash gravels and sand deposits;
- (vi) *The coastal fringe* in which the regolith is highly disturbed, where residential and industrial development is widespread and highly saline coastal lakes are present.

### ***Central Troodos***

Rapid tectonic uplift and ongoing seismic activity, steep relief, historical deforestation have resulted in limited preservation of residual weathering profiles on ridges and hilltops (Fig 1.36), pockets of colluvium or alluvium in small depressions or stream bed and either skeletal or no regolith cover elsewhere.

Up to 1 m of ferruginous and residual B-horizon soil profiles overlie thick C-horizon (saprolite) are observed in exposures on most ridges and mountain peaks in Troodos, although relatively fresh mafic rocks crop out in areas with high erosion rates (Fig 1.37). The preservation of in-situ weathered profiles has been limited by ongoing tectonic uplift (Fig 1.37b). In the gabbroic and ultramafic areas weathering generally extends down to depths of ~5 m, but is deeper along fractures (Fig 1.37c,d). In the mafic and ultramafic units the primary rock fabric is largely preserved through feldspars and spinels. In the forested areas a well-defined, organic-rich A-horizon up to 10 cm thick is commonly developed. This A-horizon overlies a variably-thick B-horizon characterised by Fe-oxide accumulation and slightly bleached underlying C-horizon (Fig 1.38).

In steeper parts of the Troodos terrain the nature of the regolith varies from extensive exposures of C/D-horizons to zones with thick sequences of preserved or partly preserved colluvial mantles (Figure 1.39). In some road cuttings, accumulations of landslide debris are seen to be surrounded by zones with skeletal regolith cover. Such relationships are difficult to detect without such exposures (Fig 1.39a). Scree chutes between exposed rock faces are common in the upper parts of Troodos (Fig 1.39c).

Layering in thick colluvium exposures on Troodos indicates both landslides and sheetwash to have transported regolith at various times. The sheetwashed material (dominantly massive red sands and silts) typically overlies the unsorted angular landslide colluvium (Fig 1.40). The massive red soils that occur on the Troodos flanks and even parts of the coastal fringe may be the result of post-settlement activities (such as deforestation and terracing).

### ***Troodos flanks***

The Troodos flanks contain a variety of rock types, including sheet-dykes, basalts, the CTSS and Mamonia Terranes in some places. These areas are characterised by a series of radial ridges and streams extending towards the coastal fringe or Mesaoria Plain. There is a transition zone between the TOC and CTSS units, with outliers of CTSS overlying areas of sheeted dykes, pillow basalts and Mamonia Terrane units (Figs 1.41 to 1.43) and basaltic and Mamonia Terrane inliers exposed at the base of the CTSS in various areas.

The CTSS units are typically deeply dissected on the southern and western sides of Troodos (Figs 1.44 and 1.45), with the original bedding dipping away from Troodos at up to 10°. Scree developed from the CTSS sediments tends to be finer grained than from the mafic units on Troodos. The erosion of the CTSS units has been accelerated by extensive terracing (1.46b).

In many parts of the Troodos flank areas there are areas of thin overlap of sedimentary rocks and colluvial mantles of various compositions. In Secret Valley on the south western side of Troodos, the CTSS cover (Pakhna and Lefkara Formations) progressively thin, exposing Mamonia Terrane basement. In the exposure above the dam in the Chapotami River, Pakhna Formation carbonates are 30 m thick along the ridgelines but thin out towards the flanks to exposure the underlying red-brown Mamonia Terrane Dhiarizos Group (Fig 1.47). Detailed profile sampling of the transition zone has been undertaken.

Colluvial pediment depths progressively increase away from central Troodos, with hills and ridges typically containing thin regolith cover (Fig 1.48) surrounded by thicker colluvial accumulations in lower parts of the topography. Zones of mixed regolith include cover of weathered basalts by carbonate-rich colluvium, cover of carbonates by mafic clast-rich and intermixed carbonate and mafic-rich colluvium and fanglomerates. To the northern side of Troodos, extensive fanglomerates have built up in areas and developed indurated surfaces. On the lower slopes, the fanglomerates are subparallel to the underlying CTSS sedimentary units bedding surfaces. These surfaces – both the fanglomerates and CTSS units – are now undergoing degradation and incision.

In a road cut near Coral Bay, Pegeia, the bleached calcareous sedimentary rocks are overlain by three different colluvial layers (Fig 1.49). The first is an indurated massive red soil that appears to be a product of sheetwash (rather than aeolian material although volcanic ash derived from various Mediterranean sources and dust storms from Africa and the Levant may be a contributor), overlain by poorly sorted and bedded gravels that have been recemented by carbonates and contain a calcrete duricrust, and a top unit of unconsolidated colluvium. The age relationship between these subunits is unknown, especially with respect to deforestation of Troodos.

The carbonate units along the south western coast display strong karstification (Fig 1.50a).

The high degree of deformation and alteration in combination with the underlying bentonitic clays and the steep topography in the Mamonia Terrane units is considered as one of the main factors of instability in the Pafos region. In addition, the earthquakes have played (and still play) a significant role.

### ***Mesaoria Plain***

This is dominated by sheetwash colluvium, deltaic deposits, palaeo-river gravels and discontinuously capped by alluvium that is commonly calcreted (Fig 1.51). The composition of clasts in the deposits on the Mesaoria Plain reflects both TOC and CTSS sources. It is noted that only a small portion of the samples collected in this study are derived from the Mesaoria Plain, which mainly lies within the UN zone and the occupied areas.

## *Coastal systems*

Along the coastal fringe the regolith is highly disturbed, especially where residential and industrial development is widespread. This zone includes highly saline coastal lakes (Fig 1.50 and 1.52). The salt pans are dominated by sodic clays, although there are some organic-rich layers at Akrotiri.

Along the southern coast, especially the Akrotiri Peninsula, the beach areas contain a mixture of sand and cobble-sized material (Fig 1.53). The cobbles include a range of mafic and ultramafic lithologies from the TOC (mainly gabbros and dolerites as the basalts tend to be friable) and CTSS calcarenites. The sands contain a mixture of mafics and shell materials (apart from some private beaches that have imported quartz-rich sands).

## *Soils*

The soil types reflect the influence of both geology and landforms. As a subset of the general regolith classifications in Cyprus, soil maps have been developed by the MOA based on the FAO classification scheme (FAO 1998) and summarised in Table 1.4. The distribution of the various soil types is presented in Fig 1.54.

The most characteristic soils of Cyprus are the dark red terra rosas developed over limestones and scattered in many areas of the island. The largest areas are found along the southern Mesaoria boundary from Morfou in the west to the Ammochostos district in the eastern part of the island (the Kokkinokhoria district), around Lemesos and over the fanglomerates in the western part of the Mesaoria Plain. The terra rosas have a clay content of approximately 35–45 %. The A-horizon of these soils has low CaCO<sub>3</sub> content (0–3%) whereas the lower B-horizon has high CaCO<sub>3</sub> content (up to 50%). The pH of these soils has been reported to be in the region of 7.5–8.0. Organic matter content is in the region of 1.0–2.0% (Koudounas 2001). These are highly fertile soils and are heavily cultivated (especially potatoes).

The TOC is characterised by calcaric leptosols and cambisols (in some areas also classified as skeletal). Some soils have preserved residual B-horizons.

The central plains of Mesaoria (consist of heavy alluvial soils with high clay content (40 %) and have been enriched over the years by material brought by Pedieos River and Gialias River. These soils have a high CaCO<sub>3</sub> content (up to 30 %). Due to the water shortages in the area the dry-land cultivation is dominant (mainly grain).

In the southwest districts of Pafos and Lemesos, the decomposition of limestones and marls produces white, lime-rich soils with clay content of up to 25%. These areas have been extensively cultivated with vines for centuries. Broad river valleys host fertile alluvial soils that are intensely cultivated because of the availability of ground water.

The volcanic rocks of the Troodos ophiolite are covered by a characteristic brown soil which is produced from the weathering of pillow lavas and sheeted dykes. This produces a fairly thin cover dominated by unconsolidated rock fragments. Higher on the Troodos slopes are very thin, brown/grey, sandy soils which sometimes are absent altogether, especially on gabbros. These depleted soils on the ultramafic rocks have low organic matter content (1.5–3.0 %) (Koudounas 2001) and are not able to support much vegetation except for a few species of plants that are hardy to the chemical conditions of this type of soils. Extensive terracing has taken place over hundreds of years of agricultural exploitation of the land especially on the mountainous Troodos range as well as the lower hills and parts of the Mesaoria plain.

Geochemical processes are likely to be dominated by mechanical dispersion with geochemical dispersion playing a less important role in the more elevated parts of the terrain. In the flatter plain areas the soils are dominated by alkaline soils (hence the abundance of calcrete cements) and geochemical dispersion of metals in such an environment will be limited, despite oxidation of sulfides present.

Due to the semi arid climate, areas with high Ca contents in the soil commonly form montmorillonitic clays (Nalbantoglu and Gucbilmez 2001). The calcareous soils also lead to fixation of superphosphate, and the arid climate further limits P solubilisation rendering little purpose in much P addition via superphosphates to the soils (Krentos and Orphanos 1979).

### ***Soil mapping***

The soils of Cyprus reflect the geology, geomorphology and climate of the island, hence the first soil classification system developed in the 1960s was mainly based on the formation, origin and parent material of Cyprus soils (Hadjiparaskevas 2005). The initial series of 1:5,000 soil maps was subsequently combined into the 1:200,000 General Soil Map of Cyprus. Soils were classified mostly as “red”, “sedimentary” and “alluvial or colluvial”. Most classification schemes included groups of soil series whose names reflected their parent geological formations.

In 1970 the unified international scheme of soil classification resulted in the FAO soil classification system, with horizon classifications including mollic, ochric, argillic, natric, cambic, calcic and gypsic. More recent attempts to map the soils of Cyprus generated a new 1:250,000 general map (Markides 1999), based on previous classifications was adjusted to the new FAO classification system (FAO 1998, Haziparaskevas 2008). Under the FAO system a number of soil orders have been recognised: lithosols, regosols, rendzinas, solonchauks, solonetz, vertisols, cambisols and luvisols.

In areas where soils have not been surveyed, extrapolation and photo interpretation methods with remote sensing imagery support have been used to map soils. A number of important information sources have been used in the preparation of the soil map of Cyprus including the 1:250,000 Geological Map of Cyprus (GSD 1995) which has been used to identify likely soil parent materials.

### ***Regolith-landform model***

On the basis of the sampling and following from the previous description, a preliminary regolith-landform model for Cyprus has been developed and can be compared with the model developed as part of the FOREGS project (Figs 1.55 and 1.56).

Apart from residual soils on restricted parts of ridges on Troodos, the majority of regolith in Cyprus has undergone some degree of transportation. Whereas regolith in pockets and valleys on Troodos may have been transported <500m, the material in the foothills and towards the coast may have been transported tens of kilometres. The accumulations of regolith at the base of the steeper slopes of Troodos and generally within the valleys would represent more a stream sediment than either a soil or colluvium.

The CTSS cover and colluvium are generally thin around the upper flanks of Troodos, permitting inliers of mafic and ultramafic rocks to crop out. Even on the lower slopes, there are outcrops of the Mesozoic cover surrounded by colluvium and sheetwash deposits. The result of this regolith-landform setting is that much of the colluvium contains a mixture of parent materials. This scheme can be compared with simpler models that divide the landforms into residual, transported and depositional (Fig 1.57 and 1.58) which correspond with Central Troodos, Troodos flanks and the Mesaoria Plain/Coastal fringe in the context of this study.

In terms of regolith materials a B-horizon is present in most areas, although this is generally not a residual B-horizon but the result of accumulation of transported material down-slope due to sheet wash erosion. This is generally referred to as transported B-horizon - B(t) - due to its local derivation from upslope. On Troodos the B-horizon is generally absent and the skeletal A-horizon (more of an A/C-horizon) directly overlies the C-horizon (Fig 1.59). In such situations, sampling is most effective on the face of road cuttings.

In the transition from the coast to Troodos, the soil (or regolith) profile varies from relatively thick C and B-horizons (although the nature of the regolith in which the B-horizon develops changes significantly) to a general absence of B-horizon and a thin C-horizon (Fig 1.60).

Whereas each of the main regolith component materials will have highly variable geochemistry, depending on processes such as reweathering, the ratios of certain incompatible elements inherited from the parent lithologies is preserved (Scott 1999). This allows some estimation of the relative proportion of regolith sources.

### **1.2.3 Climate**

Cyprus has a typical Mediterranean climate, incorporating hot and dry summers from mid-May to mid-September and rainy, rather changeable, winters from November to mid-March. These seasons are separated by short autumn and spring seasons of rapid change in weather conditions.

The central Troodos Massif, which rises to over 1900m and to a lesser extent the long and narrow Keryneia Mountain Range with peaks of about 1,000 m, play an important part in the climate of Cyprus. In the summer the island is mainly under the influence of a shallow trough of low pressure extending from the great continental depression centred over southwest Asia. It is a season of high temperatures with almost cloudless skies.

In winter Cyprus is near the track of frequent small depressions which cross the Mediterranean from west to east between the continental anticyclone of Eurasia and the generally low pressure belt of North Africa. These depressions give periods of disturbed weather usually lasting 1–3 days and producing most of the annual precipitation between December and February.

### ***Rainfall***

The average annual precipitation increases up the south-western windward slopes from 450 mm p.a. to nearly 1,100 mm at the top of Troodos. On the leeward slopes annual precipitation decrease steadily northwards and eastwards to 300 – 350 mm in the central plain and the flat southeastern parts of the island. The narrow ridge of the Keryneia range produces a relatively small increase of rainfall to nearly 550 mm along its ridge at about 1,000m.

The Troodos Ophiolite has a very significant role in the water resources of the island. Most of the rocks, especially the gabbros and the sheeted dykes are good aquifers due to fracturing. The perennial rivers running radially are feeding the main aquifers in the periphery of the Troodos and the plains.

Rainfall in the warmer months contributes little or nothing to water resources and agriculture. The small amounts which fall are rapidly absorbed by the very dry soil and soon evaporated in high temperatures and low humidity. Autumn and winter rainfall is variable. The average rainfall for the year is ~480 mm but it was as low as 182 mm in 1972/73 and as high as 759 mm in 1968/69. Snow occurs rarely in the lowlands and on the Keryneia range but falls frequently in winter above 1,000 m (Dec–Apr).

Statistical analysis of annual rainfall in Cyprus reveals a decreasing trend over the last 30 year and rising temperatures (0.8°C).

### ***Temperatures***

Cyprus has a hot summer and mild winter, modified by altitude which lowers temperatures by about 5°C per 1,000m and marine influences which give cooler summers and warmer winters near coastlines (especially on the western coast). The seasonal difference between mid-summer and mid-winter temperatures is 18°C inland and 14°C on the coast. Differences between day maximum and night minimum temperatures are quite large especially inland in summer with winters 8–10°C on the lowlands and 5–6°C on the mountains, increasing in summer to 16°C on the central plain and 9–12°C elsewhere.

In July and August the mean daily temperature ranges between 29°C on the central plain and 22°C on the Troodos mountains, while the average maximum temperature for these months ranges between 36°C and 27°C respectively. In January the mean daily temperature is 10°C on the central plain and 3°C on the higher parts of Troodos with an average minimum temperature of 5°C and 0°C respectively.

Open sea temperatures rise to 27°C in August and are above 22°C during the six months June to November. During each of the three coolest months, January to March, average sea temperature falls only to 16 or 17°C. Near all coasts in water three or four metres deep temperatures are very similar to those of the open sea and lie within the range 15–17°C in February and 23–28°C in August.

Seasonal change in mean soil temperatures is from about 10°C in January to 33°C in July at 10cm depth and from 14°C–28°C at 100cm depth. Above 1,000m these mean seasonal values are lowered by ~5°C.

In the central plain and eastern lowlands the average number of hours of bright sunshine for the whole year is 75% of the time that the sun is above the horizon. Over the whole summer six months there is an average of 11.5 hours of bright sunshine per day whilst in winter this is reduced only to 5.5 hours in the cloudiest months, December and January.

## **Winds**

Over the eastern Mediterranean generally surface winds are mostly westerly or southwesterly in winter and northwesterly or northerly in summer. Winds are generally of light to moderate strength and rarely reach gale force. Wind direction is quite variable with orographic and local heating effects playing a large part in determining local wind direction and strength. Diurnal differences of temperature between sea and land in periods of clear skies in summer cause considerable sea and land breezes. Whilst these are most marked near the coasts they regularly penetrate far inland in summer reaching the capital, Nicosia, and often bringing a welcome reduction of temperature and also an increase in humidity.

### **1.2.4 Vegetation**

Cyprus has relatively high plant diversity due to the geographic location of the island and its size. The isolation of Cyprus from the mainland since the Messinian salinity crisis and the diversity of climatic conditions and geomorphology also contribute to diversity (Figs 1.61 and 1.62).

The indigenous flora of Cyprus includes 1,614 species or 1,749 taxa at variety level of which 111 species or 150 taxa are endemic to the island. Introduced species currently includes about 240 taxa. The dominant flora are the annuals (49%) and perennial herbs (38%); however, the vegetation and the landscape are visually dominated by trees and large shrubs and small shrubs which represent only 7.5% and 5.5% of the flora respectively. The most important centres of plant diversity and endemism are the National Forest Park of Troodos, hosting 74 endemic plants, while the whole Troodos Massif hosts 95 endemic taxa. Other important areas for endemics are the Keryneia Range and Akamas Peninsula with 62 and 54 endemic taxa respectively. Some notable flora elements are the endemic trees *Cedrus brevifolia* and *Quercus alnifolia* forming endemic forest types and also the endemic shrub *Bosea cypria*, believed to be an element of the Tethyan-Tertiary period.

The long history of human influence has had a significant influence on the development of the landscape, habitats and the flora of the island through farming, introduced plants and animals, mining and forest exploitation. High forests cover about 17% of the island, mainly on the Troodos and Keryneia Ranges. The hills are covered by shrubs alternating with built-up areas and cultivations. The plains of the lowlands are covered by cultivation (about 45% of the island) and habitations, but there are also small areas of natural habitats locally. The natural and semi-natural vegetation types as well as the cultivations, especially traditional ones such as tree orchards, constitute important habitats for the flora. The vegetation distribution and classification patterns in Cyprus are indicated in Fig 1.63.

Thermophilous Calabrian pine (*Pinus brutia*) forms the most extended forests, from sea level to about 1400m, and covers the Troodos and Keryneia Ranges and parts of Akamas Peninsula. Cypress (*Cupressus sempervirens*) forests occur mainly on Pentadaktylos. The semi-deciduous Cyprus oak (*Quercus infectoria* subsp. *veneris*) forms only remnant stands especially at the western part of the island. Black pine (*Pinus nigra* subsp. *pallasiana*) forest and the stands of mountain junipers (*Juniperus foetidissima* and *J. excelsa*) are restricted to higher altitudes of Troodos, whereas the endemic Cyprus cedar (*Cedrus brevifolia*) forest is confined to a small area of Pafos forest on the Troodos range. The endemic golden oak (*Quercus alnifolia*) occurs under the conifers or in pure stands, at altitude of 700 m and above, all across the Troodos range.

Various types of shrub communities are dominant in the thermo-Mediterranean and semi-arid zones. *Olea europaea* (olive tree) and *Ceratonia siliqua* (carob tree) maquis as well as kermes oak (*Quercus coccifera* subsp. *calliprinos*) tall shrubs are rather rare, while the low and spiny phrygana are the most common vegetation type. Phoenician juniper (*Juniperus phoenicea*) is typical of the coastal zone. Dry grasslands develop in pastures and in shrub and forest openings. A unique peat-grassland (a fen) occurs at only two locations on Troodos.

The sandy coastal zone is generally narrow, with ammophilous communities on low embryonic and shifting dunes. Extended dune systems, including stabilised dunes with shrubs and dune slacks, develop at few places (Apostolos Andreas at Karpasia, Akamas), notably in connection with halophytic wetlands (Ammochostos, Agia Eirini and the salt lakes of Akrotiri and Larnaka).

A discontinuous and narrow line of riparian shrub and forest develops along the numerous streams that dissect the island, often in the midst of cultivated land. Standing fresh water bodies are only artificial storage basins and dams, yet hydrophilous vegetation has established at most of them. The rocky

habitats include chasmophytic communities developing on limestone (Pentadaktylos, Akamas) and igneous rocks (TOC). There are endemic serpentinophilous chamaephytic communities in Troodos, Akamas and the Limassol Forest.

### 1.2.5 Hydrogeology

A hydrogeological classification, based on geology and topography, is presented in Fig 1.64.

The clastic sediments are the most important aquifers of the island. These are mostly developed in broad valleys and river deltas. Such aquifers are those of western and eastern Mesaoria, Akrotiri and Pafos. Aquifers are also developed in porous rocks such as calcareous and gypsiferous units characterised by karst, and in fractured rocks such as chalks and limestones. Up to 1960 the TOC was considered to be an aquitard. After systematic groundwater exploration, however, the TOC proved to be one of the most important aquifers on the island. Secondary porosity, developed through fracturing, faulting and tectonism of the TOC rocks, resulted in the development of fractured aquifers in some gabbros and dolerites.

The fracturing and karstification of the allochthonous limestones made them excellent aquifers and gave rise to a number of significant springs at the foothills of the mountain range, close to the contact of the limestones with the underlying marly-argillaceous rocks.

### 1.2.6 Human history

Cyprus has experienced a long history of human civilisation, commencing in the early Neolithic Period (~12,000 BC) following the last Ice Age, when the first seafarers crossed the narrow straights from the neighbouring mainland to the coastal areas of the island. The deep cultural heritage of Cyprus is preserved in a wide variety of archaeological and modern cultural and religious sites.

As a result of both its position at the crossroads of vital sea routes in the eastern Mediterranean and its natural resources (minerals, wood, water and fertile soils), Cyprus was influential in the ancient world for millennia. It was a place of mixing of a diversity of cultures stretching from Asia Minor, Greece, Egypt, Mesopotamia and Syria to areas in the western Mediterranean. Control of Cyprus has reflected the dominance of various cultures, empires and countries in the Europe–Middle East region, and has culminated in a number of rich archaeological sites. It has also left an environmental imprint in terms of extensive deforestation and mineral exploitation.

The first civilisations on Cyprus were Neolithic (7000–3900 BC), with Cu mining commencing in the Chalcolithic Age (3900–2500 BC) and expanding during the Bronze Age (2500–1050 BC) (Pyatt 1999). Evidence of ancient metallurgical sites is associated with a number of the larger Cu deposits, especially west of Polis near the coast (Raber 1984). During the Late Bronze Age the island was a centre of interest for the Hittites, Syrophenecians, Egyptians and Mycenaeans from Greece because of its importance as a major source of Cu and producer of bronze. The island's wealth in Cu and other goods attracted the first Mycenaeans during the 14<sup>th</sup> century BC, who established commercial outposts in coastal areas. Pafos, Salamis, Kition and Kourion emerged as city-kingdoms. After the collapse of the Mycenaean centres in the Aegean in the 12<sup>th</sup> century BC, Greek populations moved to Cyprus, initiating the process of Hellenisation of the island. Cypriot kingdoms tried to preserve their independence but came under the domination of Assyria, Egypt and Persia. King Evagoras of Salamis (who ruled during 411–374 BC) attempted to unify the island through a revolt. After a great siege he concluded peace with Persia and lost control of the island. Alexander the Great made Cyprus an integral part of the Hellenistic world, bringing about the establishment of unified rule.

Copper mining continued throughout the various historical periods (mainly defined by the occupying powers) and peaked during the Late Bronze, Cypro-Classical to Early Hellenistic, Late Roman to Early Byzantine, Medieval (peaking during the 15<sup>th</sup>–16<sup>th</sup> Centuries) and modern eras (Koucky and Steinberg 1982). The decline of mining during the latter parts of the Roman Empire has been attributed to either the health effects of mining operations and smelting or a lack of wood to fire the smelters (Pyatt 1999). Cyprus was also a significant source of timber for ship building (Ezekiel 27:6).

In the period 58 BC–330 AD Cyprus was part of the Roman Empire. During the missionary journeys by Paul and Barnabas (Acts 4:36, 13:4 and 15:39) the Proconsul Sergius Paulus was converted and became one of the first Christian Roman governors. After the division of the Roman Empire into two

parts, Cyprus came under the Byzantine Empire. Earthquakes during the 4<sup>th</sup> century completely destroyed the main cities.

The Crusades returned European influence to the Near East. Cyprus became part of the patrimony of a Frankish dynasty, and was a crucial base for many of the military operations in the nearby Levant (Tyerman 2007). The island was subsequently inherited by Venice during its period of ascendancy as a trading and naval force in the eastern Mediterranean (Norwich 2003) before being occupied by the Ottomans in 1571. The island remained under the Ottoman rule until 1878, when Britain assumed administration of the island.

In 1914 Britain annexed Cyprus after the Ottoman Empire entered World War I. In 1923, under the Treaty of Lausanne, Turkey renounced any claims to Cyprus, and in 1925 it was declared a Crown colony. Following World War II an armed liberation struggle broke out (1955–1959). Under the terms of the Zurich-London Treaty, Cyprus became an independent republic on 16 August 1960. The 1960 Constitution of the Cyprus Republic proved unworkable and the Turkish-Cypriot ministers withdrew from the Cabinet. In July 1974 a coup was staged in Cyprus by the Military junta in Greece to overthrow President Makarios. On 20 July 1974 Turkey launched an invasion of Cyprus, and has occupied 37% of the island since then. Of the total Greek–Cypriot population, 40% sought refuge south of the subsequent UN Green Line. In 2004 the entire island of Cyprus was admitted to the EU and adopted the euro as its currency in 2007.

The deep cultural heritage of Cyprus is preserved in a wide variety of archaeological and modern cultural and religious sites (Fig 1.65).

### 1.2.7 Landuse

Landuse in the Republic of Cyprus can be subdivided into the following main classifications (Fig 1.66):

- *Undeveloped forests.* Apart from villages, much of Central Troodos and the north western flanking areas are dominated by undeveloped forests, although most of the forests have been relogged on a number of times during history.
- *Scrubland (garique-maquis) and degraded land.* This occupies much of eastern Troodos and the southern Troodos flanks as far as the coast (excluding parts of the Polis Valley and coastal fringe around Pafos and Lemesos). There are small areas with vineyards and some cropping where soil derived from the basalts has accumulated or on terraces cut into the calcareous units of the CTSS (Fig 1.67). Much of the terracing on the southern side of Troodos appears to have been abandoned and is overgrown with scrub.
- *Cropping areas.* These are mainly found in the eastern end, between Kokkinokhoria and the edge of the Troodos Mountains. The principal crop is wheat, followed by olives and vineyards. There more intense farming with irrigation west of Lemesos on the Akrotiri Peninsula and in the northern Polis Valley. Whereas ploughing is common (Fig 1.68a and d), there does not appear to be extensive use of fertiliser outside the areas of intense farming.
- *Urban areas* – incorporating industrial, commercial and residential use. The main industrial areas are located in the vicinity of Larnaca and Lemesos. New construction activity is most prevalent along the southern coastline, including the Lemesos area and between Pafos and Coral Bay.
- *Mining areas.* Environmentally the mines with greatest environmental impact are the Cu mins that ring Troodos in the pillow basalts. Other mining operations include limestone quarries (mainly for cement), and the abandoned Cr and asbestos deposits (Fig 1.69).

The mineral deposits have been discussed in Section 1.2, but further consideration of the status of these sites is relevant to the subsequent design of the current study. The Cu mines are (or were largely open cut operations (Fig 1.70). The Cyprus-type mineralisation mainly contains pyrite-chalcopyrite, with low amounts of As, Pb and Zn. This style of mineralisation is common throughout the pillow basalts, with umbers, ochres, small patches of sulfide mineralisation and secondary Cu minerals common (Fig 1.71).

The Fe content of pyrite and chalcopyrite is the main cause of acid mine drainage (AMD). The effects of AMD are similar in each of the abandoned Cu mines. This includes accumulation of low pH, high Cu-Fe-sulfate mine waters in the pits (Figs 1.72 and 1.73) derived from both groundwater leakage and rainwater, and loss of some mine waters to the local groundwater and surface waters.

Demetriades *et al.* (2006) have estimated that there are over 200 Mt of mine wastes in Cyprus derived from the last 100 years of mining. All the mines contain extensive waste piles and tailings the largest probably being the Skouriotissa Mine that is the only mine still in production. In some cases, such as Limni, the tailings and waste have been dispersing off-site (Fig 1.73b), though there is a recent action to relocate much of the tailings back to the Limni or nearby pits. In other cases the local stream contains large amounts of AMD and Cu contamination with Cu sulfate effluences and limonite (Fig 1.74).

Differentiating natural occurrences of elevated Cu and low soil pH due to sporadic hydrothermal sulfide mineralisation in the basalts, from contamination due to mining activities is a key issue for Cyprus. To assist with resolving this question, the current study has undertaken more detailed sampling and analysis in the vicinity of selected Cu mines (Limni, Skouriotissa, Mathiatis and Kalavastos).

Potential contamination derived from urbanisation, industry and waste disposal are well-documented in the literature. At the scale of sampling adopted for this study intense point sources of contamination may be detected, but detection of more diffuse sources or dispersion patterns are more likely to be detected.

## 1.2.8 Environment

### *Human effects*

Human habitation has significantly affected local environments on the island of Cyprus (Figs 1.75 to 1.77). Exploitation of natural resources such as wood for the supply of the necessary energy for extracting Cu, water and soil for food production, have taken a massive burden through the years.

Some sources estimate that the island was deforested and reforested a staggering 16 times between 2000 BC and 500 AD when the production of Cu reached 200,000 t via pyrometallurgical processes (Constantinou 2010). The marks of the extraction processes for Cu throughout the years are still evident and scattered across the island. The issue of regenerating abandoned mining areas is today a very important one with some examples of regeneration in progress. Visual evidence of the human impact on the natural environment of Cyprus is the extensive terracing systems applied on mountainous slopes to facilitate agricultural exploitation.

Today intensive agricultural as well as stock raising processes which in some cases are concentrated in relatively small areas of the island are among the highest threads of pollution of soil and underground water reservoirs. The use of large quantities of agrochemicals in the form of soil enhancers and pesticides as well as the production of large quantities of liquid and solid waste from stock raising activities are big contributors of chemical pollution of soil and water. Industrial processes of manufacturing and secondary processing have also been known to contribute to chemical pollution. Urban development of the cities has taken a massive boost, especially after 1974, and has contributed in a booming of solid urban waste production. The problem has been alleviated somewhat by the introduction of a legal framework and organised waste disposal sites and the introduction of recycling during the last few years.

### *Environmental regulations*

The Republic of Cyprus Legal framework has recently been reinforced both due to the accession of Cyprus to the European Union but also through reinforcement of domestic legislation. The EU legislation on Water and Soil Pollution Control {106(I)/2002, 160(I)/2005, 76(I)/2006} provides the main framework for the control of water pollution. Most EU directives and the environmental regulations in the water sector (and some in the waste sector) are promulgated through Ministerial Orders and Council of Ministers Regulations under this EU law. These include directives dealing with nitrates, urban wastewater treatment, dangerous substances, water extracted for drinking and sludge use in agriculture (amongst others).

The Integrated Pollution Prevention and Control (IPPC) Directive aims at minimizing pollution of air, water and soil from industrial and agricultural activities with high pollution potential (energy industries, production and processing of metals, mineral industry, chemical industry, waste management and livestock farming). This is achieved through a system of licenses, linked to integrated pollution prevention and control aiming at improved management and control of production processes. The IPPC Directive has been transposed into national legislation by the Integrated Pollution Prevention and Control law. The law serves as a link in order to achieve integration and is complimentary to the Air and Water Pollution Control laws. It is implemented through the Water and Soil Pollution Control law 106(I)/2002 and the Air Pollution Control law 187(I)/2002.

According to the Environmental Liability with Regard to the Prevention and Remedying of Environmental Damage Law (2007) which incorporates the “polluter pays” principle, economic operators should pay the cost for remedying environmental damage which includes damage to water and therefore soil resources.

The laws and regulations required damaged natural resources to be restored to baseline conditions by performing primary, complementary and compensatory remediation. The “baseline conditions” are generally unspecified. Under such laws, the economic operators are liable (a) for damage or imminent threat of damage from occupational activities specified in the law and (b) damage or imminent threat of damage from other occupational activities. The liability as to the second category arises only where the operator is at fault or found to be negligent. If the competent authority takes the remediation measures itself, it may recover the costs from the polluter.

The protection of soil has received significant attention from the EU since 2005 when a thematic strategy for soils was proposed by the Commission. The 6<sup>th</sup> Environment Action Programme has mandated development of seven thematic strategies, including a strategy on the protection of soil.

The overall objective is the protection and sustainable use of soil is based on the following guiding principles:

- Preventing further degradation of soil and preserving its functions.
- Restoring degraded soil to a level that enables at least its current or intended use, which entails considering the cost implications of restoration.

Although finalising such a strategy has a long way to go before it becomes legally binding, the Commission has given degradation of soil the same importance as degradation of water and air.

It is noted that there is no specific institution dealing exclusively with the environmental aspect of soils. Assessment and regulation depends on cross-departmental responsibilities within Cyprus and with other international soil centres.

The best known set of regulatory guidelines and limits for soil contaminants are the so-called Dutch standards or intervention levels, as set out in the framework of the Dutch Soil Protection Act. In recent years these guidelines have been simplified to a set of single-value intervention or indicative levels for metals, organics and other materials (Table 1.5). Similar approaches have been adopted by other countries, although it is noted in the National Inventory of Potential Sources of Soil Contamination in Cyprus (Demetriades *et al.* 2006) that there are “*no guidelines for soil, developed by the European Commission. Each country has its own national soil guideline values*”. This is demonstrated in the Table 1.6.

Demetriades *et al.* (2006) recommended a risk-based approach to setting soil guideline values for various landuse types (*Risk-Based Soil Guideline Values* or RBSGVs) and their values designed for metals in Cypriot soils are tabulated for industrial and residential areas in Table 1.7 (most values have been adjusted as the concentrations in the original table appears to be in µg/kg and not mg/kg).

### 1.2.9 Previous geochemical studies in Cyprus

A number of geochemical studies have been conducted in Cyprus. The majority of these are litho-geochemical and petrological studies of the main tectono-stratigraphic packages (principally the TOC). There have been a limited number of geochemical studies related to mineral exploration (EMED 2008), and these have focused on litho-geochemistry rather than soils and sediments. There have been

some environmental geochemical surveys related to current and historical mining operations, and industrial sites.

### **Lithochemistry**

Lithochemical studies in Cyprus demonstrate extreme differences between what may be considered end-member lithologies: the ultramafic units within the TOC, the mafic intrusive and extrusive units of the TOC and Mamonia Terranes, the Cu-mineralised basalts and the dominantly calcareous units of the CTSS.

The ultramafic core of the TOC is characterised by high-Mg and low alkalic lithologies with elevated Ni (in olivine) and Cr (in spinels and pyroxenes) relative to the associated sheeted dykes and pillow lavas (Table 1.8). MgO contents may exceed 30% in some of the ultramafic units, including the serpentinites. The plagiogranites, formed with associated hydrothermal fluids, are the only high-Na igneous rocks (Kelley and Robinson 1990).

Spinel from the chromitite deposits have flat chondrite-normalized PGE patterns except for the distinct negative Pt anomalies (Büchel *et al.* 2004). Concentration ranges of PGE in chromitites are presented in Table 1.9.

The lithochemistry of the dolerites, gabbros and basalts of the TOC and Mamonia Terranes has been well-characterised in previous studies. The TOC pillow lavas and the Mamonia Terrane mafic lavas are low Na+K (Table 1.10) and sit within the basalt to basaltic andesite fields of the TAS diagram (Fig 1.78). The extensive lithochemical database for the TOC, assembled by Eastern Mediterranean Minerals (EMED 2008), indicates most of the volcanics plot in the basalt to basaltic andesite fields (some of these have been subjected to various types of alteration), with a portion plotting in the more alkaline trachyte-basalt to trachyte fields.

MORB-normalised data indicates the Upper Pillow Lavas are slightly depleted in Ni and enriched in Ba, whereas the Lower Pillow Lavas are strongly depleted in Cr and Ni, weakly depleted in Co and enriched in alkalis and REE (Fig 1.79). REE abundances are lower than most MOR basalts and basaltic andesites (Thy *et al.* 1985) with slight HREE enrichment and a minor Eu depletion when chondrite normalised (Fig 1.80). This suggests a tholeiitic island arc rather than primitive MOR basalt association. The basaltic andesites of the Upper Pillow Lavas have glasses that are relatively Mg-rich [ $Mg/(Mg+Fe) = 0.59-0.64$ ] and low  $Na_2O$  (1.8%) (Fig 1.81). The Lower Pillow Lavas display lower Mg contents and contain chromite (Thy and Moores 1988).

The mafic units of the TOC have relative consistent Ti/Zr (~100) and Ti/Y (~200) ratios, whereas the Mamonia Terrane basalts display Ti/Zr ~60 and Ti/Y ~500. The upper pillow lavas are more mafic, and have higher Cr and lower Zr contents, than the lower pillow lavas. Such systematic variations in the immobile elements may assist in characterizing parent lithologies to the soils.

The EMED (2008) data indicates low  $P_2O_5$  (<0.1%) values for all intrusives and volcanics except for siltstones and umbers (Fig 1.82).

In the Mamonia Terrane, magma evolution has generated a sequence in the volcanic units from depleted tholeiites to trachytes (Lapierre *et al.* 2007). The tholeiites display both low REE and no enrichment trends, whereas the alkali basalts and trachyte show distinct enrichment in LREE and incompatible HFSE elements (Nb, Ta, Th and Zr), and relative depletion in the siderophile elements (Cr, Co, Ni and V) (Table 1.11 and Fig 1.83). The Dhiarizos Group basement pillow lavas are alkalic (Swarbrick and Robertson 1980; Malpas *et al.* 1992). The volcanics of the Ayia Vavara Formation of the Mamonia Terrane are albitic though most of the basalts have been subjected to amphibolite alteration (Malpas *et al.* 1992). The volcanics of the Mamonia Terrane range from tholeiitic basalts to trachytes

Umbers are precipitates from hydrothermal solutions associated with basaltic pillow lavas (form of mudstone). Geochemistry of some umbers and associated radiolarian mudstones and overlying carbonate-rich sedimentary units are presented in Table 1.12. The umbers, and associated sediments and ochres are REE-enriched, with Ce depletion indicative of the REE source being leached by seawater of tholeiitic lavas (Robertson and Fleet 1976). The elevated REE contents and relative LREE enrichment, along with Ce depletion, in the umbers is indicative of reaction between seawater and the precipitating Fe-oxides and a seawater source for the REE (Robertson and Fleet 1973). Relative to the

pillow basalts, the umbers are enriched in a number of siderophile elements, including Mn, Cu, Ni, V and Zn).

The results of the lithochemical analysis are consistent with radiometrically-determined U, Th and K (Tzortzis and Tsertos 2004) (Table 1.13).

The CTSS units are generally enriched in Ca and Si, with subordinate Al and Fe. Terra member of Pakhna Formation may have been originally dolomitic but diagenesis has removed most of the Mg (Follows 1992). Some of the sediments deposited in the four Messinian-Pliocene basins (including the Pissouri and Polemi Basins) contain gypsum and palaeosols, and this is indicative of a period of cycling between sub-aerial exposure and hallow highly saline shallow marine waters cut off from the ocean during the Messinian Salinity Crisis (Rouchy *et al.* 2001).

Indicative values for carbonate-rich units within the CTCC are presented in Fig 1.84. The selenitic carbonates have significantly lower values than the other carbonate units.

### **Mineral exploration data**

Despite the importance of Cu mining to Cyprus up to the 1990s, there have been few exploration geochemical studies published.

In a reconnaissance rock geochemical survey, 369 samples of basaltic pillow lavas (centres) and 1,250 samples of intrusive dykes were collected from a 20 km<sup>2</sup> zone around the Mathiatis pyrite-Cu deposit (Pantazis and Govett 1973). They were arbitrarily divided into an inner (zone within 0.5 km of the pit, but excluding samples from the pit itself) and outer zone extending to 2.5 km from the pit. Some elements (including Cu) displayed little lithochemical variation between the two zones, whereas others (such as Zn) displayed a population shift for the inner zone samples (Fig 1.85). By use of discriminant and determinative functions, samples could be classified on their Cu+Zn+Co+Ni contents into an “anomalous” class near the mine and a local “background” class away from mineralisation. Similar results were obtained for Skouriotissa (Govett 1972).

Background values for Hg in soil are 0.008–0.012 mg/kg but values up to 0.1 mg/kg occur in the vicinity of faults that intersect buried sulfide mineralisation at Sha and Mitsero (Friedrich *et al.* 1984) (Fig 1.86). Elevated Hg is typically accompanied by elevated Ba, Cu and Zn (values >2000 mg/kg) especially where the depth to mineralisation was under 50 m.

In vicinity of Limni Mine, Pyatt (2001) found significant increase in the Cu contents of organs of *Acacia retinoides*, but less increase in *Eucalyptus torquata* between a few contaminated and a presumed back ground site.

### **Contaminated sites**

Various studies have been conducted on contamination related to the old Cu mines and processing plants in Cyprus, as these constitute the largest source of metals contamination. Averkiou (1997) demonstrated that the streams surrounding the Skouriotissa mine were heavily affected by acid mine drainage and Cu contamination (into the low % levels). Contamination surveys have also been conducted in the vicinity of the Limni Mine and elsewhere. There is an extensive literature on the characteristics, effects and modelling of acid mine drainage related to sulfide-bearing deposits (e.g. Plumlee *et al.* 1999; Seal and Hammarstrom 2003; Balistrieri *et al.* 2007), including studies relevant to Cyprus-type basalt-hosted, hydrothermal pyrite-chalcopyrite deposits. Unfortunately, historical records on mining activities and methods are very limited prior to the middle of the last century.

There have been a limited number of contamination studies related to metals, outside mining, published in Cyprus. Previous studies are partially covered in the National Inventory of Sources of Soil Contamination in Cyprus by Demetriades *et al.* (2006a,b), including an extensive table of various industry types and the potential contaminants. A study of the multi-function Vasiliko Industrial site indicated a number of locations with highly elevated As, Cu, Pb and Zn related to various industrial processes (Table 1.14).

## 1.3 THE GEOCHEMICAL ATLAS OF CYPRUS

### 1.3.1 Project objectives

The principal objective of this project is the generation of a general-purpose, multi-element geochemical atlas of the Republic of Cyprus derived from a high density soil sampling survey. The project examines a number of factors controlling the distribution of elements in the soil and will provide Cyprus-specific data on soil geochemistry and mineralogy to assist in environmental planning and policies.

The project objectives are consistent with those of the global geochemical mapping project (IGCP 360) and the recently completed geochemical atlas of Europe, though the Cyprus Atlas is being undertaken at a high sampling density.

The project will also form the basis to ongoing geochemical and environmental research projects for Cyprus as well as development of geochemical data interpretation and data processing methods.

### 1.3.2 Design principles

Whereas the main recommendations of IGCP 259 and 360 and the FOREGS Geochemical Atlas of Europe form the basis for the design and implementation of this project, some specifications (including the sampling plan and regolith media) have been modified to account for the specific characteristics of the landscape, regolith and landuse in Cyprus. In particular, the Geochemical Atlas of the Barents Region (Salminen *et al.* 2004), undertaken by the geological surveys of Norway and Finland, has formed a useful model to consider in the design of the current survey.

The FOREGS sampling protocols were designed to accommodate continental scale surveys and terrains that are not typical of most of Cyprus or other arid to semi-arid environments found in the Mediterranean region. Their general strategy was however be adapted to establish a protocol more suited to the much higher density sampling proposed for Cyprus and the tectonically active, highly eroded and semi-arid terrain that characterises Cyprus.

Although previous geochemical atlases (both environmental geochemical) have utilised a wide variety of sampling media, the two media most appropriate to the Cyprus setting are soils and stream sediments. Whereas stream sediments would provide a systematic coverage of Cyprus, they provide less direct correlation between parent lithology and derived regolith. However, a series of 89 stream sediments representing the major streams draining Troodos was collected in association with this project).

The nominal density of one site per 1 km<sup>2</sup> renders this a very high density regional survey. This density provides a statistically significant number of sites within each of the major geological units and landuse zones. A more detailed discussion of these protocols is provided in Section 2.



## 2 PROJECT IMPLEMENTATION

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In this section the implementation of the project from design considerations to the sampling and analytical programs, database setup and training are presented. The quality control aspects of the project are provided in Section 3 and data processing method in Section 4.

### Project Management and Operational Controls

The technical components were supervised and implemented by the principal UNSW consultants (A/Prof D.R. Cohen and Dr N.F. Rutherford) in consultation with the GSD technical representatives (Dr A. Charalambides and subsequently Dr A. Zissimos) (Fig 2.1). Project management was provided by the GSD through its director (Dr P. Michaelides and subsequently Dr E. Morisseau), ACDS (A. Demetriades) and UNSW Global (J. Arneil and A. Ahuja), with general oversight by the project/tender committee listed in the acknowledgements.

The project implementation team and timeline for project advisor activities are set out in Table 2.1 and Fig 2.2.

### 2.1 PROJECT WORKPLAN

The project was divided into nine major tasks, based on the original terms of reference (TOR) and proposal, with minor modifications to the project design approved on the basis of the First Progress Report (Implementation) that followed completion of the orientation survey.

The progress on the following key tasks during the project is summarised in Fig 2.3.

Task 1	Orientation survey and detailed project design
Task 2	Sampling and field data collection
Task 3	Sample processing
Task 4	Physical and chemical analysis
Task 5	Quality assurance and control program
Task 6	Compilation of data
Task 7	Data processing and statistical assessment
Task 8	Training
Task 9	Reporting

#### 2.1.1 Task 1 – Orientation survey and detailed project design

The key components of Task 1 are summarised in Fig 2.4.

##### *Preliminary site assessment*

Site assessments and an orientation suite of 157 sites was collected in May 2006, covering a broad transect from Pafos to Nicosia and around Larnaca, Kokkinokhoria, Dali and Pano Arodes (Fig 2.5). Further site examination without sampling was conducted at various locations along the southern coastline. This assessment included:

- (i) Composition, nature and depth of soil cover in relation to local bedrock, topography and general landscape features (the regolith-landform relationship).
- (ii) Mapping requirements, including topographic maps and air photographs.
- (iii) Evaluation of general site accessibility and the basis for the overall sampling sequencing.
- (iv) Testing of sampling methods and timing.
- (v) Review of other logistical issues.

Coupled with the site assessment was a series of tests at UNSW on a small suite of samples to establish and validate sample processing and analytical protocols for use in the main survey.

### ***Sampling distribution – main survey***

Following from the principles outlined in Section 1 and results of the orientation study, a sampling strategy tailored to the regolith-landform settings of Cyprus was developed. Variations from the FOREGS sampling strategy reflected the higher density of the survey being conducted in Cyprus and the different physical and landuse characteristics of the terrain between northern continental Europe and Cyprus.

The grid cell model for regional geochemical sampling used in this project is a variant of the continental scale low density global terrestrial network (GTN) was adopted by FOREGS. Under the GTN model, sites were pre-selected to form the starting points for location of representative sites for sampling within the 160 km<sup>2</sup> cells. The actual collection sites were determined by local field conditions, to meet a series of pre-defined attributes and located as close as practical to the preselected coordinates.

In this project the site selection was based on a 1 km x 1 km mesh under UTM WGS84 Zone 36N metric grid. The density reflects the scale of variation in the geology at the 1:250,000 mapping scale. To retain the general structure of the grid while increasing sampling efficiency by use of existing roads and tracks, the actual sampling location was allowed to vary by 250 m from the nominal grid centre (Fig 2.6).

Such an approach does induce some potential bias in the sampling. Roads and tracks tend to follow ridges or streams. In urban areas, industrial and residential properties are more difficult to access than open fields and parkland.

Whereas the site distribution was intended to provide a nominal 1 km<sup>2</sup> grid, the Troodos Mountains contain extensive regions with near-uniform rock type, skeletal soils and limited vehicle access. In the central Troodos region such a high density of sites would have resulted in a corresponding high level of data redundancy. Hence, sampling in the 1200 km<sup>2</sup> central part of Troodos (mainly gabbro-dolerite-basaltic dykes) was reduced to a density of one site per 2.2 km<sup>2</sup> and the ensuing extra sites directed to the following special studies:

- High density sampling lines and in-fill sampling at the following mine sites:

Skouriotissa (Cu)	Mathiatis (Cu)	Hadjipavlou (Cr)
Limni (Cu)	Kalavasos (Cu)	Kokkinorotsos (Cr)
Mitsero (Cu)		Kannoures (Cr)
- High density profiles at the following sites;

Salt flats at Akrotiri	Lady's Mile Beach
------------------------	-------------------
- Variation test sites at Troulloi (basaltic soil) and Tseri (carbonate-rich soil)
- Vertical profile sampling at Coral Bay, Secret Valley and Mamonia
- Orientation sampling lines extending from Petra tou Romiou to Nicosia at 1 km spacing and Akamas Peninsula to Cape Greco at 4 km spacing, with the samples subjected to more detailed analysis as described below.

A summary of sampling distributions between the various groups is provided in Table 2.2.

#### **2.1.2 Task 2 – Sampling and field data collection**

##### ***Basemaps and navigation***

Daily sampling plans were determined by each field crew leader using a combination of Quickbird images and 1:25,000 topographic maps (Fig 2.7). Plans were designed to minimise travel distances and off-road driving. Navigation and site locating was conducted using GPS and the WGS84 Zone 36N grid (expected error ±10 m).

Each site was given a unique site number (CYPxxx) on arrival, based on the next sequential number in the site description and sample tick books. Site numbers were marked on 1:25,000 topographic maps at the time of collection. Sites sampled by crews without UNSW advisors were marked with flagging tape and a portion of such sites were subsequently checked by the advisors. Sampling locations, including

site numbers) were downloaded to a master file every evening and plotted on 1:50,000 *Quickbird*<sup>TM</sup> images. The final distribution of main sites and special sites is indicated in Figs 2.8 and 2.9.

Of the main grid sites, 104 were sampled in duplicate, with the duplicate site positioned between 10 and 30 m from the original site.

### ***Sampling location***

On arrival at the nominal sampling location, the following criteria were applied to the specific selection of the point or profile to be sampled:

- (i) The site should be visually representative of the dominant attributes of the grid cell being sampled;
- (ii) The site should be remote from immediate sources of abnormal contamination which may include rubbish dumps, formal gardens, farm buildings, adjacent to drainage line or ditches, nearer than 10 m upslope or 50 m downslope from a sealed road or major gravel roads;
- (iii) The soil should display some degree of consolidated and not just recent colluvium. In some instances this criteria was difficult to achieve in areas dominated by unconsolidated sheetwash slope deposits;
- (iv) There should be a well developed soil profile >70 cm depth. In some areas this was not possible due to the skeletal nature of the soils, and in this case material from several sites in the local vicinity was composited.
- (v) Agriculturally disturbed land and areas of recent re-forestation were acceptable as sample sites as these from a major part of the landscape at the sample density of the survey.

In urban environments, where there are restrictions to access of private property, sampling was limited to public domains such as parks, public property and vacant sites. In areas dominated by new building construction and other engineering works, sites were selected from adjacent locations that showed the least evidence of ground disturbance, although in some circumstances disturbed ground was sampled and noted in the field data.

It was judged that such an approach would not contribute significant spatial or parametric bias at the nominal 1 km grid cell size.

### ***Access***

Apart from dam sites, water-logged centre of salt flats and some rare zones lacking tracks, there were no major problems with site access. The sampling teams were afforded access to all properties by land-holders, who commonly provided useful information on the history of the land use, the nature of soil improvements and other information. The Cypriot and British military establishments provided access to bases (including Akrotiri), where sampling just around the base perimeters would create inadequate coverage.

### ***Sampling depths***

The sampling protocols for this study specified a top soil sample (0–25 cm depth) and sub soil samples (50–75 cm depth), without reference to specific regolith facies or soil horizons. This conforms to the FOREGS protocol and was close to the National Geochemical Survey of Australia protocols.

### ***Sampling procedures***

The sampling methodology is summarised in Fig 2.9.

#### ***(i) Top soil sample (the “A” sample)***

The surface was cleared of recent organic debris (leaves and twigs) and a 25 cm layer removed (or as close to 25 cm as could be excavated) using a steel pick (Fig 2.10a,b). The sample was disaggregated before sieving. The pick was cleaned using a nylon brush after each hole and subsequently “pre-contaminated” by scraping top surface of soil a few metres away from the actual sample site.

#### ***(ii) Sub soil sample (The “B” sample)***

Although the sub-sample was ideally collected from 50–75 cm depth, in areas with skeletal unconsolidated cover the sub-sample had to be collected from a more shallow depth. This was

commonly the case in the calcreted areas in the Kokkinokhoria region and parts of the Mesaoria Plain, and some of the steeper hill slopes. In the event that the C-horizon was shallower than 50 cm, collection of the sub-sample commenced immediately below the transition between the soil A/B-horizons and C-horizon and for a further 25 cm where possible.

### ***Excavation, sieving and bagging***

The main tool used for excavating and collecting the sub soil sample was a Jarrett-type auger (Fig 2.10f) with thick tungsten cutting edges. The augers were stripped of paint prior to use and cleaned with nylon brush and washed if necessary between holes. The cutting edges were resharpened every 500 samples, to a maximum of two resharpening. Five augers were used in the course of the project. Where the profile was exposed, as was commonly the case along tracks and terraces, the face was cleaned back 30 cm using the pick and then the sub-sample sample excavated laterally by auger.

Both the A and B samples were sieved in the field to <2 mm in Al-sieves with steel mesh (Fig 2.10). The sieves were cleaned between sites using a nylon brush and then “precontaminated” with material from the new site before sieving the actual sample. Where the material sieved was moist, the sieves were washed between samples.

All field samples were collected in wet-strength “Minisam” Kraft paper soil packets and dried at 40°C (in the sun or oven) prior to storage or transporting. The chemical effects of such bags on soil samples have been tested in the past and does not cause significant contamination of samples, even when completely wet (Seneshen 1991). A tear-off ticket from the field data tick books was placed in the soil bag as a means of cross-checking the site number if required.

### ***General field sampling observations***

In many areas, the soil or colluvial cover is less than 10 cm. This is commonly the case in the deeply dissected carbonate-dominated areas on the southern side of Troodos where the unconsolidated top layer could range from locally-derived carbonate-rich colluvium overlying carbonate-rich sedimentary units of the Pakhna Formation (Fig 2.11a) to basalt-derived soil overlying the carbonates (Fig 2.11b) or basalt (Fig 2.11c). The reverse was also observed with carbonate-rich colluvium overlying C/D-horizon basalts or mafic-derived sedimentary rocks (Fig 2.11d). In each of these cases the lower sample was excavated out of the C/D horizon (saprolite) of weathered rock.

In some areas there are thick residual soil profiles with up to 20 cm of A-horizon (organic-rich) overlying a B-horizon dominated by Fe-oxides and clays. This is the case along most ridge lines in the higher parts of Troodos. In other areas there is just a skeletal transported regolith horizon of only 10 cm overlying a variably weathered C-horizon (saprolite), as is the case for much of the Troodos flanks. Yet other areas had thick colluvium and alluvium with some degree of consolidation but little indication of horizon development.

In profiles where thin scree overlies residual soil, the top sample was taken in the scree and the lower sample below the scree where possible. In some cases the lower sample was collected above or below the normal 50–75 cm depth interval (Fig 2.12a, b and 2.14c,d). In some cases the top sample was collected from very thin cover (< 5 cm) requiring compositing of material from a few spots surrounding the nominal sample site and the lower sample excavated from the C-horizon. An example of weathered basalt with recent carbonate fracture infill is shown in Fig 2.12c. When sampling the C-horizon, a number of holes were required in some instances to generate sufficient <2000 µm fraction.

Thick layers of sodic clays in the salt flats at Akrotiri also display strong layering related to redox fronts and some organic build-up in the top 3 cm (Fig 2.12d). Here the top sample extended down to the base of the organic-rich plus grey clay layer and the lower sample from below the Fe accumulation zone.

Urban areas presented a number of issues regarding the selection of sampling sites. Sampling of the verge surrounding car parks or grassed areas in parks or adjacent to roads may be influenced by contamination derived from both vehicles and fill materials (Fig 2.13a,b). Golf courses and outside banks represented rare sampling sites (Fig 2.13c,d).

Where possible, undeveloped sites were sampled in urban areas (Fig 14a) or areas on properties where there were no obvious signs of cultivation or fertiliser use (Fig 2.14c – note the engagement of a local property owner to assist in the sampling). In areas with crops, sampling was generally restricted to

periods outside the growing or harvesting seasons (2.14e,f). It is noted that in most agricultural fields the plough-depth in such areas was around 30 cm (spanning the top sample).

Specific site characteristics that affected sampling were noted in the field tick books and the ensuing database.

Sampling of soils and rock samples generally proceeded irrespective of weather or other hazards (Fig 2.15).

### ***Sample numbering***

Each site was allocated a unique numbered on arrival (CYP<sub>xxxx</sub>), in the sequence determined by the next available site number in the sample tag books.

“A” sample (top soil)	A1 sample (small), ~100 g, to GSD archive (frozen)
	A1 sample (large), ~300 g, to GSD archive
	A2 sample, ~100 g, to UNSW
“B” sample (sub soil)	B1 sample, ~300 g, to GSD archive
	B2 sample, ~100 g, to UNSW

Site duplicates constituted separate sites in the numbering scheme.

Samples sequences were checked prior to sampling and by field crews at the end of each sampling day to ensure no missing samples or numbering error.

### ***Project-specific reference materials***

Three project-specific reference materials, representative of end-member lithologies, were collected. CYP-A is a calcareous sediment collected from an outcrop of Pakhna Formation west of Episkopi. CYP-B was a basalt-derived soil with minor amounts of pedogenic carbonate collected over the upper pillow basalts north-east of Sha. CYP-C was an ultramafic-derived soil from the top of Mt Olympus.

### ***Sampling depth variability***

Whereas the majority of sites in the main survey were sampled at the nominated depth of 0–25 cm for the top sample and 50–75 cm for the lower sample (Fig 2.16), for some sites the thickness of the unconsolidated part of the profile reduced sampling depths. Shallow sampling was mainly restricted to the areas of skeletal soil cover (Akamas Peninsula), areas of calcrete development and thin soil cover (Mesaoria Plain, the Kokkinokhoria region and areas underlain by Pakhna formation limestones and calcareous sedimentary rocks), and along some ridgelines emanating south from the Troodos Mountains.

### ***Field data***

Digital field data recording and direct capture of GPS coordinates using an HP iPaq 6515e with Windows CE via a series of questions and answers was tested in Oct 2006. However the system proved unstable and all data was collected using the tick books and the data transferred to computer manually at the end of each day and subsequent data entry at UNSW.

Field data collected at each site is indicated in the example tick book (Fig 2.17) and the data was transferred to the field database (Section 2.8).

Whereas most field information is objectives, the identification of rock type was prone to some variability in both nomenclature and interpolation between outcrops in areas dominated by transported cover. For example, the terms “calcareous”, “carbonate-rich sandstone/siltstone” and “marl” were used synonymously by different teams, though these have been standardised to “carbonate-rich sedimentary rock/unit” in the final database. In other cases the geology indicated at many sites was that of outcrops in the vicinity of the sampling location.

At a representative number of sites, photographs were taken to show the site characteristics and the geological or regolith characteristics of the area, as well as sampling methods (Fig 2.18). These are linked to the site numbers in the photographic archive.

### ***Teams and sampling rates***

The first sample was collected on 21 Apr 2006 (Fig 2.19). The penultimate sample was collected in the car park of the GSD by the project committee members on 19 June 2008. The final sample was collected by His Excellency the President of Cyprus, Mr Dimitris Christofias, in the presence of the Hon Minister for Agriculture, Natural Resources and Environment Dr Michalis Polynikis Charalampides, the Australian Consul Mr Andrew Szwajcer, the Director of the Geological Survey Department Dr Eleni Morisseau and project team members in the gardens of the Presidential Palace on 15 Dec 2009.

Sampling of the 5,516 sample sites was completed in 280 crew-days in a series of time-blocks yielding an average sampling rate of 19.6 sites per day per crew, or 25 minutes per site including travel. Sampling in the Akamas Peninsula area and parts of the deeply dissected Troodos flanks was under 10 sites per day, whereas in the flat agricultural areas sampling could exceed 30 sites per day. The principal source of delays was wet weather and problems with access in the Troodos area, although some easily accessible areas were set aside for such days.

Over 72% of the sites were sampled by UNSW advisors and the remainder under the close supervision of the advisors. The sampling phase allowed field orientation for eight of the UNSW consultants.

Project Sampling days	180
Individual crew days	280
Ave crews / sampling day	1.6
Sites per day of sampling	30.6
Sites per day per crew	19.6
Percent of days with UNSW staff	72.7

The main period of sampling was late Sep to early Nov 2006, during which time nearly 50% of the sampling was completed, with four field crews active (Figures 2.20 and 2.21).

The final distribution of samples between the main survey (including the Troodos and non-Troodos regions), the orientation lines and more detailed sampling around selected mines and other key sites is presented in Table 2.3.

The 5,870 km<sup>2</sup> of accessible land in the Republic of Cyprus was covered by 5,516 sites yielding an overall average density of one site per 1.06 km<sup>2</sup>.

A few grid cells could not be sampled due to the presence of wet salt flats, airports and military zones, as well as those lacking vehicular access. Coverage by the various field crews deployed is indicated in Fig 2.22.

### ***Sample delivery and archive***

The small A1 samples are stored in their original paper bags, wrapped in plastic bags and placed in a -16°C refrigerator. The large A1 and B1 samples have been stored by site number sequence at the GSD sample store in Geri, in plastic-wrapped cardboard boxes (Fig 2.23). The A2 and B2 samples were packaged in plastic-lined crates on three pallets, re-wrapped in polythene, and dispatched by ship to UNSW. The samples were subjected to gamma irradiation by the Australian Quarantine and Inspection Service on arrival to ensure compliance with Australian quarantine regulations.

#### **2.1.3 Task 3 – Sample processing**

The sample processing and analytical methods are summarised in Fig 2.24. The protocols for the main suite of samples were broadly based on the FOREGS protocols, but modified to incorporate the use of INAA in addition to ICP-MS and XRF. Additional processing and analytical work was conducted on the orientation line and mine area samples.

### ***Splitting and Milling***

Each sample fraction was randomly assigned a unique analytical number (CYPAYyyyyy) prior to milling (Fig 2.25a). The complete original sample (50–100 g) was split using a Laval Labs mini riffle splitter (Fig 2.25b). ~20 g sub-sample was extracted and placed in a number plastic *Ziploc*<sup>™</sup> bag for subsequent milling (Fig 2.25c). The analytical number was marked (in red) on the original soil paper packet for cross checking.

The selection of mill was based on the need to limit sample contamination. A Rocklabs mild steel mill was selected as the only significant contaminant would be Fe, an element that is generally present in samples in the minor to major ranges (>100 mg/kg). The same mill compositions were used in the National Geochemical Mapping of Australia project and FOREGS surveys.

To limit contamination by minimising milling times, tests were performed on two of the raw materials used in producing the reference materials. Sub-samples of 20 g of unmilled CYP-A and CYP-B were milled for periods of 5, 10, 20 and 40 seconds using a Rocklabs C-40 mild steel mill (Fig 5e, f). The particle size distributions after milling were determined using a Malvern *Mastersizer 2000*<sup>TM</sup> laser particle sizer.

The size distribution (Fig 2.26) indicates that for 20 g the required specification of <15% coarser than 75 µm is easily achieved after 30 seconds milling and there is only a marginal further decrease in grain size over the next 40 seconds. Further to this, there was a maximum loss (inability to efficiently recover) of 0.2 g of sample to the mill at 40 seconds of milling.

The entire sub-sample split was milled and the pulp returned to the plastic bag (Fig 2.25d). Between samples, each mill was washed and dried. The maximum rate of milling was around 300 samples per day, using two milling crews. During the initial stages of milling the main suite of samples, occasional samples were sieved through 75 µm nylon mesh to monitor milling efficiency.

### ***Processing of CYP reference materials***

After drying at 40°C for 24 hours, the materials were milled for 10s intervals in a tungsten carbide mill with interleaved sieving in <63µm nylon sieves. The sieved material was placed in polythene bottles and re-mixed. These three in-house reference materials were then subjected to various tests as set out below.

The major oxide and volatile components were determined using glass bead XRF (Pananalytical) and Leco CNS analysis at UNSW Analytical Centre (Fig 2.27). CYP-A has ~40% LOI due to its high carbonate content and CYP-B and CYP-C around 16% relating to Fe-oxyhydroxides, clays and minor amounts of pedogenic carbonate. The three reference materials display wide variation in major oxide concentrations.

Sample blanks were developed by milling quartz sand, leaching the material in 20% nitric acid for seven days and washing the residues in distilled water before drying.

### ***Grainsize separation***

500g sub-samples of the orientation suite samples were quantitatively wet-sieved in distilled water using steel mesh sieves into three size fractions, <125 µm, 125–250 µm and 250–2000 µm. All material (solid and water) passing through the 125µm sieve was collected and dried at 80°C. These fractions were used in subsequent geochemical and mineralogical analysis. Previous studies by Cohen and Rutherford (1995) indicated that there was no detectable contamination by the sieves or substantial loss of mobile elements.

### ***Sample dispatch***

Milled samples for aqua regia–ICPMS analysis were dispatched to Actlabs Pacific in the *Ziploc* bags. Sub-samples were weighed by Actlabs Pacific into polythene vials for the INAA analysis and shipped to Actlabs Canada.

#### 2.1.4 Task 4a – Physical analysis

A range of physical analyses were performed on the samples to assist with subsequent interpretation of the geochemical data.

##### *pH, EC and LOI*

To minimise double handling and weighing of samples Munsell soil colour, pH, EC and LOI were conducted in sequence on the sample sub-sample (Fig 2.28):

- Step 1: ~3.00 g of unmilled sample was placed in a pre-weighed and numbered crucible, and the Munsell soil colour determined on the dry sample.
- Step 2: 15 mL of DI water was then be added to the crucible, the 1:5 slurry mixed and the pH and EC measured after 30 minutes. Meters were recalibrated at the start of each batch and at 50-sample intervals.
- Step 3: The crucibles with the slurries were placed in a drying cabinet at 80°C over night to remove excess water, then be placed in a muffle furnace at 400°C and the temperature ramped to 1000°C over 2 hours. The crucibles were removed and reweighed to determine LOI.

To test the effects of pre-addition of water and concentrated nitric acid on LOI, sub-samples of the three project reference materials had LOI determined on dry material (by BEES and the Analytical Centre) and on samples that were left for 30 minutes in distilled water and for 30 minutes in 40% nitric acid. The results indicate that there was no significant difference between the dry and the water slurry LOI measurements (Fig 2.29), but that nitric acid increases LOI marginally (presumably by conversion of chlorides and some oxides to volatile nitrates).

##### *Grainsize analysis*

Grainsize analysis was performed on the orientation suit A-samples using a Malvern Mastersizer 2000 laser particle sizer with 0.02–2000 µm range (Fig 2.28d). The 84 size divisions represent a 1.15x increase between successive boundaries. Approximately 1g of unmilled sample was added to the automated ultrasonic bath and the sizing performed after 15 minutes of ultrasonication. The analyses were run in triplicate and the data averaged for each size fraction. Tests were performed to determine the minimum time for ultrasonication required and the effect of addition or absence of a dispersant (*Calgon*<sup>TM</sup>).

##### *Spectral analysis*

UV-visible spectral analysis on the top soil samples was carried out using a 1024-channel FieldSpec<sup>TM</sup> instrument co-owned by UNSW. The mechanics of the spectral analysis is set out in the accompanying UNSW honours thesis by Jumrieng (2007), but involved placing sufficient unmilled powder in a dish to fill to a depth of 10 mm and placing the dish under the scanning aperture for the ~20 s scan. The spectra were calibrated using standard reflectance plates.

##### *XRD*

Unoriented powders from milled orientation suite samples were analysed in the UNSW Analytical Centre using a Philips PW1140 XRD, scanning from 2–165° (2θ) under Cu-Kα radiation. The data were processed and mineralogy quantitatively determined using *SIROQUANT*<sup>TM</sup>. The XRD data were compared with XRF normative mineralogy data using SEDNORM (Cohen and Ward 1992).

#### 2.1.5 Task 4b – Chemical analysis

A review of existing protocols and operating procedures used in similar regional geochemical studies was undertaken and the IGCP Project 360 and FOREGS protocols formed the main basis modified by experience of the advisors in regional geochemical mapping in Australia. As regional geochemical mapping data may be used for environmental purposes, such as assessment of background concentrations of elements and setting regulatory limits, three criteria used by FOREGS to guide the analytical program (Sandström *et al.* 2007) were consider in this study:

- i. *the analytical methods used must be sufficiently sensitive to allow detection of a wide range of analytes ... at background levels;*
- ii. *the analytical precision must be good, preferably significantly better than natural geochemical variation; and*
- iii. *all data and other records pertaining to the analysis and testing must be fully documented and traceable.*

The general statement by FOREGS that “*total element concentrations are most relevant for geochemical interpretation of data*” is debatable. This would predicate the main emphasis of such surveys being relating regolith to parent material. However, the FOREGS report conceded that “*to address the needs of national and European level environmental authorities, information on leachable concentrations of the elements was also considered to be important*”. The NASGLP project utilised a four-acid digestion (total for most elements and minerals), rather than a near-total method like aqua regia, on the grounds that the sampling and analytical component of the project was designed to run over 15 years and that a total digestion was less dependent on procedural details and analyst technique, delivering data “*believed to be more consistent over the multi-year life of the planned soil geochemical*” (Smith *et al.* 2009).

As indicated by FOREGS, aqua regia digestions are the most common “near total” extraction used for such purposes, though it was emphasised, that significant variation does exist in aqua regia extraction procedures. These variations can include the order in which the component acids are added, digestion times and the vessels in which digestion occurs. Outside of analytical errors, variation between aqua regia digestions are largely restricted to elements being released from the more resistate minerals (such as aluminosilicates and some oxides) rather than the more readily soluble minerals such as carbonates. It is noted that the national geochemical survey of Australia is utilising multiple analytical methods including XRF, a total digestion ICP-MS and aqua regia ICP-MS (Caritat *et al.* 2007).

Since the establishment of the ISO 11466 method, aqua regia extraction has become one of the most common acid leaching methods in geochemistry (Sastre *et al.* 2002). Although total extraction methods involving either a high temperature fusion with various fluxes or use of HF with other strong acids to decompose silicates and some resistate oxides are useful in some applications, such methods are cumbersome and the volatilization loss of some elements may occur unless closed containers are used. However, Sastre *et al.* (2002) found little difference in the amount of Cd, Cu, Pb and Zn extracted by aqua regia versus a complex sequence of steps involving HNO<sub>3</sub>, HF and HClO<sub>4</sub> under microwave heating (Table 2.4). In the Manitoba transect of the NASGLP pilot projects Klassen (2009) found that most transition metals displayed high correlation between total and aqua regia-extractable metal contents.

In the FOREGS project, the acid leachable portion of selected elements were analysed after hot aqua regia (Sandström *et al.* 2007). Samples were digested in aqua regia by weighing 1 g of sample in a polyethylene tube and adding 6 mL HCl and 2 mL HNO<sub>3</sub>. The samples were left for 15 minutes at room temperature before heating in an aluminium block at 95°C for 60 minutes. After cooling, the samples were filtered in ash-free filter paper and made up to 50 mL in a polyethylene flask. Based on QC samples, the relative standard deviation of the measurements was typically 3–7% for concentrations exceeding three times the limit of quantification of the particular element.

Aqua regia digestions followed by inductively coupled plasma – mass spectrometry (*ar*-ICPMS) was, therefore, selected as the main analytical procedure in this study, with additional instrumental neutron activation (INAA) to provide total element concentration for a more limited suite of elements. The aqua regia technique used by the main laboratory used in this project (Actlabs) varied slightly from more conventional aqua regia in the use of a 1:2.5 HNO<sub>3</sub>:HCl rather than the more typical 1:3 to reduce the interference caused by excess Cl ions.

Other analytical procedures involving stronger acid digestions were compared with aqua regia for the project reference materials prior to commencing the main analytical program. In addition, two other selective geochemical extraction procedures were applied to the orientation suite and some mine suite samples, along with XRF major element analysis.

The project analytical method and quality control protocols were tested in mid 2008 and were detailed in an interim progress report in June 2008 (GAC06 - *Analytical Methodology Testing and QAQC Evaluations*).

### **Testing of sampling digestion procedures**

Tests were conducted at the UNSW AC to evaluate various aspects of the reference materials and various processing parameters. A standard aqua regia composition was used (1:3 HNO<sub>3</sub>:HCl) with 0.5g of sample digested in 15–20mL of aqua regia and taken to near dryness over a period of ~20 minutes before reconstituting in 10% nitric acid. Analyses were performed using either a Perkin-Elmer Elan 6000 ICP-MS and/or a Perkin Elmer Optima ICP-OES. For broad characterisation of the reference materials, only a selection of key trace or major elements was analysed.

#### **(i) Milling-digestion tests**

The milled splits produced under Section 2.2.3 were subject to aqua regia extraction and ICP-OES analysis for selected trace elements. The data are presented as the relative extraction on the amount released from the samples milled for 40s (Fig 2.30). Calcium displayed no particle size effects, indicating the dominance of calcite as host for Ca. CYP-A displayed maximum extraction after 20s of milling and CYP-B after just 10s of milling for most of the transition elements. Aluminium and Co, however, displayed progressive increases in extraction levels as grain size decreases, which may be attributed to exposure of surfaces of more chemically resistate minerals such as clays and magnetite

#### **(ii) Solid-liquid ratios**

0.5 g sub-samples of six reference materials were digested in varying amounts of aqua regia, yielding solid:liquid ratios of 1:8 up to 1:40. For some elements and materials the solid to liquid (aqua regia) ratio has no effect on element extraction (Fig 2.31). This is typically the case of Ca and Mn. For other elements related to more resistate phases, such as Al, there is a significant increase in the amount of element released as the solid:liquid ratio drops from 1:8 to 1:40. This is, however, unlikely to be an effect related to the ratio *per se*, but that the amount of time required to reduce the mixture to near-dryness is greater for the solutions with more aqua regia.

#### **(iii) Reference mixing test**

To additionally test the analytical accuracy of the analyses at UNSW AC, the effects of digestions on samples whose composition lies between the in-house reference materials and to examine the homogeneity of the reference materials, a sequence of five mixtures representing various proportions of CYP-A and CYP-B were analysed. The results indicate linear trends for all elements, within analytical error margins, indicating no significant matrix effects on the digestion efficiency (Fig 2.32).

#### **(iv) Digestion technique comparison**

To demonstrate the relationship of routine aqua regia extractions in open beakers to four-acid digestions and microwave-assisted digestion, defined in previous studies, samples of the reference materials were subjected to:

- i. Digestion in aqua regia in an open beaker at 100°C to near-dryness
- ii. Digestion in a 3:1:2:1 ratio mixture of HCl : HNO<sub>3</sub> : HClO<sub>4</sub> : HF (the typical “four-acid” digestion) in an open beaker at 100°C to near-dryness
- iii. Digestion in aqua regia at 180°C in a microwave for 10 minutes
- iv. Digestion in a four-acid mixture at 180°C in a microwave for 10 minutes

The results are presented in Fig 2.33 as the extraction relative to the open beaker four-acid digestion.

The results are quite variable between digestions, elements and reference materials. For elements typically found in alumino-silicates (primary or secondary), such as Al, K and Na, the four acid extraction is generally more effective as the HF assists in breaking down the silicate structure. Ca displays no great variation between methods for CYP-A as the host is almost completely carbonates which dissolve rapidly in strong acids, however, the extractions are significantly greater where HF is used in CYP-B and CYP-C indicative of Ca being partly distributed into clays and possibly some primary silicates such as feldspars. In the case of Cr, the extraction from CYP-B is assisted by HF, whereas in CYP-C the extraction is similar between all four methods. Although results are erratic due

to proximity to the DLs, the elements typically found in resistate minerals display substantial increase in extractions where HF is used.

In general, the effect of adding perchloric and HF to the digestions is more significant in altering extraction levels, then the effect of microwaving relative to open beakers. The ligand (F) appears more important in attacking resistate minerals than  $H^+$  in such strong acid mixtures or oxidising species.

#### **(v) Digestion time**

To test the effects of digestion time, sub-samples were digested in aqua regia for 5, 10, 15 and 20 minutes. The solutions were only taken to dryness after centrifuging and decanting the solutions into clean beakers. With the exception of aluminosilicate mineral hosted elements in CYP-A, most elements displayed over 80% of the extraction achieved after 20 minutes with the first five minutes (Fig 2.34). Elements dominantly hosted in some secondary minerals (Ca in carbonates and Fe in secondary Fe-oxides) digested at a faster rate than elements in clays or primary silicates.

It is noted that the Actlabs procedure is to leave the samples in HCl for a number of hours, followed by addition of the  $HNO_3$  to make the aqua regia.

#### **(vi) Comparison of aqua regia extractable elements versus total contents**

The aqua regia extractable element contents (from the round-robin program) are compared with the certified total metal contents for GXR-6 (Gouvenia *et al.* 1994). Relative extractions range from <5% to nearly 100% (Fig 2.35). In general again, elements associated with aluminosilicates, clay structural sites and resistate minerals display much lower extractions in aqua regia than elements typically associated with carbonates, secondary Fe-Mn oxides.

#### **Weak selective extractions**

Selective extractions have long been used in the exploration and environmental industries to determine mobility, to speciate elements or define the link between element concentrations and sample mineralogy. In this study, element speciation for the orientation suite and in the vicinity of the areas of contamination from mining will be determined using ammonium acetate in pH5 acetic acid (mobile metals and carbonate-hosted elements) and 1M hydroxylamine.HCl in pH 1 HCl (secondary Fe-oxide hosted elements).

The choice of digestions follows the work of previous studies by Hall and Bonham-Carter (1998), Gray *et al.* (1999) and Cohen *et al.* (1998). And the optimisation of the method based on the work of Dalrymple *et al.* (2005) and Dalrymple (2007).

1.5g of unmilled material was placed in polythene tubes and 15 mL of 1 M ammonium acetate in pH 5 acetic acid added. The tubes were agitated for 1 hour, centrifuged and the supernatant fluid placed in disposable polythene tubes containing 2 drops of conc. nitric acid for subsequent multielement ICP-MS analysis at Actlabs. To the remaining solid material 1M hydroxylamine.HCl in pH 1 HCl was added, the tubes remixed and placed in an oven at 60°C for 4 hours. The tubes were centrifuges and the supernatant fluid placed in a disposable polythene tube for subsequent ICP-MS analysis at Actlabs.

#### **Cation exchange capacity**

CEC was determined using the methylene blue absorption (MBA) test (Santamaria-Fernandez *et al.* 2002; Yukselen and Kaya 2006). Methylene blue (MB) is a highly soluble cationic dye ( $C_{16}H_{18}N_3S$ ) which can readily exchange for cations at the surface and internal exchangeable sites of clay minerals.

2.00g of soil was added to 20mL of MB solution. The amount of MB absorbed from the solution was measured by spectrophotometer - MB having a very strong absorption in part of the blue light spectrum – and converted to a cmol/g basis. Only the orientation suite and some of the mine suite samples were analysed.

#### **Reference material calibration**

Samples of project specific reference materials CYP-A, CYP-B and CYP-C, and certified reference material USGS GXR6 were forwarded to seven ISO-certified commercial laboratories as part of a round-robin analytical program to determine the expected concentrations of elements extractable by aqua regia. These were:

- ALS-Chemex (Brisbane, Australia)
- Genalysis (Perth, Australia)
- ALS-Chemex (Vancouver, Canada)
- Ultratrace (Perth, Australia)
- Acme Laboratories (Vancouver, Canada)
- Actlabs (Perth, Australia)
- SGS Laboratories (Toronto, Canada)

In all labs the Actlabs-preferred 1:2.5 HNO<sub>3</sub>:HCl aqua regia ratio was used.

The results are presented and discussed in Section 3, but the results from Actlabs were statistically similar to those achieved for other laboratories for most elements, indicating good methodological precision and analytical accuracy (for the digestion solutions). Digestion of USGS GXR-6 (a contaminated Fe-rich soil) in nitric-rich aqua regia resulted in near-total digestion of most siderophile transition metals, but only partial digestion of elements associated with silicates, aluminosilicates and resistate mineral phases.

### ***Soluble ions***

Soluble ions were determined using an in-house ion chromatographic method developed at the GSD. About 5g of sample and 200mL of deionised water were transferred to a shaking bottle and the slurry was shaken for 120 minutes using a mechanical shaker and then filtered through an ashless filter paper. The conductivity of the filtrate was measured using a conductivity meter. The filtrate was then filtered through a membrane filter of pore size 0.45 µm to remove any particulate matter. The dissolved anions were determined by liquid chromatography. All the calibration curves had squared correlation coefficient >0.99. All chromatographic analysis was carried out using a Shimadzu ion chromatograph with a 50µL sample loop. The system components consisted of one anion guard column Shim-pack IC-SA2(G) and a separator column Shim-pack IC-SA2 (250 mm x 4.0 mm) used for the simultaneous separation of anions, an anion self generating suppressor package HK-10Asuper, a pulsed electrochemical detector CDD-10Asp and an advanced gradient pump LC-10ADsp. The eluents were delivered to the columns by a Shimadzu eluent degasser module DGU-14A and all the above were used in combination with the SLC-10Asp system controller.

### ***C and S analysis***

Selected samples had *tot*-C, *tot*-S and SOC determined using an Eltra CS-800 analyser at GSD, as well as soluble anions (chloride, fluoride, nitrate and sulfate). Some cross-check *tot*-C and *tot*-S analyses were performed on the orientation sample suite using a LECO at UNSW.

### ***XRF***

Major oxide contents were determined by XRF at the GSD. The orientation suite was also analysed by XRF at the UNSW Analytical Centre using a PW2400. The Norrish and Hutton method for glass disks was used.

### ***Actlabs procedures***

The “Ultratrace 3” package at Actlabs, involving *ar*-ICPMS and INAA was used for the analyses. Some of the procedures are shown in Figures 2.36 and 2.37.

#### ***(i) Weighing***

From the sample manifest provided by UNSW, Actlabs allocated a project number and set up the analytical numbers and sequences within their LIMS. Samples were stored and weighed in a balance room, separated from the main laboratory weighing room. With data digitally captured, 0.5 ± 0.001 g was weighed into boron-free disposable glass reaction tubes for aqua regia digestion and 2.0 ± 0.001 g into polythene vials for INAA. Weighing balance calibrations were checked at the start of the project run. The polythene vials were dispatched to Actlabs, Canada for INAA.

### **(ii) Digestions**

The reaction tubes were placed in heating blocks and 0.5 mL of HCl added slowly to prevent spluttering of carbonate-rich samples. A further 3.0 mL of HCl was then added and the tubes covered and left at 80°C overnight. The following day 2.0 mL of HNO<sub>3</sub> was added and the samples digested for a further 2 hours. This brought the solid:liquid ratio to 1:10. After digestion 10 mL of DI water and an Rh spike was added via an autodiluter and the solutions forwarded to the instrument room for ICP-MS analysis.

### **(iii) Analyte determinations**

The program of geochemical analysis of samples was designed to meet the requirements of the tender and to expand the number of analytes; (especially the rare earth elements and some incompatibles). The inclusion of extra elements to the TOR is a function of the selection of instrumental neutron activation (INAA) to complement the *ar*-ICPMS.

Samples were analysed in sub-batches of 80. Each sub-batch was preceded by a 16-solution calibration (or calibration check) series and interspersed with a series of UNSW and Actlabs reference materials, duplicates and other quality control samples. The quality control results are discussed in Section 3.

The reference materials used were:

- **CYP-A, CYP-B & CYP-C** In-house reference materials developed for this project representing end-member soil types.
- **GXR-6** Certified by the USGS for total analysis.
- **ORES100-A & ORES47-P** Certified for a limited range of elements by HCl-HNO<sub>3</sub>-HClO<sub>4</sub>-HF digestion and ICP-MS; used in the *ar*-ICPMS analysis by Actlabs.
- **Till-1 to Till-4** Certified for totals analysis and were used in the INAA analysis by Actlabs
- **Sample blanks** Acid-leached quartz blanks.

### **2.1.6 Task 5 – Quality control**

The details for this task are presented in Section 3 of this report.

The DLs for the various method used (including a comparison with FOREGS) is presented in Fig 2.38 and Table 2.5. A summary of the analyses performed is presented in Table 2.6.

### **2.1.7 Task 6 – Compilation of data**

#### ***Files***

The data has been divided into a series of Excel files (flat tables). The index or descriptors of the key files are set out in Tables below.

#### ***Field data logs***

Columns in purple are derived from the GSD-supplied digital database (cadastral information, geology, soils and vegetation).

#### ***Data platforms***

The principal spatial data platform is ArcGIS v.10, with some presentations via Mapinfo. An example of the Mapinfo output of the 1:250,000 geology map and RGB colour codings for lithologies and geological formations are provided in Tables 2.7 and 2.8. The geological map used in this study is derived from the 1995 digital geology rather than the current GSD OneGeology compilation.

#### ***Standardisation of terms and descriptions***

Some standardisation of geological terms from the field tick books was required. In most cases this was to reduce synonyms or similar terminology to a single descriptor. For example “marl” is synonymous

with “calcsiltstone”, with the former name now archaic. Similarly, the terms “silt-sand-gravel (SSG)” is effectively the same as “alluvium-colluvium” in the context of the present study. The modern or most generally accepted term has been used in the field database.

To simplify the subsequent processing of the geological data and the geochemical interpretation, the myriad of geological descriptors derived from slight variations in the geology observed, have been reduced to a set of 15 main rock groups (Table 2.9). The original descriptors remain in the database, however dunite, harzburgite, pyroxenite, plagiogranite, wehrlite and mixtures of these lithologies have been simply grouped as “ultramafics”.

Similarly, the main rock types of the geological formations in Cyprus have been distilled from the digital database and added to the field data logs. This permits a comparison between the geology observed at each given site in the field by the advisors with the geology assigned to the site in the digital geological database. When the project database is reduced to the 15 main rock types and the main geological formations are reduced to similar rock types, a contingency table can be produced (Table 2.10).

The direct correlation between the field data and geological map is 72%. However, the advisors attempted to determine the underlying geology at each site, even where there was colluvium and alluvium by noting nearby (within 200 m) outcrops. Excluding sites where either the field teams noted the geology when the geological map indicates alluvium-colluvium or the reverse, the match is over 90%. This does not imply the remaining 10% of sites where there was conflict between the field data and map is indicative of inaccurate field observations; at 1:250,000 scale, there is a degree of smoothing of the variation in the observed geology, especially near the boundary between formations where there may be a zone of “overlap” involving outliers and inliers (especially where an on-lapping formation thins). There are small outcrops of calcarenites for some distance into Troodos despite the geological maps indicating the TOC units. Similarly, where the CTSS units are thin, there are sporadic outcrops of the underlying the TOC units (mainly basalts). Hence, the major of disagreements are calcarenites versus basalts.

### **2.1.8 Task 7 – Data processing and statistical assessment**

This aspect of the project is discussed in detail in Sections 4 and 5.

### **2.1.9 Task 8 – Training**

#### ***Short courses***

Five half-day seminars were held at the GSD by project advisors:

3 Nov 2006	A/Prof G.R. Taylor	<i>Remote sensing in soil geochemical mapping.</i>
2 Mar 2007	A/Prof D.R. Cohen	<i>Geochemical mapping – reason and approach</i>
18 Feb 2008	A/Prof D.R. Cohen & Dr N.F. Rutherford	<i>Geochemical sampling, analysis and data quality control</i>
20 Feb 2008	A/Prof D.R. Cohen	<i>Statistical analysis of geochemical data</i>
16 Dec 2009	A/Prof D.R. Cohen	<i>Geochemical atlases and project update</i>

#### ***Field training***

Field training for GSD staff was conducted at various stages in the project, but mainly in 2006 and 2008. A total of 50 person-training days were completed involving 12 individual GSD staff. This training focussed on various aspects of geochemical sampling and site assessment.

#### ***Visit of GSD staff***

Four visits by GSD staff to UNSW and other sites in Australia were completed, for training and visits to various organisations.

Dr Charalambides, project coordinator for the GSD, visited UNSW from 28 March to 6 April 2007. The main activities during this time were inspection of the UNSW Analytical Centre and some preliminary laboratory work relating to the implementation of the analytical quality control protocols. Visits were also made to the New South Wales Geological Survey (Maitland offices and Londonderry

core archive facility), the Sunny Corner abandoned mine site, the Cadia Au-Cu Mine and SGS Laboratories in Sydney. A series of discussions were held with UNSW Global and the project advisors and consultants.

Dr A. Zissimos and Mr E. Kyriakou visited UNSW from 4 to 20 March and a further 3 days in Perth for Dr Zissimos. The main activities during this time were inspection of the UNSW Analytical Centre, some further preliminary laboratory work relating to the implementation of the analytical quality control protocols and training in GIS techniques. Visits were also made to Geoscience Australia in Canberra and the New South Wales Geological Survey (Maitland offices). During the two days in Perth, there were two visits to Actlabs. A series of discussions were held with University of New South Wales Global and the project advisors and consultants.

Dr E. Morisseau, the GSD Director, visited UNSW in February 2011 to review the data, finalise details of the Atlas and Symposium, and to consider related publications and future projects. Visits were also made to Geoscience Australia (Canberra) and the New South Wales Geological Survey (Maitland offices) with meetings held with the survey directors (Dr C. Pigram for GA and Mr B. Mallard for NSWGS).

### **2.1.10 Task 9 – Reporting**

#### ***Progress reports***

Progress reports were provided at the 3, 12, 24, 36 and 48 month stages of the project, as well as an interim report summarising the analytical quality control program. Various presentations were made to the project committee on progress as well as a general presentation to a broader group of government representatives in Dec 2009.

Along with the progress reports, manuals relating to sampling, analysis, sample preparation and analysis were produced. Three honours these were also completed on aspects of the orientation studies. The list of reports is presented in Table 2.11.

#### ***Papers***

Various conference presentations have been presented on preliminary aspects of the project. The abstracts and accompanying poster papers are presented in the Appendix

- D.R. Cohen and N.F. Rutherford, *Regolith Characteristics of Cyprus*, 23<sup>rd</sup> IAGS, Oviedo, May 2007
- A. Zissimos, E. Morisseau, E. Stavrou and D.R. Cohen, *Total and soil organic carbon, and total sulfur determinations of soils from Cyprus*. 24<sup>th</sup> IAGS, Fredericton, June 2009.
- N. Webster, D.R. Cohen, N.F. Rutherford, A. Zissimos and E. Morisseau, *Selective geochemical extraction patterns in Cyprus soils: responses to geology and land use variations*. 24<sup>th</sup> IAGS, Fredericton, June 2009.

Various papers are planned for the 25<sup>th</sup> IAGS, Rovaniemi in 2011 and the IGC in Brisbane in 2012, together with various journal papers.

#### ***Honours theses***

##### ***(i) Mines suite geochemistry***

The honours project conducted by Carlos Constantinou (2008) identified strong spatial relationships between the location of the mines and tailings at Limni and Mitsero, and the amount of elements that can be extracted by pH 5 ammonium acetate (AAC) designed to attack carbonates and adsorbed metals and the subsequent pH 1 hydroxylamine.HCl (HXL) designed to attached Mn and some Fe oxides. The data indicate little evidence of contamination (wind-borne) up-slope of mineralisation at either site and the down-slope contamination does not extend for much more than 1500 m at maximum.

##### ***(ii) Orientation suite geochemistry***

The honours thesis of Nyree Webster (2007) investigated the physical and selective geochemical extraction characteristics of the N-S orientation line. The work demonstrated a number of key effects in the data including very abrupt changes in the geochemical characteristics of the regolith when major

geological boundaries are crossed (e.g. between the Pakhna Formation carbonates and the lower pillow basalts of the Troodos Complex) and when approaching the coast. The Mesaoria Plain displays a highly variable and mixed geochemical signature. There are only small variations in soil pH across the orientation traverse. The selective geochemical data displayed a number of multielement characteristics that are also parent geology dependent.

***(iii) Classification of regolith in Cyprus using FDA of soil spectra***

The honours thesis of Hunsamon Jumrieng (2007) evaluated the suitability of functional data analysis as an approach for the classification of regolith using IR-visible reflectance spectra of soil samples from Cyprus. Soil samples were obtained from the A and B horizons of a grid of sites at approximately 1 km spacing. Data sets were created using infrared spectrometer.

***The Atlas***

This report forms the basis to the Geochemical Atlas of Cyprus, published in July 2011 and released at an international Symposium in Lefkosia September 5-7, 2011 (Fig 2.39).



## 3 QUALITY CONTROL

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### 3.1 OVERVIEW

A detailed set of quality control procedures was implemented, covering all project tasks from field sampling and geochemical analysis to final data compilation (Fig 3.1). These procedures were based on various protocols used in the exploration and environmental geochemistry sectors (Reimann and Wurzer 1986; Reimann 2005; ISO-1994 1995) and were designed to deliver data fit-for-purpose through meeting the data quality objectives (DQOs) outlined in the following chapter.

The sampling and analytical methods in particular were designed to conform, as closely as possible, to the protocols used in the Geochemical Atlas of Europe (FOREGS 2007). Consideration was also given to the protocols for the National Geochemical Survey of Australia project (Caritat *et al.* 2007, 2009), the geochemical mapping of China (Xie 1995) and the NASGLP project for North America (Smith *et al.* 2009), although in some of these projects the principal sampling media was stream sediment and not soils *per se*.

It is noted that most large-scale regional geochemical mapping studies are not specifically aimed at mineral discovery but defining a hierarchy of broader geochemical patterns and geology-regolith-landform -landuse controls on the geochemistry (Xie 1995). Such studies typically require lower detection limits and higher methodological precision than in mineral exploration. The analytical protocols were also implemented to permit direct comparison of data from this survey with that of similar studies at regional to global scales (Darnley *et al.* 1995).

#### Project Control

All stages of the project were conducted or closely supervised by the project advisors (Cohen and Rutherford) to ensure conformity with the design principles and implementation of the quality assurance procedures agreed with the GSD. All procedures were documented in a series of manuals, with various components of the design, such as the analytical protocols, being tested prior to implementation.

Field sampling crews spent a number of days with the consultants being trained in sampling and field data collection. All staff involved in the sample preparation stages were provide detailed training and closely supervised. Detailed logs were completed during the sample collection and processing stages.

Quality assurance was partly based on a series of cross-checks, including repeat sampling of various sites by different sampling crews and a large set of quality control samples in the analytical runs independently generated by the advisors and the laboratory.

#### Setting Data Quality Objectives

The background to the setting of the DQOs was presented in Progress Report (GAC06-2008).

#### 3.1.1 Sampling and field data collection

The key DQOs for field sampling were:

- i. Sample locations (as determined by GPS) to be within 10 m of the true location.
- ii. Site numbers to be recorded on sample bags and in field log books, along with field data, without error.
- iii. Sampling methods to be conducted in accordance with the Manual for Field Sampling (GAC01-2006) or variations noted in the field logs.
- iv. Field data to be completed for each site, without gaps, and recorded in accordance with the Manual for Field Sampling.
- v. Samples to be properly dried and delivered securely to the GSD and UNSW.
- vi. Samples to be properly archived and stored for subsequent work at the GSD and UNSW sample storage areas.

### 3.1.2 Analytical quality control

The following analytical DQOs were set:

- i. No error in the identification of samples, allocation of laboratory numbers or entry of data to the digital database.
- ii. Analytical accuracy for the ICP-MS and INAA analyses to be;
  - a. Minimum  $\pm 8\%$  accuracy with no exceedences for any analytes at concentration above 10x the Actlabs reported detection limits (DLs).
  - b. Minimum  $\pm 15\%$  accuracy with no exceedences for analytes at concentrations 5–10x the Actlabs DLs.
  - c. Values  $< 5x$  DL to be reported without DQOs specified.
  - d. Only one reference material (CYP-A/B/C or GXR-6) to report at worse than  $\pm 5\%$  accuracy at concentrations  $> 10x$  the Actlabs DLs per sub-block of 80 analyses.
- iii. Sub-sample methodological precision, incorporating sample dissolution and analysis, to be  $< \pm 10\%$  at the 95% confidence limit for concentrations above 10x the Actlabs DLs. This is to be determined using both Actlabs and UNSW duplicates and utilising the Thompson-Howarth method for calculations.
- iv. No contamination to be detectable in field or solution blanks, with the exception of trace Fe in low-Fe samples (due to the milling) at 3x the Actlabs DLs.
- v. Review of quality control data to be undertaken by a suitable qualified person independent of Actlabs, UNSW and the GSD.

### 3.1.3 Other data

Digital data provided by the GSC had DQOs defined by that organisation.

Monitoring Data Quality objectives

### 3.1.4 Accuracy

Establishing the accuracy of the ICP-MS and INAA analyses was largely based on a set of project-specific reference materials developed on material from Cyprus (CYP-A, CYP-B, CYP-C and quartz blanks) and a series of reference materials routinely used by Actlabs (ORES100-P and ORES45-A for aqua regia ICP-MS analysis, and TILL-1 to TILL-4 for INAA), plus an international reference material (USGS GXR-6). Accuracy was also maintained for the ICP-MS analyses by frequent re-calibration against a set of 16 multi-element solutions containing various combinations and concentrations of analytes<sup>2</sup>.

The use of reference materials largely followed the approach suggested by Xie (1995), though the frequency of inclusion of reference materials far exceeded the typical rates (Table 3.2).

Variations in accuracy (or calibrations for some elements near detection limits) using the reference materials was monitored using standard analytical control charts.

Whereas there are no agreed international standards on the setting of accuracy targets for regional geochemical mapping (partly because of the variation in analytical method used), the NASGLP project pilot study has specified a methodology accuracy requirement, defined on the basis of recovery of elements from a series of reference materials, as  $\pm 15\%$  (Smith *et al.* 2009).

### 3.1.5 Precision

Data precision was examined at three levels – analytical precision, methodology precision and site variability. It has been noted in a number of previous studies that a very large component of total measurement error may be introduced during the sample collection, in addition to natural

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<sup>2</sup> The Actlabs protocols require 16 different multielement reference solutions be analysed for calibration checks after every 80 analyses.

geochemical variability in sampling media and at given sites, and that subordinate amounts of error are introduced during preparation and analysis (ISO 1993; Geelhoed and Glass 2001; Ramsey *et al.* 1992; Ramsey and Argyaki 1997; Stanley and Lawie 2007; Squire *et al.* 2000).

Problems exist for extensive sampling programs in inhomogeneous systems (e.g. regional geochemical mapping) where the site variance plus sample variance components vary substantially across a region, but where the subordinate components (processing and analysis) do not vary substantially. The use of sample duplicates has been shown to be a practical and applicable method of estimating uncertainty from sampling in large-scale surveys (Thompson *et al.* 2002; Lyn *et al.* 2007), and was therefore used in this study. Precision and components of variance were subsequently determined using the method of Thompson and Howarth (1976) and ANOVA.

### 3.1.6 Detection limits

The definition of “detection limit” by the Analytical Methods Committee of the Royal Chemical Society (RCS 1987) is *the minimum concentration that can be detected above a field blank*. This may be calculated as  $3\sigma$  units above the (analytical) value for a “zero analyte”, where  $\sigma$  is the standard deviation of the responses of field blanks under a given (and complete) analytical procedure. In this study, the practical quantification limit took into account processing errors and natural sample variability at the sub-sample scale. In some cases the detection limit reported was higher than the analytical detection limit quoted by the laboratories.

### 3.1.7 Contamination and blanks

Multi-step sampling, processing and analytical procedures are subject to various sources of contamination. With the use of Cr-steel spades and W-tipped augers, cleaning between samples, precontamination of digging equipment and the Al+steel field sieves (using soil at each site) and, given the large volumes of samples collected (>500 g), detectable levels of sampling-induced contamination was unlikely. Contamination at the sample processing or analytical stages was monitored using quartz blanks developed from milled and acid-washed quartz sand.

### 3.1.8 Quality control samples

The proportion of quality control samples within the set of 12,700 unknown samples is summarised in Table 3.1 and Fig 3.2. Sample analysis was broken down into batches of ~250 samples with the positioning of quality control samples in the ICP-MS analytical run set out in Fig 3.3. The structure was similar for the INAA runs, except for the lack of solution references.

The percentage of quality control samples in this study is compared with those of the FOREGS project in Table 3.2, indicating a higher proportion within-lab reference materials and duplicates in this study. The table excludes a number of other in-house reference materials used by Actlabs but which were not included in the QC assessment.

### 3.1.9 Determination of precision and detection limits

Analytical precision is partly a function of concentration (Fig 3.4), and DQOs are typically defined at concentrations well above the detection limit or practical quantification limit. Precision estimations were performed using duplicate samples, and analysed using both simple scatterplots as well as the precision control chart and calculation methods based on duplicate sub-sample analyses technique of Thompson and Howarth (1976) (Fig 3.5).

## 3.2 ANALYTICAL ACCURACY

### 3.2.1 Establishing target values

The need for geological reference materials (GRMs) that reflect the typical composition of unknown samples to be geochemically analysed is emphasised by Xie (1995). The three “end-member” GRMs developed for this study were CYP-A (a calcareous soil), CYP-B (a basaltic soil with a trace of pedogenic carbonates) and CYP-C (an ultramafic soil).

Results of the seven laboratory round-robin analytical program to determine the expected values for CYP-A, -B, -C and a comparison with USGS GXR-6, are presented in Appendix 3.1 and summarised in Table 3.3. In all laboratories (except Lab 3) the Actlabs-preferred 1:2.5 HNO<sub>3</sub>:HCl aqua regia ratio was used. Reported detection limits for the various elements vary between the seven commercial analytical laboratories. It is emphasised that, unlike total geochemical analytical methods, aqua regia extractions and other partial extraction methods are subject to varying behaviour depending on the exact digestion conditions (time, temperature, order of addition of reagents) and the nature of the sample matrix and mineralogy.

Although USGS GXR-6 is certified for total metal analysis, Actlabs results for elements that typically occur in contaminated soils in mobile form or in mineral matrices readily digested in aqua regia were statistically equivalent. This included Cu, Co, K, Mn, Ni, Pb, Sr, Zn and, somewhat less expectedly, Fe, Cr and most of the REEs. For refractory elements where aqua regia does not typically extract high proportions, the Actlabs values were higher for a few elements than other laboratories (e.g. for Hf, Li, Sc and Ti) but were otherwise similar.

The average RSD on the three analyses performed on each of the three project GRMs and USGS GXR-6 by the seven commercial laboratories were determined to assist in setting DQOs and for calibrating the analytical control charts.

For the vast majority of the elements and GRMs the RSDs were <5%, even for some where analyses were between 3 and 5x DL (Fig 3.6). For some elements the RSDs were much higher (Fig 3.7), but this is normal for analytical values <5x DL. For all elements except Te and Sb, at least one UNSW reference material (and at least two other GRMs used internally by Actlabs) had concentrations well above the DLs and with RSDs below 5% for subsequent analytical quality control applications.

### 3.2.2 Evaluation of accuracy

Analytical quality control charts for the key GRMs – CYP-A, CYP-B and CYP-C for aqua regia extraction ICP-MS and Till-1, 2, 3, 4 for INAA – are provided in the Appendix. The structure of the control charts is indicated in Fig 3.8. The INAA data for CYP-A, B, C were included to assist in monitoring sub-batch consistency rather than evaluating absolute accuracy. Data are included for two other GRMs used by Actlabs for ICP-MS (ORES100-A and ORES45-P).

The target zone for each analyte was defined as the certified or recommended values  $\pm$  one standard deviation of the GRM analyses after trimming values outside the 10<sup>th</sup>–90<sup>th</sup> percentile for the entire analytical run. Providing the analytical means obtained for the GRMs are close to the recommended values and errors normally distributed, then the target zone statistically contains 68% of the values. A more rigorous criteria was applied where values were >10x DL, such that no more than 10% of observations were permitted outside the target zone and all values in excess of two standard deviation from the recommended value were followed up with the laboratory to check calibrations and, if necessary, reanalysis of the sub-batch. Indications of other analytical problems, such as drift, were also examined.

A full statistical summary of the GRM results in comparison with the recommended or certified values is presented in the Appendix. The structure of these tables is set out in Fig 3.9. The DQOs for accuracy were determined as having been met if analytical averages were within one standard deviation of the recommended or certified value, for any analyte with a mean / recommended value ratio >5.

There was overall close agreement between the means for the reference materials and certified or expected values (Fig 3.10 and 3.11). A few element means for GXR-6 were significantly below the certified (totals) concentrations under aqua regia extraction ICP-MS, but this is expected as the aqua regia digestion is not a total extraction method. Also, some elements have INAA detection limits well above the aqua regia ICP-MS expected value for CYP-A, B, C.

Whereas CYP-A, B, C were also submitted for INAA analysis, the results for ICP-MS are typically lower than for INAA due to a number of elements being contained in minerals that are not readily digested in aqua regia. Similarly, the results for the two ORES reference materials were relatively consistent for all elements reporting at >10x detection limit but some resistate elements also reported slightly below the recommended values. It should be noted that the primary checks of calibrations (and

corrections) for the ICP-MS analyses were the 16 multielement solutions that were re-analysed after every 80 samples. The reference materials were then largely used to monitor inter-calibration precision. The analytical sequences for the reference materials show no indication of long-term drift or changes in relative precision or accuracy for any of the elements (emphasising the advantages of having run the ICP-MS analytical program as essentially a single batch). There is short-scale cycling in analytical values for some of the reference materials (for example in the Ba and Ce data) but this was within the target zone. There were no broader trends observed in the full analytical sequence beyond some clustering of high and low values which related to the areas of Cyprus from which the various blocks of analytical samples were drawn (i.e. CTSS sampled versus Troodos sampled).

INAA concentration for a number of the orientation line samples were analysed by XRF and indicated very similar total metal contents for Ca, Na and Fe (Fig 3.12).

Variations in the values for GRMs submitted in the batch of samples analysed by selective geochemical extractions (ammonium acetate and hydroxylamine) are presented in the Appendix. There are no established certified values, but accuracy of the analytical determinations was based on the calibration solutions using the digestion matrices and blanks.

### 3.2.3 Contamination

Data from the sample blanks (acid washed milled quartz) indicated no significant sources of contamination or miss-calibration of analytical “zero” values. Milling tests indicated minor contamination by Fe and Mn, but at levels well below natural Fe and Mn concentrations in the samples.

### 3.2.4 Analytical and methodological precision

Precision has been monitored at various hierarchical levels by way of analytical duplicates, sample processing duplicates and site duplicates (including development of two soil variation test sites over basaltic and calcareous soils). Precision was also monitored as part of the monitoring of accuracy. The results for the site, processing and analytical duplicates are presented as both scatterplots and Thompson-Howarth plots in the Appendix. An example of the precision control charts is presented in Fig 3.13.

Correlation between analytical duplicates was high ( $r_{\text{corr}} > 0.9$ ) above 10x DL with variation then increasing with increasing proximity to detection limits. Correlation above 10x DL was partly dependent on the form of elements and their association with major “control” elements. For example, the form of the scatterplots for Ba, Sr, and most REEs were similar to Ca indicating carbonates to be their major host. Conversely, elements that are closely related to Fe in soils (Cr, Co, Ni, Cu and Mn) displayed very high correlation between duplicates across the entire concentration range. In general, the processing duplicates (separated prior to milling) display higher variation than the analytical duplicates (analyses of duplicates from the same milled sub-sample).

Site duplicates are plotted against processing and analytical duplicates for selected elements in Fig 3.14. For all elements, whereas there is still good correlation between site duplicates, the site variation was larger than the variation observed for the processing and analytical duplicates. The correlation between the analyses for sites that were resampled by different field crews and sample processes by different laboratory assistants were also high indicating minimal sources of additional variance due to variations in procedures of different crews.

The Thompson-Howarth plots indicate most elements analysed by ICP-MS display a subsample methodological precision better than  $\pm 10\%$  for values exceed 10x DL and, in many cases, even within the range 5x–10x DL. For INAA, the analytical precision was generally poorer, but this reflects a high proportion of values being less than 10x DL. Based on these plots and other data, a comparison between the reported Actlabs detection limits (DLs) and the methodological practical quantification limits (PQLs) is presented in Table 3.4. The detection limits and RSDs on element analyses are compared with those of the FOREGS data in Table 3.5.

Correlation between particle sizing duplicates was high (Fig 3.15) and was the correlation between selective extraction (AAC and HXL) duplicates.

As a further test of sample processing and analytical quality, the determined bulk element concentrations was compared with the reconstructed bulk composition based on the element

concentrations and eight percent of the component fractions for the orientations sampled. The correlation was again high (Fig 3.16).

### **3.2.5 Sources of variance**

A comparison of variance at the sub-site (1 m) and site (10–100 m) levels was undertaken for two field variation test sites. The location of samples within the two test areas is shown in Fig 3.17. Bar charts for selected elements in Fig 3.18 and ANOVA partitioning of variance in Fig 3.19.

For elements where values are well above the detection limit, such as Ca, Cr, Cu and Fe, there is a significant proportion of variance due to real variation in soil chemical composition at the sampling scale of 10–100 m compared with the scale of 1m. For elements with either high natural variability or values near detection limit, there was no significant difference in the variation at the two scales. The effect of difference in detection limit between ICP and INAA is shown for Mo, where 80% of the site variance is between sites for ICP, whereas 100% of the variance is within sites for INAA. There are no systematic differences between the A and B samples in terms of partitioning of variance, though this is unlikely to be the case where sample were collected in areas with thin transported top soil and residual sub soil.

## **3.3 DQO CONCLUSIONS**

In summary, the DQOs for analytical accuracy and precision were met for all analytes required for the project, for both ICP-MS and INAA. Although some elements routinely reported close to the detection limits, most key elements critical to the project – those related to mineral deposits, contamination, salinity and major controls on trace element distributions – reported well above detection limits.

## 4 RESULTS PART A – THE ATLAS AND OTHER MAPS

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The results are presented in two sections. This Section focuses on the raw element maps that form the basis of the Atlas itself, together with other maps derived from processed data or statistical models. Section 5 presents more general statistical analysis, the orientation lines, regolith profiles and the detailed mine site surveys.

### 4.1 ATLAS DESIGN

#### 4.1.1 Data presentation

There are a number of options for the presentation of geochemical maps derived from independent point observation but where there is a demonstrated degree of spatial continuity (the geostatistical concept of a “regionalised variable”). Plotting options can be divided into:

- (i) *Symbol plots* that represent the value of each point *in situ* without interpolation of values or conversion to a continuous surface or regular grid. The relationship between values and symbols depends on the aspect of the data intended to be highlighted. This can range from proportional representation linking values to symbol size, shape or shading, in a linear or non-linear relationship, to quantised values representing a number of pre-determined ranges.
- (ii) *Gridding and contouring procedures* that interpolate point data to create a continuous surface that can be colour sliced or proportionally shaded to represent spatial variations in values. Interpolation of non-gridded data is typically based on a weighted averaging of surrounding point values for which methods of assigning weights and setting limits to the search ellipses range from “rule-of-thumb” techniques such as inverse distance squared and spatial filtering methods described by Chork and Mazzuchelli (1990), to the more objective variography–kriging techniques routinely used in geological resource estimations.

Both approaches have conceptual advantages and disadvantages in balancing the need to preserve data integrity and limit processing artefacts versus the need for visual impact.

A number of presentation methods were tested based on the approaches by GTK and others (Björklund and Gustavsson 1987, Gustavsson *et al.* 1997) and techniques used in recent geochemical atlases. A variety of symbol plots and pseudo-contouring colour schemes are presented in Fig 4.1. Proportional size dot-plots with linear or non-linear scaling between geochemical value and circle diameter, and colour dot-plots preserved the spatial relationships between the samples. This is especially the case for central Troodos where sampling was less regular than the surrounding areas. However, individual point plots failed to visually convey the lithologically-controlled spatial patterns and edges with the same degree of visual impact as the more continuous colouring methods. Part of this is related to the large number of samples. Most of the data are effectively gridded anyway by virtue of the sampling design.

Multi-coloured (rainbow) contouring was visually more dynamic than simpler two-colour plots. Spatial patterns were more distinct with the 11-colour than the 5-colour scheme. Adding aspect shading to the plots provided some improvement in detail for areas with very high values and extreme variability at the 1 km scale (e.g. Cr values in the ultramafic core of the TOC and Mamonía Terrane), but otherwise shading added unnecessary complexity to the plots. Incorporating dot-plots with an underlying continuous coloured plot (as per the FOREGS Atlas of Europe) also provided too much visual “noise”. The 11-division rainbow plots were, therefore, selected as the optimum presentation method, although dot-plots are used in some detailed maps of the mine areas and profile studies where the data density in the maps is lower.

It is noted that the map colours are roughly linked to fixed-interval percentiles (10%). Variables with very limited ranges and RSDs (e.g. *ar-P*) have similar scaling to those with very high ranges and RSDs (e.g. *tot-Cr*), hence the red zones may correspond to areas with extremely high values compared with the bulk of the data or to areas with geochemical values just marginally higher than the global means.

### 4.1.2 Data gridding

Gridding methods were tested using data from three detailed sub-areas containing a variety of lithologies (Fig 4.2). Dot-plots for Ba, Fe and Cr demonstrate the strong controls on geochemistry by lithology, with Ba elevated in the carbonates, Fe in the basalts and Cr in the ultramafics.

*Mapinfo* offers two gridding methods, based on inverse-distance weighting (IDW). Under IDW, the estimate for a variable at point  $P_{x,y}$  (typically the grid cell centre) is given as:

$$P_{x,y} = \frac{\sum (X_i / w_i)}{\sum w_i}$$

where:

- $w_i$  =  $1 / D_{xi}^a$
- $D$  = the distance to point  $X_i$ .
- $a$  = the exponent selected by the user.
- $X_i$  =  $1 \rightarrow N$  for all  $N$  points within the search radius (SR or  $D_{max}$ ) selected by the user.

The exponent  $a$  (hence  $D^a$ ) controls the balance of weightings between close and distant neighbours.  $D_{max}$  is set to limit the potential unwanted influence of distant points with very high or outlying values and accelerate data processing. Values of  $a$  close to 2 have traditionally been used, based on empirical observations.

The final parameter to select is that of the grid size. This is influenced by a number of factors, including spatial sampling density, the search radius (SR),  $a$  and the degree of visual smoothing required in the data. Excessively large grid cells relative to the sampling density produced over-smoothing and loss of localised groups of points (or single points) with high or low values. Excessively small grids increased processing time and gave the illusion of spatial data smoothness that rarely reflects actual soil geochemical patterns.

For the three areas and elements selected (Fig 4.2), the cell size was varied between 0.2 and 0.5 km, the exponent between 1.0 and 2.0 and SR between 1 and 3 km. The results of the gridding and a comparison with the raw data dot-plots are provided in Figs 4.2 and 4.3.

For the Cyprus data, the parameters that had the most control or visual effects were the SR, followed by grid cell size. An SR of 1 km generated gaps in the plots due to variations in the sample distributions (especially over Troodos), whereas an SR of 3 km resulted in the loss of some short scale spatial variation and blurring of geochemical edges related to major lithological boundaries. Variation in the grid cell size did not generate significant change to the perceived patterns in the data. Increasing  $a$  to  $>1.6$  preserved point anomalies, although there was little difference between  $a = 1.3, 1.6$  and  $2.0$ , for the grid cell size and SR values selected.

Based on the variables and parameters tested, the final model selected was:

Grid cell size	0.33 km
Exponent ( $a$ )	1.6
Search radius (SR)	2 km

Variography and kriging was performed on *ar-Al\_A* and *tot-Cr\_A* for sub-area 1 (Fig 4.4). Using an unoriented search ellipses, both elements displayed spatial correlations and smooth variograms to a range of 10–15 km. Most other elements with values well above detection limits displayed similar spatial correlation patterns. The spatial characteristics of the dataset are the subject of a subsequent paper.

A comparison was made between the selected *Mapinfo* IDW gridding and variography approaches, based on a common 0.33 km grid cell size (Fig 4.4). Kriging generated similar visual spatial patterns, but the loss of some localised maxima and minima values and blurring of lithology-related geochemical boundaries (a similar effect to that of a large search radius under IDW). Whereas the kriging parameters could be varied to better preserve some of the granularity and edges in the geochemical data, it appeared to offer no advantages over the simpler IDW gridding.

### 4.1.3 Map format

The maps are designed to deliver the maximum amount of visual geochemical and statistical data in the simplest visual form. The design followed a review of the presentation methods used in a number of recent regional atlases.

Seven major lithological groups have been used for statistical and graphical purposes:

- i. ultramafics – including the various cumulate units and the serpentinites
- ii. mafic intrusives – including the gabbro cumulates in central TOC and the sheeted dykes.
- iii. basalts – basal to upper pillow lavas.
- iv. mafic (and ferruginous) clastics
- v. silicic clastics
- vi. carbonates
- vii. alluvium-colluvium

The three main components to the maps are:

- i. Two geochemical maps with the images generated using the IDW procedure described above and sliced into 11-colour divisions. The selection of the divisions was initially based on an equal percentile spread for each variable plotted but with the boundaries subsequently modified to simplify the numerical scale and to highlight desired spatial features in the data.
- ii. Comparative boxplots, based on the seven main lithological groups, and global normal probability plots for the top soil and sub soil values for the two maps. In most cases the boxplots and probability plots were plotted on log scales. The fences extend for a distance of 1.5x the difference between the 25<sup>th</sup> and 75<sup>th</sup> percentiles values (known as the “hinge-spread”), below the 25<sup>th</sup> and above the 75<sup>th</sup> percentiles. Values falling outside the fences are deemed “outliers”. In some of the derived variables (such as ratios), the boxplots and probability plots were replaced by scatterplots. The boxplots are the standard Tukey-type (Fig 4.5).
- iii. Traverse plots for the two variables for the X-X’ and the Y-Y’ orientation lines, with the lithological groups co-plotted.

The derived maps (Volume 3 of this report) are grouped according to various element and element-lithology associations. General overviews of most elements are provided in the FOREGS atlas documents (<http://www.gtk.fi/publ/foregsatlas/text/>), Reimann and Caritat (1998), other atlases and texts on exploration geochemistry such as Levinson (1980).

## 4.2 PHYSICAL CHARACTERISTICS

The majority of soils in Cyprus display near-neutral to alkaline pH values when slurried with water. This reflects the influence of carbonates in the CTSS and colluvium-alluvium areas and alkaline earth oxides and hydroxides derived from the dominant mafic and carbonate-rich lithologies in the TOC and Mamonia Terranes. Most of the carbonate-dominated formations (e.g. The Pakhna and Lefkara Formations) generated soil pH >8.3, which is significantly more alkaline than the average for the rest of Europe (pH 5.5–5.8), although there is a distinct increase in pH in Europe going from north to south. With few exceptions, no soils with >5% Ca had pH <7.5, and no samples with >4.5% Ca had pH <5. This was demonstrated in the Limni study by Constantinou (2008).

Landuse and vegetation type does not appear to affect soil pH. Values below pH 6.4 are largely restricted to the vicinity of the sulfide mines. The samples containing sulfidic mine wastes have pH <3.5. Sporadic low pH values throughout the sheeted dykes of the western end of Troodos reflect isolated zones of sulfide mineralisation; a feature indicated by secondary Cu minerals such as malachite observed in various locations. Where Fe contents exceed ~5%, alkaline conditions generally produce strong red-brown colouration in the soils, whereas in neutral to acidic conditions there is a yellow-red colouration due to the greater degree of hydration in the secondary Fe minerals.

EC is simply a reflection of soluble salts and other conductive materials in the soils. Values are very high in the salt flats and along much of the coastal areas, excluding the cliff-dominated areas between Episkopi and Mandria and parts of the Akamas Peninsula. The areas of elevated EC ( $>0.3$  mS/cm) extend into the agricultural areas on the eastern side of Troodos. There is no spatial correlation between *ar*-Na and EC (outside the salt flats). Overall EC values are low compared with the rest of Europe (outside Fennoscandia) and probably reflect high drainage rates in all areas except the coastal salt flats. EC is typically higher in the valleys than the ridges on the southern side of Troodos.

### 4.3 MAFIC-ULTRAMAFIC INTRUSIVES AND VOLCANIC ASSOCIATED ELEMENTS

In referring to analytical methods, the aqua regia-extractable (ICPMS-analysed) values for each element are abbreviated to *ar*-, and the total (INAA analysed) values as *tot*-.

The top soil samples are labelled A and the sub soil samples as B.

#### 4.3.1 Iron

Iron is the fourth most abundant element in the Earth's crust. It is one of the main constituents of mafic and ultramafic rocks (the ferro-magnesian minerals) and sulfide deposits (pyrite, chalcopyrite and other sulfides). In the secondary environment Fe is a major element in many weathered profiles, due to the low mobility of Fe<sup>III</sup> oxides and hydroxides, where it generates strong yellow to red colouration. Most ferromagnesian minerals (such as olivine, Fe-pyroxene, Fe-amphiboles and chlorite) and sulfides, are unstable in the surface environment. Magnetite and chromite, common minerals in ultramafic and some mafic rocks, are more resistant to weathering and contribute to the mechanical dispersion of Fe.

There is a marked difference between the Fe contents of soils in the TOC and volcanic units of the Mamonia Terrane, and the surrounding CTSS units. The soils in the ultramafic core of the TOC contains *ar*-Fe contents in excess of 6% and *tot*-Fe in excess of 7%. The basaltic areas also display high soil Fe contents. The gabbros surrounding the ultramafic core display a zone of low *ar*-Fe values compared with *tot*-Fe (hence the low *ar*-Fe/*tot*-Fe ratio). In the gabbro cumulate areas a significant proportion of the Fe is present in unweathered or partially weathered primary minerals in those areas as immature soils are skeletal and erosion rate high. The *tot*-Fe in the mafic intrusives is relatively uniform (7 – 10%).

The CTSS and other carbonate-dominated areas display low soil Fe contents (<2%). There are very sharp soil geochemical boundaries (at the 1 km scale of sampling) between high and low soil Fe values along the southern boundary of the TOC. The *tot*-Fe contents are slightly elevated along the coastal fringe, reflecting the accumulation of magnetite grains and cobbles derived from the TOC. Whereas the general patterns are identical between the two sampling depths, the ratio of *ar*-Fe between top soil and sub soil is highest along the southern boundary of the TOC and the middle sections of the CTSS. This may reflect elevated amounts of Fe in the thin layers of sheetwash and colluvium that overlie the weathered carbonates. The *ar*-Fe/*tot*-Fe ratio (a rough indication of element mobility) is highest in the former Polemi Basin on the western side of Troodos and in the pillow basalts.

#### 4.3.2 Manganese

Manganese is geochemically closely related to Fe in most environments, substituting in a number of primary minerals and co-precipitating with Fe<sup>3+</sup> in the secondary environment. Manganese is generally depleted in ultramafic rocks and most mafic intrusives relative to basalts. In the secondary environment Mn is present as pyrolusite (MnO<sub>2</sub>) plus an array of Mn and Mn-Fe oxyhydroxides and carbonates.

There is less variation between median *ar*-Mn values of the various lithologies than other major elements (as shown in the comparative boxplots). The pillow basalts display the highest soil *ar*-Mn contents at 1,500–8,000 mg/kg whereas the cumulate gabbros and Pakhna Formation carbonates have the lowest Mn values at 200–350 mg/kg. There is a 5–10 km zone with low *ar*-Mn around the TOC ultramafic core corresponding with the gabbro cumulates. As with Fe, the Mn oxides and hydroxides in the surface environment have the capacity to scavenge a number of siderophile and chalcophile metals in neutral to alkaline soil pH conditions via co-precipitation or adsorption. Both Fe and Mn values are elevated in the vicinity of the sulfide deposits and this may be due to ochre and umber deposits derived

from hydrothermal activity. The few areas sampled where soils were derived from Peripedhi Formation sediments, including umbers and shales, display elevated Mn (and Ni and Cu).

### 4.3.3 Sodium

In igneous and metamorphic rocks, Na is mainly bound up in feldspars, with lesser amounts in micas, amphiboles and other aluminosilicates. In the secondary environment and sedimentary rocks, Na is present in various clay minerals in both structural and exchangeable sites and as chlorides and carbonates in saline areas and evaporitic deposits. Despite its high mobility in the surface environment, there is a substantial influx of Na to the landforms in many regions from dissolved salts in rainwater and aerosols.

The distribution of Na is controlled by two separate factors, yielding large differences in the *ar*-Na and *tot*-Na patterns. The highest *ar*-Na values (>5%) are found in the saline lakes and salt flat areas such as Akrotiri and Larnaka. In the main drainage basins and coastal flats, where the effects of sea spray, elevated groundwater tables or seawater intrusion into aquifers may add Na to the soil, *ar*-Na values commonly range from 0.3% to 0.5%. Elevated *ar*-Na on the western side of the TOC corresponds with the Karkotis Valley in which groundwater also has high elevated Na. There is some elevation of *ar*-Na in the pillow basalts relative to the mafic intrusives, which may be related to release of Na from seawater-altered basalts (spilitisation). The *tot*-Na values are spatially more consistent than the *ar*-Na, and are highest in the mafic intrusives and the pillow basalts, including a 10-km-wide north–south corridor on the western side of the TOC. This reflects both minor amounts of Na in the primary feldspars and possible subsequent spilitisation of the basalts. There is a marked contrast between the ultramafics and the surrounding gabbros.

Aqua regia does not easily attack feldspars and this is demonstrated by the *ar*-Na:*tot*-Na ratio, which is uniformly low across the TOC. In effect this ratio is a measure of the amount of (unweathered) feldspar remaining in the soils and sediments as well as a potential indicator of the amount of Troodos-derived materials in the regolith. The *ar*-Na:*tot*-Na ratios are lowest on Troodos and along the southern coastline. The spatial pattern in the ratio of *ar*-Na between top soil and sub soil is erratic and indicative of discontinuous zones of Na accumulation at the surface, related to spring and groundwater seepages. Values are lowest over the ultramafics and the carbonates.

### 4.3.4 Aluminium

Aluminium is the most abundant metal in the crust and a fundamental component of the aluminosilicate mineral groups, including the feldspars and micas. Silica-deficient mafic rock may carry corundum and Al-bearing spinels. Aluminium values are typically low in ferromagnesian and carbonate minerals. In the secondary environment Al displays low chemical mobility, with most Al bound up in clays and substituted for Fe in Fe+Mn oxyhydroxides such as goethite. Aluminium mobility increases at low pH (e.g. near areas with acid mine drainage) and in strongly alkaline conditions (pH >9). The end-point of very intense weathering is commonly just Al oxides and hydroxides (bauxites).

*ar*-Al is a relatively uniformly 2–5% in the mafic units and <1.5% in the remaining units, apart from some elevated values relating to clay accumulation in a few of the coastal estuaries and salt flats. Peak values occur in isolated residual soils derived from mafic units on ridges over Troodos. The concentrations are particularly low in the carbonates (<1.5%), indicating a lack of clays. There is a very sharp boundary shown in the X–X' traverse at the CTSS–TOC contact in both top and sub soil.

### 4.3.5 Gallium, germanium, scandium and vanadium

Gallium, Ge, Sc and V can substitute for Al (and Fe, depending on valency) in various minerals, hence, the patterns for those elements closely follow those of Al. Vanadium can also substitute for Fe in minerals such as magnetite, which is a common component of ultramafic and mafic rocks. The only variations in this trend are the more elevated Ga, Sc and V in the pillow basalts on the northern side of Troodos. The association of Sc with feldspars in the mafic units (and derived clays in the weathered zone) is more strongly shown in the *tot*-Sc patterns with very uniform 30–40 mg/kg Sc. Scandium appears more closely associated with Al than the more typical association with Fe. *ar*-V values are

very low in the ultramafics, gabbros and carbonates. Although the detection limits for Ge are high, there appears limited variation between lithologies.

#### 4.3.6 Magnesium

In igneous rocks, Mg is associated with Fe in ferromagnesian minerals (olivine, pyroxene and mica) and various phases in metamorphic rocks such as chlorite, talc and serpentinite. In the surface environment and sedimentary rocks, Mg is typically hosted by carbonates (magnesite-dolomites) or smectitic clays. Calcite may be converted to dolomite ( $\text{CaMgCO}_3$ ) during diagenesis of carbonate sedimentary rocks, although dolomite can precipitate directly in hypersaline environments or sabkhas.

Magnesium contents are highly elevated in the ultramafic-derived soils (Mg typically >4%) and the pillow basalts (especially upper pillow lavas) relative to the other mafic intrusives. This is consistent with the lavas being at the mafic end of basaltic compositions. Magnesium is a contributor to the soil alkalinity in Troodos. The soil *ar*-Mg content of the CTSS units is very low, indicating a general absence of dolomite. Slightly elevated *ar*-Mg contents along the coast may be related to Troodos-derived cobbles.

The Akamas Peninsula mafic units tend to have higher Mg and lower Mn than the equivalent lithologies in the Troodos area, and through both rock composition and weathered profile development, commonly have thin calcrete layers directly overlying the weathered mafic units.

#### 4.3.7 Titanium

Titanium substitutes for Fe and Al in oxides and some aluminosilicate. A significant proportion of Ti, especially in weathering or sedimentary environments, is bound up in the two highly resistate minerals rutile ( $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_3$ ). In the secondary environment there is some substitution of Ti for Fe in goethite. Apart from very low values in the ultramafics, the overall distribution of Ti does not vary greatly between lithologies with most units delivering soils with 0.04 to 0.2% *ar*-Ti. It is emphasised that aqua regia will only extract a small proportion of *tot*-Ti. *tot*-Ti values were consistently high in the mafic units due to the presence of ilmenite and along the coast where heavy minerals accumulate.

#### 4.3.8 Chromium, nickel and cobalt

These elements are typically highly elevated in ultramafic lithologies due to substitution for Fe in various ferromagnesian minerals and the formation of their own minerals. Chromium mainly substitutes for Fe in spinels as well as forming its own spinel - chromite ( $\text{FeCr}_2\text{O}_4$ ). There were economic chromite mines associated with harzburgites and dunites in Troodos, with sporadic chromite accumulations spread throughout the ultramafic units (including the serpentinites where chromite tends to survive the hydrothermal alteration). In the secondary environment, Cr is typically preserved as chromite which disperses mechanically.

In the absence of a sulfide melt component, Ni (and to an extent Co) substitute into olivine and pyroxene. Otherwise Ni is typically present in sulfides such as pentlandite ( $(\text{Ni,Fe})_9\text{S}_8$ ) or millerite ( $\text{NiS}$ ), and Co in cobaltite ( $(\text{Co,Fe})\text{AsS}$ ) or linnaeite ( $\text{Co}_3\text{S}_4$ ). Most sulfide deposits contain elevated Ni and Co due to substitution for other chalcophile elements. Hence, Ni and Co can display associations with either the siderophile elements (especially Cr) or the chalcophile elements, depending on igneous rock bulk composition. In the secondary environment, Ni and Co-bearing minerals are generally very unstable, although both elements display complex supergene and hypogene mineral assemblages. Nickel and Co released during weathering typically associate with secondary Fe and Mn oxides.

Soil *ar*-Cr and *tot*-Cr concentrations are an order of magnitude higher over the ultramafic lithologies than any other lithology (including the mafics). This includes the Arakapas Transform Sequence. Chromium is also elevated in the vicinity of the slivers of serpentinite on the Akamas Peninsula and to the east of Pafos, low-lying areas along the southern coastline, the Kokkinokhoria region and the northern end of the Polis Valley. A comparison of the *ar*-Cr and *tot*-Cr data (including the ratio map) indicates significant variations in signature between these areas of elevated soil Cr contents. There is generally a converse relationship between soil *tot*-Cr and the *ar*-Cr/*tot*-Cr ratio, suggesting that in areas with low Cr values most of the Cr is in extractable form (e.g. associated with Fe oxides) rather than bound up in chromite or Cr-substituted magnetite. The ratios are very low along the entire southern

coast, and especially in the fanglomerate-dominated Kokkinokhoria area, indicating the majority of Cr in those areas is present in either clasts of transported ultramafics or as chromite in the heavy mineral component of the sands observed at many of the beaches. The top soil/sub soil ratio of Cr is commonly >1, which is probably the result of lag accumulations of chromite at surface. The elevated Cr values in the Upper Pillow Lavas compared with the other basalts are related to their picritic nature.

Nickel typically follows the Cr trends with respect to the ultramafic areas. There is over 1.5 orders of magnitude difference between Ni in the ultramafic areas and other lithologies. There are a number of areas within the basalts containing slightly elevated Ni contents, especially in the vicinity of the major sulfide deposits. Elevated *ar*-Co values strongly define the ultramafic units and the pillow basalts. *tot*-Co contents are consistently high in the ultramafic areas, and values in the other mafic units are significantly higher than the sedimentary units, especially in the vicinity of the sulfide deposits. Unlike Cr, the proportion of aqua regia extractable Co is between 0.5 and 1 suggesting most of the Co in the soils is associated with secondary Fe+Mn oxides rather than resistate primary phases. There are no strong patterns in the ratio of top soil to sub soil Ni and Co concentrations.

### 4.3.9 Phosphorus

Most primary P is contained in apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ ) which is a common accessory mineral in felsic to mafic rocks. Apatite was observed in some of the heavy mineral concentrates. Apatite slowly breaks down to a variety of secondary phosphates, though many of these are quite insoluble. Significant amounts of P cycles between the biosphere and soils, and a number of P mines involve guano deposits. Superphosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ) is commonly added to soil to improve pasture growth, as apatite is relatively resistant to weathering or biological attack.

Despite the low overall variation in the P content of the soils in Cyprus (0.01–0.1%), there are very distinct and consistent patterns related to two sources – the basalts and agriculture. There are very low *ar*-P and *tot*-P (by XRF) in the ultramafics (generally <0.01 %), 0.02–0.03 % in the sedimentary units and 0.07–0.2% P in the mafic units. There are slightly elevated P values in the agriculture-intensive Kokkinokhoria region, compared with the remaining CTSS. The data suggests there may be some use of superphosphate in the agricultural areas around Larnaca and possibly Kokkinokhoria. The FAO indicates that 100–700 t of superphosphate is imported annually to Cyprus but some of this may be then exported.

## 4.4 SULFIDE ASSOCIATED (CHALCOPHILE) ELEMENTS

The sulfide-associated elements (chalcophiles) generally display similar behaviour as a group in both the primary environment and the secondary environment. In the primary environment chalcophile elements will partition into the sulfide component of a melt, with excess S generally taken up by Fe to form pyrite ( $\text{FeS}_2$ ). There are a wide variety of sulfides and sulfosalts, for which the most common for each of the chalcophile elements are;

Pyrite	$\text{FeS}_2$	Arsenopyrite	$\text{FeAsS}$
Pyrrhotite	$\text{Fe}_{1-x}\text{S}_x$	Orpiment	$\text{As}_2\text{S}_3$
Chalcopyrite	$\text{CuFeS}_2$	Realgar	$\text{As}_3\text{S}_4$
Bornite	$\text{Cu}_5\text{FeS}_4$	Acanthite	$\text{Ag}_2\text{S}$
Chalcocite	$\text{Cu}_2\text{S}$	Sperrylite	$\text{PtAs}_2$
Tetrahedrite	$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	Sphalerite	$\text{ZnS}$ ( $\pm$ Cd and Fe)
Tennantite	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$	Galena	$\text{PbS}$
Stibnite	$\text{Sb}_2\text{S}_3$	Molybdenite	$\text{MoS}_2$
Pentlandite	$(\text{Fe}, \text{Ni})_9\text{S}_8$	Bismuthinite	$\text{Bi}_2\text{S}_3$
Gersdorffite	$\text{NiAsS}$	Cinnabar	$\text{HgS}$

There are also various metal alloys including electrum (Au-Ag) and Plat-iridium (Pt-Ir).

As a result of weathering and oxidation, beyond the complex zone of supergene and hypogene alteration above mineralisation most of the chalcophile elements co-precipitate or adsorb onto Fe+Mn oxides or carbonates, with transitory associations with clays and soil organics. The oxidation of sulfides generates sulfate and, in the case of Fe-bearing sulfides,  $\text{Fe}^{\text{III}}$  oxides and acid. This potentially

generates a number of environmental problems in Cyprus given the number of abandoned sulfide mines. In anoxic environments, such as swamps and estuarine muds, sulfate is reduced to sulfide and can cause precipitation of secondary sulfides such as pyrite and co-precipitation of other chalcophiles.

The mobilities of chalcophile elements are highly variable. Antimony and As are less mobile than Pb, which is less mobile than Cu and finally the more mobile Zn. Mobility also depends on the general composition of surface waters, with the presence of  $\text{Cl}^-$  ions reducing Ag mobility but increasing Cu and Zn mobility. pH is also a major control on mobility. Most common divalent chalcophile elements (Cu, Zn, Cd, and Pb) are much more mobile in acidic conditions due to the stabilisation in solution of the cations and prevention of adsorption to Fe oxides and organics. In neutral to alkaline conditions, most of the cations precipitate as hydroxy-carbonate species such as (malachite  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ). Conversely, trivalent to hexavalent cations may become more mobile in alkaline conditions through the formation of soluble oxyanions such as the arsenate oxyanion ( $\text{AsO}_4^{3-}$ ) and similar complexes of Mo, U and V.

In terms of spatial patterns in Cyprus, the chalcophile elements can be subdivided into three sub-groups:

#### 4.4.1 Copper, zinc, indium and gold

Apart from the low values in the vicinity of the ultramafics and some mafic intrusives, median soil *ar*-Cu concentrations do not vary greatly between the main lithology groups. Values are highest (>200 mg/kg) in the pillow basalts, especially near sulfide mineral deposits which represents the set of high outliers in the boxplots. The *ar*-Cu values in the ultramafics, CTSS and most of the Mamonnia Terrane are the lowest (<60 mg/kg). One feature of the *ar*-Cu is the 10 km-wide corridor of elevated values that runs north-south through the western side of the TOC, across the sheeted dyke complex. Elevated values for *ar*-Cu top soil / sub soil ratios are scattered but the highest values tend to occur in the vicinity of the sulfide deposits and the sheeted dyke complex. Most of the major urban areas (Pafos, Lemesos, Larnaca and Lefkosia) display slightly elevated *ar*-Cu values relative to non-urban areas with similar lithology.

Both *ar*-Zn and *tot*-Zn generally follow the Cu patterns. There are more pronounced top soil *ar*-Zn anomalies in the urban and industrial areas. The high *tot*-Zn values are mostly restricted to the vicinity of the sulfide mines. Indium is a relatively scarce metal in the crust and values are generally low across the region (<0.1 mg/kg). The pillow basalts and the Kokkinokhoria areas have In values (0.03–0.07 mg/kg). There are a few clusters of sites with *ar*-In >0.8 mg/kg and these are typically situated within the Cu mining areas. Unlike Cu and Zn, there are no detectable In anomalies in the urban areas.

Most sites displayed Au values below the detection limit (1  $\mu\text{g}/\text{kg}$ ). The sites with *tot*-Au values >20  $\mu\text{g}/\text{kg}$  are largely restricted to the known Cu deposits, some of which carry sub-economic Au grades. An example is the sub-economic supergene Au zones over parts of Skouriotissa. Gold geochemical patterns are generally erratic due to the particle scarcity effect, but elevated Au values in the top soil commonly correspond with elevated value in the sub soil. There are a number of elevated Au values in the urban areas (?slow pedestrians). There are more sites with elevated Au values in the sub soil, suggesting some elutriation of Au grains down through the soil profiles.

#### 4.4.2 Arsenic, antimony and cadmium

The *ar*-As and *tot*-As data includes a series of narrow anomalous zones (As >8 mg/kg) over known sulfide mineralisation. The Kokkinokhoria region displays consistently high As contents. Values are also elevated in the fanglomerates and Mesaoria Plain units surrounding Lefkosia, the Polis Valley (including the former Polemi Basin) and various sites along the southern coastal strip. The ratio plots indicate minor accumulation of As in the top soil and *ar*-As/*tot*-As ratio >0.7 mg/kg. The *ar*-As and *tot*-As values are generally higher in the carbonates than the mafic units (<5 mg/kg), indicating a regional carbonate affiliation especially along the valleys incised into the Pakhna and Lefkara Formations.

The Sb patterns are similar to As, although there is less of a general increase in Sb in the carbonates and fanglomerate, relative to the peak values associated with the sulfide deposits.

Cadmium normally follows Zn geochemically. Whereas Cd values are high (>3 mg/kg) near the sulfide deposits, unlike Zn the regions displaying the highest *ar*-Cd values are in the Lefkara Formation and lower Pakhna carbonates along the southern side of Troodos and the mixed lithologies in the south-west. The high Cd values do not extend completely across the carbonate areas, and in the Pakhna+Lefkara Formation carbonates to the north of Lemesos the elevated *ar*-Cd values only extend half way down from the TOC, dropping from >0.35 mg/kg to <0.15 mg/kg across an east-west line. There is no obvious explanation for this “barrier” apart from the possibility of the Cd accumulation being syn-depositional and that this concentration change is the result of some physicochemical boundary related to water depth of the original carbonate deposition.

#### 4.4.3 Bismuth and molybdenum

Bismuth and Mo display an antithetic relationship over the Lefkara Formation with Bi values enriched and Mo values depleted. Otherwise, these elements display some similarity to As and Se in terms of locally elevated values near mineralisation but more general elevations in the carbonates a relative to the ultramafics and mafic intrusive. In the Polis Valley, elevated Bi values flank the sides of the valley, whereas elevated Mo are more confined to the valley centre. This converse pattern between Bi and Mo probably reflects differing solubilities versus pH, with Bi precipitating as BiOCl at low to neutral pH and Mo forming CaMoO<sub>4</sub> at higher pH.

#### 4.4.4 Lead and platinum

Soil *ar*-Pb is elevated near some sulfide deposits and in most of the Kokkinokhoria region. Other elevated values appear more closely related to urban areas (Lefkosia, Pafos, Lemesos and Larnaca) where top soil *ar*-Pb values are generally higher and form more contiguous anomalous areas than the sub soil. Sporadic anomalous Pb values with no obvious geological controls probably relate to the presence of shot gun pellets. Pellets were observed in heavy mineral concentrates extracted from a selection of these samples. Shooting ranges and field sites generally have elevated Pb.

Due to the analytical detection limits for Pt (1 µg/kg) the map is relatively “flat”. Small areas with >2 µg/kg Pt in both top and sub soil samples occur at a number of areas south of the Akamas Peninsula, near Lefkosia and a line of five anomalies along a line just to the west of the X-X’ traverse and which intersects the TOC ultramafic core.

#### 4.4.5 Silver and selenium

The patterns for Ag and Se are somewhat erratic, as indicated by both the maps and the traverse plots. Peak values are mostly within the TOC and coastal strip. For Se there is little variation between lithologies.

### 4.5 ALKALI AND ALKALINE EARTH ELEMENTS

#### 4.5.1 Calcium

Calcium is one of the most common elements in the crust and a major component in many rock types due to two ubiquitous minerals - feldspar and calcite. In igneous rocks Ca mainly occurs in feldspar (plagioclase), as well as pyroxene and other aluminosilicates. In sedimentary rocks, sediments and soils, Ca is mainly present as calcite, gypsum or Ca-bearing clays such as smectites. Calcretes (carbonate duricrusts) are common at the regolith surface in arid environments.

*ar*-Ca is derived from calcite and gypsum in the carbonate-containing sediments, and carbonates derived from calcrete development and alteration zones within the basalts. Both *ar*-Ca and *tot*-Ca range from <1 % to ~40% (pure calcite) and are highly correlated. This indicates that even in the soils over Troodos, most of the primary feldspars have broken down to clays and other minerals that are leachable in aqua regia. Calcium displays the most consistent correlation between soil chemistry and parent lithology. The values across the TOC are uniformly <4%. Conversely, the CTSS carbonate-rich units display spatially contiguous Ca values between 18 and 40%, reflecting the simple balance between calcite and other clastic materials (mainly quartz and clays). The boundary between the CTSS and the TOC is very sharp, with Ca values dropping from >20% to <4% within the 1 km grid sampling distance. The variability in *ar*-Ca to the south-west of the TOC is a reflection of the complexity of the

geology with small outcrops of a variety of lithologies relating to the Troodos, Mamonia and CTSS terranes. Some of the elevated Ca values for samples in areas mapped as basalts or mafic intrusives relate to soils of mixed compositions derived from both the TOC and CTSS materials (e.g. colluvium containing cobbles ranging in composition from calcarenite to weathered gabbro). The Ca data show the distribution of CTSS outliers on the TOC margins.

The ratio of top soil to sub soil Ca is generally in the range 0.8–1.4, but some of the ultramafic areas display higher ratios reflecting transfer of Ca from feldspars to smectitic clays and carbonate due to weathering in the upper parts of residual soil profiles. The top soil/sub soil ratio is low for Ca in much of the Kokkinokhoria region due to the development of terra rosa (red dermasols) over the carbonates and to the probable influx of clastic sediments from other areas. Similarly, the *ar-Ca/tot-Ca* ratio displays greatest variability in the sheeted dyke complexes, which reflects variations between sites with skeletal regolith profiles dominated by weakly weathered clasts to residual soil profiles where a higher proportion of the top soil Ca was leachable.

The absence of dolomite and magnesian calcite in the CTSS sedimentary units is reflected in very low *ar-Mg/ar-Ca* ratios. The ratios are high for the ultramafics and Akamas mafic units.

#### 4.5.2 Barium and strontium

Barium and Sr substitute for Ca and K in a number of minerals, most typically feldspar. In weathered materials Ba forms its own minerals but is mainly present in baryte ( $\text{BaSO}_4$ ). Baryte is also a common mineral in the vicinity of hydrothermal seafloor systems where Ba extruding from the seafloor vents reacts with seawater sulfate. Baryte and other Ba minerals may also form within intrusive rocks due to hydrothermal alteration of feldspars. In seawater, Ba precipitates as baryte if Eh rises above ~290 mV.

As was the case for Ca, both *ar-Ba* and *tot-Ba* values closely reflect gross lithological variation in Cyprus. Elevated Ba is, however, more closely associated with the deep-marine Lefkara Formation that onlaps the pillow basalts of the TOC, than with the other carbonate dominated lithologies such as the Pakhna Formation. This probably reflects either variations in the depositional environment of the carbonates of the CTSS between the Lefkara and Pakhna Formations, or the geochemical trapping of Ba dispersing from the basalts in the immediate surrounding CTSS units. The low *tot-Ba* in the mafic units indicates low-Ba feldspar. Whereas baryte was observed in a number of heavy mineral concentrates, Ba concentrations are low over much of the basalts, indicating only small amounts of baryte were precipitated from the hydrothermal systems that generated the Cu deposits.

Strontium is very closely correlated with Ca and reflects its tendency to substitute for Ca rather than form its own minerals in most environments. Celestite ( $\text{SrSO}_4$ ) was mined near Maroni (Zygi) in the past. The reported occurrence of Sr-rich shells in the mine suggest the celestite may be a product of diagenesis.

#### 4.5.3 Potassium, lithium, rubidium, caesium, thallium, beryllium

This group contains the alkali elements, as well as Tl and Be. Potassium is one of the major crustal elements. In igneous and metamorphic rocks K is present in orthoclase feldspar and micas, hence concentrations tend to be highest in felsic rocks or in shoshonitic basalts. The remaining elements in this group can substitute for K in various minerals, however their ionic radius generally inhibits high levels of substitution. They tend to concentrate in the final stages of crystallisation of igneous melts and deposit as rare minerals such as lepidolite (Li mica), spodumene (Li feldspar), beryl (Be) and pollucite (Cs). Excluding evaporates, sedimentary rocks and sediments generally contain very low abundances of all these elements except where K has been preserved in K-micas such as sericite or substituted into clays. Radiogenic isotopes  $^{40}\text{K}$  and  $^{87}\text{Rb}$  are used in long-term radiometric dating (K-Ar and Rb-Sr systems). The  $^{40}\text{K}$ -channel is one of the three elements routinely measured in radiometric surveys (the others being U and Th) which allows some remote sensing of surface geochemistry.

All these elements are elevated, to varying extents, in the Kokkinokhoria region and Pakhna Formation carbonates. Potassium has low values in the Lefkara formation but higher values in the Pakhna Formation. Potassium is elevated in coastal areas, presumably due to the influence of seawater and sea spray, though this feature is also present in the Rb data. Caesium and Li are also elevated in the ultramafic units. Like Ca, Cs is more elevated in the top soil than the sub soil over Troodos and has the

highest *ar-Cs/tot-Cs* in the areas of sediment deposition near the coast, suggesting the main host for Cs in the mafic units is feldspar (as with Na) and probably clays way from Troodos.

Beryllium and Tl display slightly more erratic patterns with some similarities to both Ca and K. Again, the generally elevated concentrations of those elements in the Kokkinokhoria region is difficult to explain, unless it relates to deposition of clays containing those elements deposited at the distal ends of the fanglomerates.

#### 4.6 INCOMPATIBLE (HFSE) ELEMENTS

The incompatible elements, by virtue of their ionic radius and charge (HFSE), do not easily substitute for other major ions in common minerals. They are typically the last to crystallise out of igneous melts, and are more elevated in felsic than mafic rocks. They tend to form their own array of minerals which are the main component of their ores. Examples include tantalite-columbite and pyrochlore (Nb and Ta), cassiterite and stannite (Sn), uraninite (U), thorianite (Th) and zircon (Zr). Uranium, Th and Hf can substitute into zircon (where it forms one of the main radiometric dating tools via the U-Pb series) and Th into monazite (REE phosphates). All these minerals tend to be both physically strong and chemically unreactive, hence they are stable in the surficial environment and mostly resist dissolution in aqua regia. The distribution of the heavy minerals is strongly controlled by hydraulics and they accumulate in stream beds and beach sands.

##### 4.6.1 Niobium, tin, uranium, hafnium, thorium and zirconium

Niobium is concentrated in an arc that extends from the Akamas Peninsula around to Cape Greco, and which cuts across number of geological boundaries. It probably represents the base of slope or major river systems where the Nb-containing heavy minerals that originated in the basalts have deposited as the velocity of streams or sheetwash velocities drops. This is supported by higher concentrations in the top soil (a lag effect) which is shown in the separation of the population distributions in the probability plot. It may also explain the high Nb concentrations in Kokkinokhoria to be the result of deposition at the distal end of the fanglomerates.

The patterns for Sn are erratic. Apart from elevated Sn values over the plagiogranites and adjacent to major streams below the plagiogranites, the lack of felsic intrusives has contributed to low Sn values in the soils generally. As with Pb, one feature that stands out for Sn is the higher elevation of values in the top soil and the high top soil values in the urban areas, which is probably related to anthropogenic sources.

Uranium displays a similar trend to Ca. Values are low relative to other parts of Europe due to the lack of felsic igneous rocks. There are few *ar-U* or *tot-U* values >10 g/kg. The high *ar-U/tot-U* ratios indicates most U is not substituted into zircon, but more likely substituted into the carbonates as  $\text{UO}_2(\text{CO}_3)$ . Uranium values are elevated in the former Polemi Basin and are spatially correlated with elevated Ca, again suggesting precipitation from seawater rather than zircon accumulations. In seawater, U is mobile as the  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$  ions in slightly oxidising condition (Eh >~100 mV), but will precipitate as  $\text{UO}_2(\text{CO}_3)$  if pH drops below 6.2 and as  $\text{U}_2\text{O}_9$  if Eh drops below ~100 mV. Hence, there is a seawater depth (Eh)–U solubility relationship with U accumulation under reducing to slightly oxidising conditions (deeper water). Organics present in the seafloor sediments lower pH or can even directly reduce U causing precipitation.

Thorium displays similar patterns to some of the alkali elements, but the low *ar-Th* to *tot-Th* indicates most of the Th in the CTSS and coastal areas is in monazite (or possibly thorianite). Hafnium, thorium and zirconium patterns are nearly identical, presumably due to the substitution for Hf and Th into zircons. Whereas the limited mobile component of the Hf (and by inference Zr) displays highest values in the pillow basalts, the peak total values largely mimic trends for Th. The question as to where the zircons and monazites originated needs further study, and in the Kokkinokhoria area these may be derived from either the Keryneia region or more distally from the Eurasian Plate.

#### 4.7 RARE EARTH ELEMENTS

The REEs typically display very high mutual correlations, though the relative concentrations of the various REEs vary between different geological and landform settings. All REE display a 3+ valency,

but Eu can also take a 2+ and Ce a 4+ charge, leading to potential for depletion or enrichment of those two elements relative to the remaining REEs. Many studies on igneous and metamorphic processes involved analysis of trends across the REE suite normalised against chondrite (meteorite) or MORB values. The REEs can substitute for Ca or Al in feldspar, but are more commonly found in association with P in apatite or monazite. The REE are much more elevated in felsic rocks than ultramafics. In the secondary environment, the REE will be retained by heavy minerals such as apatite and monazite, or substitute into carbonates.

In general the *ar*-REE abundances are highest in the Kokkinokhoria region, along the boundary between the TOC and CTSS and in a discontinuous arc along the southern coast. There is another zone of slightly elevated values for the heavier REE in the corridor that runs across the western side of the TOC. REE contents are generally very low throughout the ultramafic and mafic intrusive units, though the values are slightly higher in the top soils as with other feldspar-hosted elements. A high proportion of the *tot*-REE contents are extractable in aqua regia (suggesting the main form the REEs is apatite). Europium/La and Ce/La ratios are high in the sheeted dykes and basalts, indicating those elements are substituted into feldspar. Otherwise, the close relationship between the REE and Th indicates a significant proportion of the REE outside Troodos are held in monazite and possibly apatite.

The *tot*-REE data indicates the light REEs are slightly enriched in the CTSS relative to the TOC units.

## 4.8 OTHER ELEMENTS

### 4.8.1 Boron

Boron is mainly present in igneous rocks substituting for Al in feldspar, or in B minerals such as tourmaline and axinite. In evaporate deposits borates such as borax may precipitate. The main form of B in soil is typically undissociated boric acid, which is highly mobile. Boron tends to accumulate in the soils of arid terrains.

*ar*-B contents are highest in the salt flats (in some cases in excess of 10 mg/kg. Other areas of elevated values (>3 mg/kg) are the main drainage systems, the coastal flats and a zone that runs from Larnaca to Lefkosia (one of the main agricultural areas). The lavas have elevated B (mainly in the glass) which is a significant source along with seawater. Some agricultural areas have B values in excess of regulatory limits. It is noted that B was used in detergents until the 1990s.

### 4.8.2 Bromine

In igneous rocks, Br and I are found in fluid inclusions and some alkali salts. Bromide salts may precipitate in some evaporite deposits, otherwise the Br (and other halogens) in soils are largely derived from meteoric water influx.

Soil *tot*-Br contents are elevated along the southern coastline and extending inland for ~20 km. A key feature of the Br data is the significantly higher values in the top soil for values <30 mg/kg but much higher values in the sub soil where Br >30 mg/kg. This suggests flushing of Br from the top soil to the lower soil horizons where it is presumably fixed by organics.

### 4.8.3 Mercury, rhenium and tellurium

Mercury is normally associated with the chalcophile elements. In the case of Cyprus there are three clear controls on the *ar*-Hg distribution. The first is weakly anomalous values associated with the known sulfide deposits. The second is the elevated sub soil values in the major urban areas and the entire northern end of the Polis Valley (and not limited to the area down-slope of the Limni Mine). The final trend is a series of anomalies in a line that runs parallel to the X-X' traverse and which cuts across a number of lithological boundaries. This lineation of anomalies is mirrored in the Re and, to a lesser extent, the Te and Pt data. Rhenium displays no correlation with Mo.

The *ar*-Hg values display an inverse relationship to EC, except around Limni and Mitsero where there is extensive low-level accumulation in the sub soil.

#### 4.8.4 Tungsten

Most tungsten originates as either scheelite or wolframite (Ca or Fe tungstates) in the final stages of crystallisation of differentiated granites, or related skarn deposits. Tungsten and Mo can substitute for each other in primary minerals. With the high detection limits and resistance to acid attack exhibited by W minerals, there are few *ar*-W values >0.2 mg/kg. There is also the potential for some W contamination related to the use of W-tipped augers in the survey.

#### 4.9 SOLUBLE IONS, TOTAL AND ORGANIC CARBON, TOTAL SULPHUR AND PHOSPHORUS

Soluble Cl<sup>-</sup> and F<sup>-</sup> values are highest in the salt flats (as expected). Other areas with elevated values (>300 mg/kg) occur along the coastal fringe and near the base of major river valleys draining Troodos. These are likely to be zones of groundwater seepage and evaporative salt deposition. Elevated F<sup>-</sup> values display little correlation with Cl<sup>-</sup> and appear more closely linked to the sedimentary basins that existed during the Messinian (Miocene) salinity crisis.

Sulfate ion concentration patterns can be broadly divided into the TOC (low SO<sub>4</sub><sup>2-</sup>) and CTSS (moderate SO<sub>4</sub><sup>2-</sup>). More-elevated values (>100 mg/kg) are largely restricted to the salt flats and the sulfide mines. SO<sub>4</sub><sup>2-</sup> >1,000 mg/kg is highly correlated with *tot*-S, but below 1,000 mg/kg *tot*-S more closely follows the trends for F<sup>-</sup>, which is again indicative of a palaeodepositional control in the various Tertiary basins.

P<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub><sup>-</sup> are important indicators of soil nutrient levels. Apart from the salt flats, there is little correlation between these variables. As for *ar*-P, the highest values are in the basaltic units of the TOC. The close agreement between *tot*-P and *ar*-P indicates the main forms to be organic-P species and apatite. High nitrate values are found along the coastal areas, the Kokkinokhoria area and the Mesaoria Plain, all of which suggests an agricultural control on soil nitrates.

Total carbon (*tot*-C) is heavily influenced by the presence of carbonates in the soil and is strongly correlated with *ar*-Ca. The abundance of soil organic carbon (SOC) is in the range 0.5–5%. The distribution of values is erratic and reflects localised variations in both soil type and vegetation characteristics. A preliminary assessment indicated that the areas with skeletal and immature soils, which dominate the steeper parts of Troodos, contain lower SOC. A small group of samples (mainly from Troodos) display SOC ≈ *tot*-C. Another group from the skeletal soils overlying the carbonates has very low SOC and a third group displays a rough trend of SOC ≈ 50% of *tot*-C.

Elevated values of F<sup>-</sup> are observed in the vicinity of salt lakes in Cyprus. The average F<sup>-</sup> concentration is 17.4 mg/kg and the maximum 1,380 mg/kg (world average: 200–300 mg/kg). Low correlation between F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> suggests that elevated F<sup>-</sup> is not related to fertilisers, given that a major source of F<sup>-</sup> contamination is in agricultural soils due to F in superphosphate (Neumüller 1981). Apatite is a common accessory mineral in basalts that slowly breaks down in soils (Kabata-Pendias & Pendias 1992). Apatite was detected in heavy mineral concentrates at various sites across Cyprus. The main source of Cl<sup>-</sup> is meteoric waters, although saltwater intrusions occur along the coast. In the salt lakes Cl<sup>-</sup> values range up to 0.3%; elsewhere the mean Cl<sup>-</sup> value is 587 mg/kg. The major source of NO<sub>3</sub><sup>-</sup> in Cyprus soils is synthetic fertilisers. The mean NO<sub>3</sub><sup>-</sup> value is 63.2 mg/kg and the maximum 3,000 mg/kg. Most high values are within 'nitrate-vulnerable zones', where the mean is 130 mg/kg. The main geogenic source of SO<sub>4</sub><sup>2-</sup> is sulfide oxidation; otherwise, contents closely reflect parent geology. The mean is 150.2 mg/kg, with a maximum (near a Cu mine) of 1.6 %.

The results of chemical analysis indicate a correlation between the concentration of some soluble salt ions (F<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) with the parent lithology of the soils (geogenic processes), and of others (NO<sub>3</sub><sup>-</sup>) with non-geogenic processes related to land use.

#### 4.10 XRF MANGANESE, MAGNESIUM, ALUMINIUM AND POTASSIUM

*tot*-Mg (as MgO) is mainly elevated in the areas of the ultramafic units, where it weathers out of olivine and other Mg-substituted ferromagnesian silicates to form Mg-rich smectites, brucite and possibly talc in the soils. Some of the Mg may also form dolomitic pedogenic carbonates, although the lack of Mg over the Pakhna and Lefkara Formations indicates there is very limited Mg mobility away from the TOC. Manganese follows Mg to some extent (Mn substituting for Fe in ferromagnesian

minerals) but is also elevated in various zones around the pillow basalts, especially in association with umbers.

Alumina is closely associated with the mafic cumulates and extrusives where is derived from the feldspars (either forming clays or remaining as partially weathered feldspars in the soil profile). *tot-K* is generally only elevated in the pillow basalts (which may be a function of the weathering of spilitised basalts) or along the coastal strip where it is presumably recently derived from seawater spray.

## 5 RESULTS PART B – STATISTICAL ANALYSIS AND DETAILED STUDIES

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### 5.1 PRELIMINARY ANALYSIS

#### 5.1.1 Basic statistics

A summary of basic statistics for all geochemical variables is presented in Table 5.1 (and associated dataset *Main geochemical\_data\_basic\_stats.xls*). Variations in average element abundances of soils within the seven main lithological groups are presented in Table 5.2.

The basic statistical summary tables again demonstrates that parent lithology exerts the dominant influence over major and nearly all trace element geochemistry in the soils. Values generally reflect global averages related to different rock types indicated in compendiums such as that of Levinson (1980). Iron and Mg values are naturally highest in the mafic+ultramafic rocks and sulfide deposit, whereas Ca is highest in the carbonates and Al in the mafic rocks. Some trace elements, including Cr, Co, Ni and Sr, display orders of magnitude concentration differences in soils overlying mafic+ultramafic units from soils overlying the carbonate-rich units. Others elements, such as Br, Be and Ti, display little statistical variation between lithologies, reflecting either less variation in the parent lithologies or that the bulk of such elements in soils are derived from other sources than weathering of parent lithologies (such as rainwater or anthropogenic sources).

Compared with the FOREGS Atlas of Europe, the mean aqua regia extractable and total soil values are higher in Cyprus for most of the mafic and ultramafic-associated elements (Cr, Co, Cu, V, Fe) and sedimentary carbonate-hosted elements (Ca, Sr and Ba), but lower for most other elements including the REE and HFSEs (Fig 5.1). The *ar*-As is higher for Cyprus and lower for Pb and Zn, than the remainder of Europe.

Most of the elements display highly skewed distributions, which probably represents a series of overlapping distributions relating to various parent lithologies and small anomalous zones related to entities such as sulfide deposits or urban areas. The results emphasis the observations of Garrett *et al.* (2006) and others that “background” distributions must be determined locally rather than over large regions if the regolith and geology is inhomogeneous. For subsequent multivariate modelling, the data were de-skewed using the Box and Cox (1964)  $\lambda$ -transformation:

$$X' = (X^\lambda - 1) / \lambda \text{ where } \lambda \text{ is a scalar value selected to reduce skewness to 0.}$$

Given the size of the dataset, the transformation was performed without prior removal of outlying values (Table 5.3).

#### 5.1.2 Correlations

Parametric correlations between top soil and sub soil geochemical values are listed in Tables 5.3 and 5.4, and scatterplots for selected elements presented in Figs 5.2 and 5.3. Correlations between *ar*-ICPMS and INAA data in Table 5.5.

The main observations from the various tables of correlations are:

- the ubiquitous high correlation between all the REEs;
- a more general correlation between the REE, K, Tl and various incompatible elements such as Be, Sn and Th; and
- correlations between the overlapping suits of mafic+ultramafic associated elements (Cr, Co, Mg and Ni) and some siderophile and chalcophile elements (Fe, Cu, Co, Mn, V and Zn).

Although the suite of elements is more restricted for INAA (including a number of elements where >50% of samples reported below the detection limit), there are strong correlations between the *ar*-ICPMS and INAA values for all elements except Na. The highest correlations are for elements tended to occur where *ar*-ICPMS extracted >75% of the total values determined by INAA (e.g. Ca).

There is generally a very high correlation between the *ar*-ICPMS and INAA concentrations of top soils versus sub soils. Most outliers occurred in samples where the top soil was clearly transported a substantial distance, such as the skeletal red or brown B(t) soils overlying bleached and carbonate-rich C-horizon. Some of the scatter at lower concentrations is a function of detection limits rather than actual differences between top and sub soil. Elements that generally reside in heavy minerals or adsorb strongly to Fe oxides are commonly more elevated in the top soil than sub soil.

Calcium, Fe and Mn typically control trace element geochemistry in soils due to co-precipitation, substitution or adsorption to carbonates and secondary Fe-Mn oxyhydroxides. Various elements are plotted against these three control elements, separated by lithological group (Figs 5.4 to 5.14). Aluminium and V are largely uncorrelated with Ca in the basaltic and sedimentary rock-derived soils if Ca is <10%, but negatively correlated if Ca is >10%. The negative correlation is likely to be a statistical “closure effect” as Ca, Al and Fe constitute the bulk of the extractable elements. In the intrusive igneous rocks Al and V are positively correlated with Ca if Ca is <10%, and negatively correlated if Ca is >10%. Samples with high Ca values (>15%) in soils overlying the basaltic and some intrusive lithologies generally reflect influx of material derived from adjacent carbonates, although in Akamas calcretes have developed directly over basalts. Aluminium and V are strongly correlated with Fe and, to a lesser extent, Mn in the basalts and sedimentary lithologies. This is likely to be the product of Al-substitution in secondary Fe-oxides such as goethite.

Chromium, Co and Ni display similar patterns of correlation to those of Al and V, although they are uncorrelated with Ca in the ultramafics and mafic intrusive areas. These elements display stronger correlations with Fe than Al or V, reflecting both the primary lithological associations and also adsorption of those elements by Fe+Mn oxides in the secondary environment (a common feature observed in most soil and sediment geochemical surveys globally).

Strontium is strongly correlated with Ca in all areas and moderately strongly anti-correlated with Fe. This reflects the tendency for Sr to substitute for Ca in carbonates, feldspars and clays, and the effects of “closure” within the Ca-Fe-Al relationship. Patterns for Ba are similar but weaker. Again, it is noted that high Ba and Ca values in some samples grouped with the mafic intrusives are likely to be derived from soils that have a significant input from up-slope outcrops of CTSS carbonate units (mainly Lefkara Formation). High Sr values in the carbonates may correspond with celestite deposits (SrSO<sub>4</sub>), and there is a former celestite mine SE of Kalavassos.

Elements typically hosted by primary sulfides – As, Cu and Zn – display no correlation with Ca and only weak correlations with Fe and Mn. The correlations with Fe and Mn are strongest for Zn which is the most geochemically mobile of the three metals. Samples with highly elevated Cu are generally associated with elevated Fe and such samples are typically within 1 km of known sulfide mineralisation.

Lanthanum, along with the other REEs and most of the incompatible elements display no correlation with Ca, Fe or Mn.

These patterns of correlation are further described and analysed in the factor analysis section.

## 5.2 PHYSICAL PROPERTIES

A range of variables are plotted against CEC in Figs 5.15 and 5.16. Low LOI (<15%) is moderately correlated with CEC, but the high LOI samples that are dominated by carbonate-rich soils samples display no correlation with CEC. When plotted against Ca, the high Ca values have a weak negative correlation with CEC and loc-Ca samples no correlation. There are three trends for *ar*-Al; low Al (<2%) and mid Al (2.5–6%) populations displaying a moderate correlation with CEC, and a small high-Al group with low CEC (probably related to Al extracted from secondary Fe-oxides rather than clays).

Three other physico-chemical variables – pH, EC and clay proportion (<5µm size fraction) – display no correlation with CEC. There is no correlation between *ar*-Fe, *ar*-Cu or *ar*-Na and CEC. *ar*-K and *ar*-Zn display a weak correlation with CEC.

Based on these trends it would appear that CEC is related to clay (mineral) content, though not related to clay (size) content. The high carbonate samples appear to have low content of clays with high exchange capacity (probably kaolinitic rather than montmorillonitic clays). Clay content is better

predicted by *ar*-K (implying most K is hosted by clays) than Ca and Na which are mainly hosted by carbonates, sulfates and possibly NaCl.

pH values dominantly range between 6.5–11 (Fig 5.17), but there is a small population with values in the range 2.5–6.0 that are related to the presence of oxidising sulfide mineralisation (mainly the mines areas). It is noted that the low pH samples typically have elevated Fe (>10% *ar*-Fe), but low *ar*-Ca (<5%) and EC (<5 mS/cm). The EC trends are unusual, in that the high EC values (>8 mS/cm) are restricted to a more restricted pH range of 7.5–9.

The close relationship between *ar*-Ca and LOI indicates carbonate to be the dominant control on LOI, with some additional control by ?kaolinite (Fig 5.18). There is a large mass of samples displaying LOI 5–25% and *ar*-Fe 2–10% but no correlation between these variables. At *ar*-Fe >25% there is a negative correlation with LOI, suggesting most of the Fe in this range is present in hematite/magnetite/chromite rather than goethite.

EC (based on a 1:5 soil water slurry) appears largely to be controlled by *ar*-Na for EC >10 mS/cm, and these samples are largely drawn from the salt flats and agricultural areas near the coast (see Section 4 maps for EC and *ar*-Na). EC is largely unrelated to *ar*-Ca, with the two main trends being low-EC (<5 mS/cm) with highly variable *ar*-Ca and a band of samples between 15 and 20% *ar*-Ca where EC values extend up to 30 mS/cm.

High *ar*-Na samples mostly lie along the NaCl dissolution line (Fig 5.19), though some appear more closely linked to sulfate. For EC >0.3 mS/cm, there is a high correlation with the sum of soluble  $\text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^-$  (as mmol.eq) indicating a limited contribution of carbonate-bicarbonate to total soil soluble ion contents.

### 5.3 DETAILED STUDIES AT MINES AND OTHER SPECIAL SITES

The detailed sampling at the mines and other sites was conducted to examine dispersion of elements away from mine sites and factors controlling element mobility.

#### 5.3.1 North-eastern mines (Cu)

Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.20 to 5.27.

This area spans a series of 10 abandoned Cu mines (some with multiple pits), including Kokkinopezoula in the “Mitsero camp” and Sha<sup>3</sup>. There are records of some minor Au workings. The deposits occur in the upper and lower pillow lavas, with the on-lapping CTSS and younger fanglomerate units extending down drainage to the north. Mining operations have left a number of pits that are now partly filled with highly acidic sulfate waters and surrounded by extensive oxidising tailings piles. Detailed sampling was conducted around the Kokkinopezoula and Kokkinonero deposits.

Elevated soil *ar*-Cu values occur around most (but not all) of the mines. The central group of four mines (Pytharachoma, Kokkinonero, Kapedhes and Peristerka), are surrounded by a number of sites with anomalous *ar*-Cu (>80 mg/kg) and these extend down the main drainage to the north-east for >10 km. The northern side of Mitsero is protected by a ridge of preserved fanglomerate. Sporadic Cu anomalies elsewhere in the basalts probably reflect small zones of Cu mineralisation, with numerous sitings of malachite-stained basalt outcrops in the region. The *ar*-Fe data reflects topography, with the western side of the area more eroded and with less weathered colluvium. Elevate Fe occurs in soils immediately adjacent or within the tailings areas.

Mercury and Zn anomalies tend to coincide with elevated Cu, although there are sporadic high Zn values (>160 mg/kg) at various locations within the basalts and carbonates+clastics. The three main cluster of anomalous *ar*-Hg values (>0.2 mg/kg) are around Kokkinonero and 5 km east of Sha. It is possible that some of the Hg is anthropogenic and related to small-scale Au mining activities.

Soil *ar*-Pb displays marked differences between the top soil and sub soil patterns suggesting a significant input of Pb at surface due to the mining activities. *ar*-Pb is almost invariably elevated in the top soil near the mines (certainly within 1 km), though there is some transportation downstream or

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<sup>3</sup> Sometimes spelt Sia

downslope to the north and east along drainages from the mines. The sub soil *ar*-Pb appears more strongly controlled by lithology, with generally low values in the basaltic areas, high values in the vicinity of the alluvium (Recent sediments) and almost no spatial relationship to the mines (except a very limited dispersion around Kokkinonero).

Both soil *ar*-Re and *ar*-As values are slightly elevated near some of the mines, but the patterns are erratic. Soil *tot*-Au values are elevated near the mines. There are a series of Au anomalies ( $>7 \mu\text{g}/\text{kg}$  and many  $>20 \mu\text{g}/\text{kg}$ ) associated with some of the main drainage sub-basins near the mines. There is also a series of Au anomalies in a stream to the southwest of the area and it may be a detrital train from a zone of Au mineralisation in the basalts. *tot*-Cr values are highly elevated in the vicinity of many of the mines, though it is uncertain whether this is a function of contamination from mining operations rather than derived from the mineralisation (which does not contain elevated Cr). Most of the elevated Cr is located along the main streams.

The Cu/Fe ratio provides no patterns related to known mineralisation, but nearly all the mines display elevated scores for *ar*-ICPMS Factor 6 (see Section 5.9) which is elevated in the vicinity of most known sulfide deposits in Cyprus.

Barium displays zones of sub soil accumulations that may again be detrital as they generally follow the Cr and Au patterns to varying extent

Most of the soils collected within the mine sites and a number down-slope displayed slightly acidic soils, though samples containing tailings had lower pH values. pH values are typically neutral to slightly acidic in the modern drainages compared with the surrounding (and underlying) carbonate-rich sedimentary rocks.

### 5.3.2 Kalavastos (Cu and Au)

The Kalavastos deposit and mine workings are on the south-eastern edge of the exposed Troodos basalts between two SE-draining streams. These are among the more extensive mine workings in Cyprus. Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.28 to 5.35.

Despite the extensive mine tailings in the area, soil pH is uniformly alkaline and this is reflected in the relatively uniform *ar*-Ca values in the area, with the exception of a small set of low Ca values from the orientation sampling line on the eastern side of the mine workings. The low-Ca value samples correspond with elevated Cu and Fe indicating they contain or are affected by mine tailings.

Gold, Hg and Pb values are elevated within the mine site and sporadic elevated values away from the mine. *Ar*-ICPMS Factor 6 scores are highly elevated at most sites within and adjacent to the mine and at a number of sites downslope (to the south east).

Total-S is elevated near the mine whereas soluble  $\text{SO}_4^{2-}$  is not elevated, implying most of the S around the mine itself is either present as sulfides or baryte. Sulfate is higher to the SE and may represent contamination derived from the mine area. Total-C reflects the distribution of basalts and carbonate rocks, rather than mining effects.

### 5.3.3 South region

Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.36 to 5.43.

The region contains the boundary between the TOC and CTSS, Cu and Cr mines, the Lemesos urban area and northern part of the Akrotiri salt flats.

Soil pH largely follows the geology, though the pH values are slightly acidic in parts of the ultramafic units and Mamonia Terrane mafic clastics on the western side of the area. Soil Ca is high within most of the Pakhna Formation carbonates and surrounding central Troodos where residual soil profiles are preserved and Ca is present in clays and pedogenic carbonates, rather than partly weathered feldspars. There are zones within the Pakhna Formation with Ca  $<15\%$  and this represents more quartzose arenitic units.

Elevated *ar*-ICPMS Factor 6 scores occur along the southern boundary of Troodos in the Lower Pillow Lavas and then progressively dilute south across the CTSS sediments, in the vicinity of the Kalavastos

Mine and within the Lemesos urban area. *ar*-Cu/*ar*-Fe ratios tend to be elevated laterally to these zones, indicating that there is some elevation in Fe within the areas of high Factor 6 scores.

The Pb and Hg patterns are erratic but there are a series of elevated values associated with the Kalavastos Mine. Elevated Au values extend down a number of the major drainages, indicating alluvial Au derived from sources in the pillow basalts.

There are zones of elevated As associated with the Kalavastos Mine, and areas of the pillow basalts, but a key feature is the elevated As within the Pakhna Formation. This may be due to an original sedimentary component to the As distribution (co-precipitation or substitution for Ca in the carbonates) or that As shedding from Troodos is mobile across the carbonate-dominated areas and deposited in areas where pH drops towards neutral conditions. The As pattern is followed by both La and Cr in the Pakhna Formation, which again suggests a sedimentological aspect to the patterns as Cr and La tend to be mechanically transported in sedimentary systems as heavy minerals.

Soil *ar*-Ba is elevated along the southern side of Troodos, along the main drainages and some of the coastal areas, indicating transportation of Ba as baryte (a heavy mineral).

#### 5.3.4 Limni (Cu)

Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.44 to 5.52.

The Limni Mine area was the subject of a detail study by Constantinou (2008). Limni was one of the largest Cu mines in Cyprus and the tailings pile sits between the mine and the coast, with dispersion of the tailings down to the beach. The effects of the tailings are currently being remediated by returning them to the Limni pit. Three detailed sampling lines were placed between the mine and the tailings pile, below the tailings and along the beach. Three vegetation test sites (olives) were also sampled.

The patterns for pH and Ca follow similar trends to other areas described, with higher Ca away from the basalts. The pH drops towards the coast below the tailings pile.

Elevated Cu and Fe occur along most of the sampling traverses below the tailings and along the beach where longshore drift appears to be carrying tailings towards the north east. Olive leaves have elevated Cu near the mines.

Although the data are more erratic, there are elevated Au and Hg values near the mines, with progressive elevation in the Au contents of the olive leaves going from the background site up-hill from the mines down to the site adjacent to the tailings. There is, however, elevated Hg generally in the lower parts of the Polis Valley. Further work needs to be undertaken to determine whether this pattern is natural or anthropogenic.

Soil *ar*-Pb is elevated around the mines area, especially in the top soils, and also shows up in the vegetation. Zinc is elevated below the mines, as is Re which displays strongly anomalous values in the vegetation adjacent to the mines and tailings but very low values in the background area.

*ar*-ICPMS Factor 6 scores are very highly elevated adjacent to mineralisation and in the entire area between the two boundary streams to the coast. The scores gradually decrease towards the north east, but display a very sharp boundary on the western edge of the anomalous zone on the beach, which again points to the dominant west to east current.

Total-S and soluble sulfate display similar trends (some *tot*-S values exceeding 0.2%). Total C again reflects whether the underlying lithology is basalt or carbonate lithology. Organic-C is highly elevated in across the mine dumps and beach.

#### 5.3.5 Kokkinonero-Sha (Cu)

Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.53 to 5.58.

This gives a more detailed view of the data from the vicinity of the Kokkinonero mine to that described for the general NE mines area. The deposit was ringed by a detailed sampling traverse, which was then extended past the Sha Cu Mine towards the coast. This included a series of vegetation (olive) samples collected adjacent to the mines samples.

*ar*-Ca is relatively uniform except around the mine site itself where values are depleted. *ar*-Pb is relatively elevated in the top soil, compared with the sub soil and in the vegetation. Copper is also elevated in both soil and vegetation within 500 m of the mine (but not much beyond that distance) and high Cu values generally correspond with lower pH values.

Mercury displays a series of anomalous values in an east-west line across that intersects the deposit and some sites on the northern side of the mine. Gold and Re are elevated around the mine, in both soil and vegetation.

### 5.3.6 Kokkinorotsos, Kannoures and Hadjipavlou (Cr)

A series of traverses were sampled in the vicinity of the three chromite deposits in central Troodos – Kokkinorotsos, Kannoures and Hadjipavlou. Selected geochemical data are plotted as semi-proportional dot-plots for soils in this area in Figs 5.59 to 5.65.

With relatively consistent geology at each site, most elements display only minor local variations (including for Fe, Pb, Au, Co and La). The variations are probably related to zonation within the ultramafics (dunite versus harzburgite).

Calcium was slightly elevated in the vicinity of mineralisation at Kokkinorotsos and Kannoures, but not Hadjipavlou. Chromium values were elevated on the road leading down to Kannoures but not along the road on the northern side of the actual mineralisation where the old workings are still preserved. The proportion of mobile Cr (*ar*-Cr/*tot*-Cr) was elevated in the vicinity of the chromite mineralisation *ar*-Mo values were highly elevated near mineralisation.

### 5.3.7 Profiles

A series of detailed profile samples were collected from boundary zones between mafic and calcareous units.

Ten samples were collected across the transition between the Dhiarizos Group mafic sediments and overlying calcareous sediments and colluvium of the Lefkara Formation at Mamonia and 24 at Secret Valley (Figs 5.66 and 5.67). At both sites, most elements displayed relatively consistent concentrations within each of the mafics and calcareous units and a sharp transition across the 50 cm mixed lithology zone. Calcium and Sr are an order of magnitude and Ni is 50% higher in the carbonates, but the other elements have either higher concentrations in the mafic sediments (Ce, Fe, Th and Sc) or no specific trends. Copper, Cr, Ni and Pb display a small spike in values at the transition zone at Mamonia, whereas Cu, Mn, Mo and Ni display much larger spikes at Secret Valley.

There are sharp changes in the concentration of most elements across the boundary between the basalts and overlying Pakhna Formation near Prodomos (Fig 5.68), with little evidence of weathering-induced depletion at the top of the basalt.

The duplicate profiles through the B(r) into the underlying C-horizon weathering profile in ultramafics collected near the Kannoures Mine, indicate surface enrichment for a number of elements, especially Cr, Pb and the Ca-associated elements (Fig 5.69). Otherwise, the C-horizon displays little vertical element concentration variability.

The Coral Bay profile was sampled at seven locations over a 60 m section at various levels. The profile contains a number of horizons, commencing with the bleached calcarenite subcrop at the base of the profile that is overlain by a massive red soil, two colluvial sub-units, a discontinuous calcrete crust and top soil with coarse lag. The profile geochemistry is presented in Fig 5.70 to 5.74. The calcarenite contains consistently high Ca (>25%) and low Fe (<0.7%), whereas the top soil contains the opposite (Ca <10% and Fe >2.6%). The intervening colluvium and massive red soils contain variable amounts of both Ca and Fe reflecting the distribution of calcareous and mafic clasts. Some elements follow the Ca trends (e.g. Sr) but most (e.g. Cu, Pb, Zn, Co and Cr) follow the Fe trends.

There is Fe enrichment in the top soil without associated increases in other siderophile elements resulting in low metal/Fe ratios in the top soil. The top soil geochemistry, including various trace element ratios, is far less variable than the underlying colluvium and typically contains the highest values for most elements. These data suggest that the top soil is derived from a relatively homogeneous source compared with the underlying colluvium.

## 5.4 TRAVERSES

### 5.4.1 Orientation lines

#### *Grainsize-geochemistry relationships*

Detailed sizing analysis of the orientation samples indicates a number of systematic trends related to lithology, topography and sampling depth. The grainsize distribution is typically marginally finer and less spatially variable in the top soil than the sub soil (Figs 5.75). The grainsize distribution is coarse over central Troodos (>50% of soil particles coarser than 250  $\mu\text{m}$ ). The grainsize becomes finer on the Troodos flanks, coarsening slightly at the base of slope (and over the Akamas Peninsula), and fining again towards the coastal fringe and the Mesaoria Plain on the N-S traverse.

Based on the detailed analysis of the orientation samples, various elements were plotted against the proportion of fine (<125  $\mu\text{m}$ ) and coarse (250–2000  $\mu\text{m}$ ) grainsize material (Fig 5.76). Lanthanum (and other REE) and Pb display a weak correlation with the proportion of fine material in the soils, otherwise there is no clear direct relationship between grainsize and element abundances.

#### *Physico-chemical properties.*

Loss-on-ignition is largely controlled by parent lithology with the maximum values of ~40% corresponding with soils that were predominantly calcite (Fig 5.77). LOI was highly correlated with Ca. Over the carbonates, the top soil had marginally higher LOI, presumably due to some calcrete duricrust formation in areas. pH ranges from ~7–9 over the mafics and ultramafics and 8–9.5 over the carbonates.

Whereas electrical conductivity did not vary greatly outside of the saline lake and coastal fringe, the top soils generally had higher conductivity due to near-surface accumulation of salts due to evaporation (Fig 5.78). The CEC was generally higher in the carbonates than the mafic/ultramafic areas, with the difference between top soil and sub soil values on the southern part of the X-X' traverse possibly due to more intense weathering of surface materials or the influx of clays from Troodos.

#### *Selective extractions*

The aqua regia and total metal contents in the soils, previously described in the regional maps and detailed mine site studies, is compared with the two weaker partial extraction, ammonium acetate for exchangeable and carbonate-hosted metals and hydroxylamine for the forme plus secondary Fe+Mn oxides (Figs 5.79 to 5.86).

All the analytical methods dissolve calcite and attack exchangeable metals. Hence all four sets of patterns are very similar (especially *ar*-ICPMS and INAA). Little Fe is released by ammonium acetate indicating relatively pure calcite (low Fe and Mg). On the southern extent of line X-X', there is a higher mobile Fe fraction in the top soil towards the base of the Troodos flanks. Only a fraction of the *ar*-Na is extracted by hydroxylamine, suggesting the aqua regia is removing Na structurally bound up in clays and possibly in feldspars, rather than just dissolving simple Na salts. Conversely, K is released at similar levels by ammonium acetate and aqua regia suggesting most of the soil K is present in very mobile forms.

Whereas the ammonium acetate releases very little Cr or Co (Fig 5.81), there is around 1% of the Cr released by hydroxylamine, indicating a small amount of mobile Cr that is associated with secondary Fe oxides. A high proportion of Mg is mobile in the soils, especially in the Kokkinokhoria area where nearly 75% of the Mg is extractable in hydroxylamine.

Lead and Zn display strongly contrasting behaviour. Whereas only a small fraction of Pb can be extracted by ammonium acetate or hydroxylamine, nearly all the Zn can be extracted by hydroxylamine. This indicates the very strong association between Zn and secondary Fe oxides in the surface environment, and that Pb is partly associated with less mobile or soluble phases (e.g. secondary phosphates). The REE and Th data display very low levels of soluble component, but clearly the highest levels are in the carbonates adjacent to Troodos.

### 5.4.2 Other traverses

Various traverses were sampled to examine the level of element variation in soils at the scale of 10s–100s of metres.

One of the key traverses extended from the Kokkinonero Cu mine past the Sha Cu mine and into the carbonates to the east of Sha. This traverse included vegetation sampling (Fig 5.87 and 5.88). In the vicinity of both mine sites, increased concentrations of Cu, Pb and Au in soils were detected, although some elevated Au also occur downslope of the mines. There are highly elevated Au, Cu and Pb in the olive leaves around the Kokkinonero Mine. In addition there were very high Re values in the leaves near Kokkinonero (a feature also observed in the samples collected from the test sites near the Kokkinopezoula Mine). The existence of Re anomalies in vegetation has not been previously reported in the literature.

The results of various traverses - along beaches near Acheleia (beach traverse #1) and at Lady's Mile (beach traverse #2), Akrotiri salt flats, Pedoulas (mafic intrusives) and Kannoures (ultramafics) - are presented in Figs 5.89 to 5.91. Most major elements displayed far less variability within each traverse than between the areas traverses, with the salt flats displaying the highest degree of local variation. For the various trace elements selected, variation within the traverses was typically less than the average differences between traverses. Soil *tot*-Cr displayed far less variation than *ar*-Cr; this would reflect natural variation in the amounts of heavy minerals (mainly chromite) in those areas. Similarly the high variability in aqua regia Ce in the Kannoures traverse related to heavy minerals such as monazite (though far less variation was observed along the Acheleia beach traverse. There is a single spike in the Cu and Zn values in the Pedoulas traverse and such sporadic high values for Cu and other sulfide-hosted elements is a feature of much of the Troodos terrain. Zircon displayed a regional trend along the Pedoulas traverse. The REE are also enriched in the top soil relative to the underlying colluvial layers and massive red soil.

### 5.4.3 SOIL TYPE VERSUS GEOCHEMISTRY

Based on the MOA regional soil maps, the geochemical data has been divided according to soil type (Fig 5.92). As expected, calcareous soil types display elevated Ca, Sr and some associated elements, whereas the ferruginous soils display high concentrations of the siderophile and chalcophile elements.

### 5.5 VEGETATION TESTS

A comparison between element contents of sets of pine needles at three test sites (one mineralised and two distal to mineralisation near Mitsero) indicated no significant variation between test sites for most major elements (Al, Fe, Si and K) and slightly elevated Mg at one of the background sites (Figs 5.93 and 5.94). Although Cu displayed no differences between the mineralised and background sites, Re, Co, Mn were generally elevated at the mineralised test site. As with the olive leaves in the vicinity of Kokkinonero and Sha, Re exhibited the strongest response to sulfide mineralisation.

In the limited comparison of the different organs in olives near Sha, Rb, K, Ga, Al, Se, Cs, U, Ag and Lu were more concentrated in the fruit (the olives) whereas Sr, Ca, Mn, Fe, Ni, Cd and a few other elements were strongly partitioned into the leaves (Fig 5.95).

### 5.6 RATIO PLOTS

Maps for various statistical processing procedures are presented in Volume 3.

The *ar*-Ba/*ar*-Ca ratio is generally high throughout the Lefkara Formation and low in the overlying Pakhna Formation. Values are also high across most of Kokkinokhoria, near the sulfide deposits and in parts of the western side of the Troodos sheeted dykes. Alteration of feldspars may result in transfer of Ba to secondary carbonates, clays and near sulfides to baryte (although the Cyprus style deposits do carry some primary baryte. Conversely, the *ar*-Mg/*ar*-Ca ratio mainly maps the ultramafics by high values, the other mafic rocks and central Kokkinokhoria with intermediate values, and the remaining CTSS with low values. This again emphasises that the ultramafics and basalts are Mg-rich, and the carbonates are Mg-deficient.

The *ar*-U/*ar*-Ca ratio mimics the Mg/Ca ratio, with high values across the ultramafics, Kokkinokhoria and at various sites within the sheeted dykes (especially near the plagiogranites). Given that aqua regia

does not attach zircon to any great extent, the ratio probably measures progressive accumulation of U in areas with preserved residual profiles.

The various ratios involving La, Ce and Eu effectively differentiate carbonate-hosted REE (high La/Sm) focussed around the Lefkara Formation, the palaeo depositional basins such as Polemi and the terra-rosa dominated Kokkinokhorio and feldspar-hosted REE (high Eu/La and Ce/La) in the gabbros and sheeted dykes.

High *ar*-Cd/*ar*-Zn ratios map the Lefkara Formation but there are slightly elevated across some of the agricultural areas, indicative of superphosphate use. The ratio is low in the vicinity of the sulfide deposits.

The *tot*-Cr/*tot*-Fe and the inverse of the *tot*-Hf/*tot*-Cr ratios present five very clear trends. This ratio is effectively the chromite normalised against magnetite+pyroxene+olivine on Troodos and chromite against magnetite elsewhere. The ratio is uniformly high in the vicinity of the ultramafics (especially the serpentinites), but uniformly very low across the remaining mafic intrusive and extrusive units. Values are slightly higher in the CTSS, but uniformly high again along the entire southern coastline except the cliff-dominated areas between Episkopi and Pafos Airport. There is a narrow zone extending east from the ultramafics near Pafos with elevated ratios and these cuts across the middle of the main Pakhna Formation outcrop along the southern flank of Troodos. The Kokkinokhorio area also displays elevated ratios across most of the area.

A series of plots for the ratio of the concentration differences between top soil and sub soil, normalised against top soil have been used as a measurement of either the degree of leaching of elements from the areas with residual soils and transportation in the other areas. The Ca ratio suggests the Kokkinokhorio soils to either be classic terra rosas (leaching of nearly all Ca from the soil overlying carbonates) or that the soil is derived from material that is exotic. The erratic patterns over Troodos represent variation in the amount of preservation of the in-situ regolith versus transported regolith. The Rb ratio is consistently high over Troodos (retention of feldspars relative to the ferromagnesian minerals leading to Rb enrichment) but depletion of Rb (stripping from clays) at surface in the CTSS. Lanthanum display some similarity to Rb, again implying most of the La is in feldspars over Troodos and in clays and carbonates in the CTSS.

The Cr and Ni patterns are erratic.

The Hg ratio is spatially erratic with the exception of two zones. The first is the Polis Valley where the sub soil has near-uniform elevated Hg. The second is the zone extending from Petra tou Romiou across Troodos towards Lefkosia and corresponds with the Re anomaly. This again appears to be the result of some regional structural feature (probably a major fault).

## 5.7 ANOMALY AND CONTAMINATION MAPS

To further investigate the source and distribution of elements and controls on element behaviour, a series of anomaly and contamination maps have been developed.

Maps of the high values (focussing on the top 10% of the data, are plotted with the river systems. *ar*-ICPMS Factors 1 and 2 are strongly controlled by lithology, but with the Cr and other heavy-mineral hosted elements showing some accumulation along the coastal areas and the floodplain areas either side of the main streams. Factor 6 is again observed to be mainly controlled by the location of sulfide mineralisation.

Mercury has some sulfide mineralisation effects, but is otherwise highest in the Polis Valley and in the NE-trending lineament previously described. Boron is shown to be derived largely from the basalts and to accumulate in the surrounding major stream valleys, as well as areas with salt accumulation along the coastal strip.

Chromium, Ni and Co, again map the ultramafics and to a lesser extent the sheeted dykes (low values generally in the cumulate gabbros). Chromium is elevated in Kokkinokhorio whereas Ni and Co are not, suggesting most of the Cr is present as chromites there.

The anomaly map for Pb emphasises pollution in the major cities and sporadic elevated values in the Troodos flanks that is likely a result of shooting. The elevated Fe values most probably relate to iron-ochre deposits within the pillow basalts, as well as the highly ferruginous ultramafics.

*tot*-Sm values are typically high along the coast, Kokkinokhoria and the northern flank of Troodos at the boundary with the Mesaoria Plain. There is some accumulation in the vicinity of the old basins. This again suggests Sm is being transported and preserved as a heavy mineral (probably monazite).

Using the comparative boxplots presented in the element maps, the “outside” values (those higher than the third quartile plus 1.5x the interquartile spread) for each of the seven rock groups have been plotted for *ar*-Cu, *ar*-Cr and *ar*-Ni in top soil. Outside Cu values are most common in the basalts and relate to zones of sulfide mineralisation within the basalts and the western zone in the sheeted dykes. Chromium and nickel are most anomalous around Akamas, the Mamonía Terrane surrounding Pafos and various areas along the coastal fringe which probably represents sites of deposition and sediment reworking of mechanically dispersed Cr and Ni.

Based on the maps and results of the factor analysis, a number of linear combinations (indices) of elements can be used to enhance various “signals”. The  $ar\text{-}(\text{Hg}*\text{Cu}*\text{Pb}*\text{Sn})/\text{Fe}$  is a measure of urban contamination with the divisor reducing the influence of sulfide deposit areas. The largest areas and highest values are associated with the major urban areas of Pafos, Lemesos, Larnaca and Lefkosia, as well as the Vaselike industrial area. There are elevated values along the sides of the Polis Valley but this does not appear to be related to urban pollution. The  $\text{Ag}*\text{As}*\text{Cu}*\text{In}*\text{Zn}$  index is a strong indicator of sulfide mineralisation and the majority of anomalies are associated with known sulfide mines. There are a few other anomalies scatter around the pillow basalts, which are also likely to be sulfide mineralisation. There are no anomalous zones outside the TOC basalts.

The ratio of  $\text{Cr}*\text{Mn}*\text{Ni}$  to  $\text{Cu}*\text{Fe}*\text{Ca}$  is designed to enhance the ultramafic signature. This ratio strongly maps out the ultramafic units and the zone of heavy mineral accumulations in the Akrotiri Peninsula. The other area of moderately high values is Kokkinokhoria.

Contaminated sites have been defined for a number of key elements based on the so-called “Dutch Values” and other regulatory limits set on soils for investigation and cleanup elsewhere in Europe. The first feature to note are the wide variations in such regulatory limits. Both Pb and Hg display contamination values in the vicinity of the major urban areas and along main road. There are no sites with high Hg values (cleanup required), but there are three sites with significant Pb contamination. Moderate to high Cu “contamination” occurs throughout the pillow basalts and the highest values, as expected, generally relate to the mine areas. The only high B values are in the salt flats, with a few marginally “contaminated” levels in the pillow basalts.

As with Cu, a number of zones are defined as highly contaminated based on their Cr and Ni values, but these are almost exclusively associated with the ultramafics, where the Cr is likely to be mainly present as chromite which makes the Cr relatively unleachable from soils. Arsenic displays a few contamination values surrounding the major mines and Vasiliko industrial site.

By strict application of European regulatory limits, the entire Lefkara Formation is contaminated by Ba (the implications of this are discussed below). As with Cr, Ba is largely contained in a relatively immobile form (baryte). Antimony displays some contamination levels, sporadically distributed across the region. Indium and Zn contamination is mainly associated with the basalts and sulfide deposits. The high Cd values occur in a belt that extends from the southern Polemi Basin around the southern side of Troodos. This cuts across the geology and may represent some palaeodepositional control (probably Eh/pH).

## 5.8 MULTIVARIATE DATA MODELLING

Two forms of multivariate data modelling have been undertaken – factor analysis and K-means clustering. The results for these are presented in support of the observations described above, as they relate to the Atlas. Various other modelling methods are being pursued and will be the subject of subsequent reports and papers.

### 5.8.1 Factor analysis

Using  $\lambda$ -transformed variables, factor analysis was performed on the *ar*-ICPMS and INAA data for both the top soil and sub soil. The factor loadings are listed in Tables 5.7 and 5.8 and plotted in Figs 5.95 and 5.96.

In each model, the first eight factors accounted for >80% of the variance with the remaining factors explaining only small proportions of the total variance and dominated by just one variable. Hence, in the final model, eight factors were retained.

In the *ar*-ICPMS data Factor 1 accounts for 26.3% of the total variance and contains strong loadings for the REE and some of the incompatible elements. The factor scores are highest in the Kokkinokhoria region, along the boundary between the TOC and CTSS, a discontinuous arc along the southern coast and the corridor that runs across the western side of the TOC. Factor 2 accounts for a further 19% of the variance and is a combination of the suite of elements whose concentrations are highest in the basalts and mafic intrusives (positive loadings) and the opposing suite concentrated in the CTSS carbonates (negative loadings). There are generally sharp boundaries along the edge of the TOC. To the north the factor loadings are still elevated and this probably represents a mixture of small outcrops or subcrops of the TOC and areas of deposition of transported TOC material towards the base of the fanglomerates and Mesaoria Plain. The elevated value in the Kokkinokhoria region may have a similar explanation. In the plot of Factor 1 versus Factor 2, Fe and Ca display the greatest separation.

*ar*-ICPMS Factor 3 relates to the ultramafic-hosted elements, with high scores in the vicinity of the ultramafic unit outcrops and the areas of accumulation of transported ultramafic clasts along the southern coast. Factor 4 is related to the elements that are elevated in the Lefkara Formation and the Polemi Basin, as well as the known sulfide deposits. Factor 5 contains the lithophile element that are generally elevated in the mafic units and which, apart from the coastal areas is the converse to Factor 5. Factor 6 contains elements closely associated with the sulfide mineralisation, though there are patches of elevated scores throughout the CTSS and coastal areas.

For the INAA data, the REE split into the light REES in Factor 1 and heavy REES in Factor 3. This may represent different fractionation trends in the Troodos rocks or secondary environment behaviour. Elevated Factor 3 scores are largely restricted to the mafic intrusives whereas Factor 1 is strongest in the Kokkinokhoria region and the Mamonía Terrane. Factor 2 relates to the ultramafic (positive loadings) and carbonate-hosted (negative loadings) lithologies. Factor 4 contains just As and Sb loadings and picks up both the sulfide deposits and the coastal or fanglomerate base accumulations.

### 5.8.2 K-means clustering

An eight-cluster model was run on the  $\lambda$ -transformed data with the mean values for selected elements in each of the clusters plotted in Fig 5.98. The clustering, in terms of both variables and spatial distribution of allocated clusters, follows the trends previously described. The “ultramafics” cluster, has high means or relative loadings for Co, Ni and Cr and negative loadings for Ca, Na and P. Conversely, the “sulfides” cluster has high loadings for Cu, Pb, Zn and Fe. The two “carbonates” clusters spatially correlate with the Pakhna Formation (carbonates I) and Lefkara Formation (carbonates II). The clusters are spatially contiguous (Fig 5.98), with the main sulfide deposits defined by cluster 8.

### 5.8.3 Sampling density effects

The question of the effect of variation in sampling densities on the detection of spatial patterns in geochemical data was tested by progressively reducing the number of samples plotted by randomly excluding a proportion of the sites and regridding the remaining data. This required changes to the IDW parameters. Sampling densities of one sample per 1 km<sup>2</sup> and simulated densities of one sample per 2, 4, 10, 20 and 100 km<sup>2</sup> were tested for a number of key elements. The results for *ar*-Ba\_A, *ar*-Cu\_A and *ar*-Cr\_A are presented in Figs 5.99 to 5.101.

At all sampling densities, the major geological domains are preserved. The sharpness of the boundaries is better preserved in Ba than in Cr due to the higher degree of spatial variability in the Cr data related to clastic dispersion of ultramafic materials away from Troodos and deposition along the southern coast. The most obvious changes in spatial resolution in the data are between the one per 20 km<sup>2</sup> and the one per 100 km<sup>2</sup> densities. Such a pattern is largely controlled by the scale of variation in the outcrop area of the different lithologies.

From an exploration or environmental perspective, the Cu patterns define the known mineral deposits at 25% of the original sampling density (i.e. one per 4 km<sup>2</sup>) but below this only broadly outlines the pillow basalts which generally have elevated Cu values.

#### **5.8.4 Spectral classification of soils**

Two hierarchical clustering approaches were applied by Jumrieng (2007) – non-parametric functional data analysis (NP-FDA) and agglomerative clustering analysis (ACA) of a suite of 300 samples from a N-S swath across the island (Fig 5.102). NP-FDA is a divisive clustering method that breaks up the whole data set into smaller nodes and illustrates results in the form of a descending hierarchical tree. ACA is used to create regolith clusters by merging individual data object until the one large cluster is constructed. A hierarchical dendrogram is used to depict the results. Derived regolith classes using ACA show more consistency with the distribution of geological formation and soil types in the study area than NP-FDA (Figs 5.103 and 5.104). The dominant minerals affecting the IR spectra appear to be palygorskite, brucite and halloysite. The presence of these minerals is controlled by parent lithology, hydrothermal alteration and geomorphological processes such as transportation and re-deposition. In addition, the spatial distribution of opal and chrysotile can also be explained by these landform processes. The results suggest that hierarchical clustering approaches adopted by this research have application in a variety of regolith settings. Even though the derived regolith classes comprise of only the two dominating minerals, they can be used as a preliminary regolith classification for further research into similar classification methods based on spectral data.

## 6 DISCUSSION AND CONCLUSIONS

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### 6.1 DESIGN AND IMPLEMENTATION OF THE SURVEY

This project was designed and implemented using principles developed for a number of major regional geochemical atlases, including the FOREGS Atlas of Europe, the NRAC survey of NE NSW and the principles set out in IGCP Project 360.

The ability to undertake a soil survey at such a high density (1 sample per  $\sim 1 \text{ km}^2$ ) and at two depths, as well as the use of both near-total (aqua regia) and total (INAA) analytical methods, has delivered a database that allows for very detailed analysis and subsequent modelling of the effects of lithology, landscape and human activity on soil geochemistry. A limited empirical analysis of the data indicates a significant loss of detail in the geochemical patterns would have occurred had the sampling density been reduced from one site per  $1 \text{ km}^2$  to one per  $4 \text{ km}^2$  and more severe loss at lower sampling density. This is especially the case where the outcrops of various different rock types in an area is of the order of  $1 \text{ km}^2$  or less. As a general observation, the scale of sampling much correspond with the “wavelength” or dimension of the phenomena being measured (variation in lithology, towns and villages, the extent of pollution or natural geochemical dispersion trains).

The use of the grid-cell sampling model, by which sample locations may be shifted by small distances, assisted logistics and ensured samples are visually representative of the area being sampled, while still preserving the regular spatial coverage of the region. With careful planning of routes, an average 20 sites per day per field crew was achieved, despite the access problems in Akamas (due to the roads) and Troodos (due to rain). The use of professional geologists to lead field crews was also essential to ensure field data was accurately and consistently recorded and atypical conditions identified.

Analytical quality control is an essential component of such studies and a significant proportion of the analytical budget was devoted to quality control analyses, including development and testing of project-specific reference materials, certified referenced materials, duplicates derived from various stages of the process (sampling to analytical), blanks and other cross-checks. It was concluded that the dataset is fit-for-purpose for most envisaged applications of the data, although detection limits for a number of INAA variables were too high to allow adequate mapping of regional variations at the lower end of the concentrations. In subsequent studies it would be advisable to use XRF in addition or as a replacement for INAA.

The close cooperation between the commissioning organisation (the GSD), the advisors and consultants (mainly UNSW), the project management staff (ACDS and UNSW Global) and the analytical laboratories (Actlabs and UNSW-AC) has contributed to the successful completion of the project.

It would be appropriate for further studies of this type to incorporate more extensive orientation studies to aid the design of the main survey within the project TOR, rather than set highly prescriptive methods in the TOR itself. Fortunately, the concurrent orientation studies supported the pre-defined design of the main survey in this project.

### 6.2 MAIN CONTROLS ON SOIL GEOCHEMISTRY

The soil geochemistry of Cyprus is dominated by parent lithology and subsequent regolith processes. This is the observation of a number of previous geochemical studies at this scale. The sharpness of soil geochemical transitions across the major lithological boundaries indicates more limited distance of soil transport down-slope than initially predicted based on the assessment of regolith-landform relationships.

Along the coast, there is physical reworking and concentrating of heavy minerals shedding from Troodos and possibly northern Cyprus and their component elements (Cr and Ni), and mobile elements reflecting either seawater influences or hydromorphic dispersion of elements from the mountains (Na

and Br). However, there is still some control exerted by underlying geology. The significant differences between the soil geochemistry of the Kokkinokhoria area and other coastal plain areas indicates either input of Mesaoria Plain sediments, the Keryneia Terrane or possibly more exotic sources from the north.

The geological controls shows up strongly in the major and minor elements – Cr in the ultramafics, Fe in the mafic units, Ca in the carbonates – and is reflected in trace elements that are controlled by the major elements (Sr by Ca; Ni and Co by Fe). Various combinations of elements, determined using multivariate techniques such as factor analysis and other more subjective indices, serve to map the geology with even subtle differences between rock types being mappable using soil geochemistry. Examples are the cumulate gabbros versus the sheeted dykes; the Lefkara Formation versus the Pakhna Formation carbonates. Zonation of the REE within the soils may be linked to evolving magmas within the TOC, particularly in relation to feldspars.

Geochemical lineaments defined by various combinations of rare elements (Hg, Re and others) suggests the influence of some deep structures that cross the island. These may represent transcurrent faulting or other crustal discontinuities that divide the TOC into separate structural blocks. Further analysis of these trends must be done in conjunction with detailed structural and tectonic analysis.

In urban and industrial areas there is detectable contamination by a number of metals (Pb, Sn, Cu) and mining activities have contributed to increased concentrations in the soils of commodities contained within the deposit and element associated with the mining activities (Cu, As and Zn). In agricultural areas there are indications of soil contamination linked to fertilisers and possibly groundwater irrigation, but these are very weak.

At the regional scale, the soil geochemistry indicates a number of “landscape geochemical terrains” can be defined:

1. Ultramafic lithologies in deeply dissected areas
  - (a) harzburgites, dunites, wehrlites and pyroxenites
  - (b) serpentinites
2. Mafic intrusives in deeply to moderately dissected areas
  - (a) cumulate gabbro surrounding TOC ultramafic core
  - (b) remainder of the sheeted dykes with gabbro-dolerite-basalt
  - (c) the high chalcophile N-S corridor in western Troodos
3. Basalts (mainly pillow)
  - (a) general suite (which may be subdivided into upper and lower pillow lavas)
  - (b) major sulfide deposit areas
4. Circum-Troodos Sedimentary Sequence
  - (a) lower carbonate units (Lefkara)
  - (b) upper carbonate units (Pakhna)
  - (c) mafic or ferruginous clastic sediments
5. Mixed terranes
  - (a) Akamas
  - (a) Polemi Basin / Polis Valley
6. Depositional areas
  - (a) Coastal fringe
  - (b) agglomerates (e.g. Kokkinokhoria and some areas around Lefkosia)
  - (c) salt flats
7. Urban and industrial areas

### 6.3 MINERAL EXPLORATION

Cyprus has one of the longest histories of mineral exploration and any deposit with a strong surface expression (such as extensive malachite staining or acid bleaching and alteration of rocks) has probably been found. The question is whether there are significant deposits that are masked by either thin outliers of CTSS units, colluvium or simply buried by unmineralised pillow basalts.

The project has identified a combination of elements – Ag, As, Cu, Zn and In – offers stronger soil geochemical indications of significant sulfide mineralisation than commodity elements alone (e.g. Cu). For this method to be further developed, lower detection limits for Ag and In may need to be developed, as well as further studies on the exact physical (e.g. grainsize) and chemical (e.g. partial versus selective extractions) that will best differentiate mineralised from non-mineralised areas. Further orientation studies over some of the targets defined in this study but which are not related to known sulfide deposits would be useful in this regard.

An area this may be worth follow-up investigations in the short-term is the sheeted dykes on the western side of Troodos which appear to have an extensive N-S zone containing elevated Cu and also other geochemical indices indicating mineralisation.

The second outcome of this study, in respect of mineral exploration, is the identification of pines (*P. brutia* or *nigra*) and olives as offering strong biogeochemical indications of mineralisation (and contamination). A surprising discovery was the strongly elevated Re contents of the leaves near mineralisation. This needs systematic follow up studies to determine how consistent the geochemical patterns are around both existing mineral deposits and other areas with known sulfide mineralisation but with limited surface disturbance by mining.

The third aspect of this work would be follow-up of the soil geochemistry with some regional groundwater studies of trace element distributions to determine the link between soil and groundwater geochemistry (and possibly at the isotopic level).

### 6.4 ENVIRONMENTAL ISSUES

The soil geochemistry indicates a number of environmental issues – some significant (and generally known) and others of uncertain significance. Metals contamination of soils in the vicinity of the (mostly-abandoned) sulfide mines, generally extend for 1–2 km outside the limits of the pits and processing plants, but which may extend further down the major drainages (e.g. Skouriotissa, Limni and Kalavassos). The main contaminant is Cu itself but there is also moderate-level Pb and low-level of As contamination. There is the question of how much of the elevated Cu in soils surrounding the deposits is natural. By virtue of the amount of carbonates in the vicinity of the pillow basalts, there are only minor indications of any surface acid mine drainage related to the sulfide mines, affecting the soils.

Significantly elevated concentrations of a number of metals, including Pb, were detected in the urban areas, at the 1 km scale of sampling. Few of those sites would be classed as highly contaminated under the various regulatory limits. Urban contamination is generally indicated by a significant elevation in the top soil/sub soil metal ratios, compared with non-urban or industrial areas.

There are some very atypical areas, containing a range of elevated metal value, including the single U high value at Akamas, the Vaselike industrial area and the many sites scattered throughout the mountains with elevated lead due to either amateur or professional shooters.

Indications of slightly elevated Na, Cd and other elements in the main agricultural areas indicate of some diffuse source pollution (use of fertilisers, insecticides and irrigation) but the values are almost all below investigation levels specified in a number of European countries.

The continuous zone of sub soil elevated Hg value in the northern Polis Valley needs follow up investigation. It is unclear from the data whether this is the result of natural accumulation of (the volatile) Hg in the sub soil due to dispersion from the western side of Troodos, or is the product of anthropogenic contamination. The latter may be related to artisanal use of Hg in Au extraction, agricultural application or some other purpose, over an unspecified timeframe.

It is absolutely clear that there is no single “background” level for most of the metals in the soils of Cyprus that can be set to differentiate the “natural” from the “potentially polluted”. Median concentrations of elements like Cr, Ni and Cu vary by orders of magnitude between the soils derived from the different lithologies. In the case of Ba, some regulatory authorities in Europe would identify the soils covering the entire Lefkara Formation as being contaminated with Ba, though the Ba levels are clearly natural and simply associated with carbonates or possibly sulfates. Boron levels are elevated along the major streams that drain the pillow basalts, and certainly in the salt flats, but this again is a natural process.

Even natural levels for elements may still pose health risks, but there are few indications of this being a major problem in Cyprus at the scale of the survey. The atlas will, however, guide the setting of lithology-specific and terrane-specific indicator levels for natural element abundances against which the results of any subsequent detailed geochemical surveys can be compared.

**In conclusion, this project has delivered a high quality, high density, multielement, regional geochemical database for the southern and central parts of Cyprus. The data have general application in environmental management, agriculture, mineral exploration and provides a basis for various studies on the nature of spatial geochemical data and its relationship to lithology, landscape evolution and the effects of human activity.**

## 7 RECOMMENDATIONS FOR FUTURE PROJECTS

The project has provided a basis for a number of future projects ranging from fundamental science and data analysis to environmental monitoring and management. Whereas some following-on projects are already in train, a number of additional projects are recommended for consideration by the GSD and other organisations:

### 7.1 ON-GOING PROJECTS BASED ON THE EXISTING DATASET AND SAMPLES:

Project	Outline	Contributors	Resources	Duration	Est. Cost
<b>Spatial and parametric analysis of a high density regional soil geochemical data (Cyprus)</b>	Development and testing of various spatial and multivariate data processing methods to isolate patterns in the data and increase our understanding of the geochemical evolution of the soils in Cyprus	Joint work by GSD and UNSW staff, plus associated groups (Queens, CUG).  Honours, MSc and PhD students  UNSW staff contacts: Laffan, Cohen and Gatehouse	Minimal beyond student scholarships and access to computing resources (all available at UNSW)	1 to 3 years for main projects but an area that can generate studies almost indefinitely	EUR 5,000
<b>Risk mapping</b>	Geostatistical analysis and risk assessment studies for deriving regulatory action limits for known toxic elements in soils of Cyprus.	Various Cyprus Govt Department, UNSW and Univ Cyprus  UNSW staff contact: Laffan	Minimal beyond time commitments  1 trip Aust-Cyprus	6 months	EUR 10,000
<b>Mineralogical and environmental controls on element distributions in soil</b>	More detailed mineralogy to complement the soil geochemistry	UNSW and GSD staff  Honours, MSc and PhD students  UNSW staff contacts: Graham, Cohen, Rutherford and Triantafilis	4 trips Aust-Cyprus  Access to UNSW electron microscope facility  Additional geochemical and mineral processing facilities  Geochemical analysis	1 to 4 years depending on level of student	EUR 20,000
<b>Extend geochemical work around mines to determine controls on mobility and risk assessments</b>	More detailed geochemical work, including selective geochemical extraction studies on mine environments	UNSW and GSD staff  Honours, MSc and PhD students (possibly junior GSD professional staff)  UNSW staff contacts: Cohen and Rutherford	4 trips Aust-Cyprus  Access to analytical facilities (UNSW and GSD)	1 to 3 years depending on level of student	EUR 50,000

## 7.2 EXTENSIONS TO THIS PROJECT AND NEW PROJECTS:

Project	Outline	Contributors	Resources	Duration	Est. Cost
<b>Complete the geochemical atlas of Cyprus (areas outside effective control of the Republic of Cyprus)</b>	Direct extension of the current project	To be determined, but preferably involving UNSW UNSW staff contacts: Cohen and Rutherford	As per this project	2 years	EUR 800,000
<b>Detailed mapping of urban and industrial geochemistry</b>	A detailed follow-up study on the urban areas to map the distribution of various contaminants, and to identify significantly polluted areas and assist with general environmental management. Probably target the four main urban areas looking at both soils and dust	MOA and local authorities UNSW and Univ Cyprus UNSW staff contacts: Cohen and Rutherford	Field crews Geochemical analysis 4 trips Aust-Cyprus	2 years	EUR 150,000
<b>Mineral exploration methods development - 1</b>	Closer investigation of vegetation geochemistry in relation to both mineral exploration and environmental assessment. Target three existing deposits and two areas with known mineralisation but no significant mining.	GSD, UNSW and Univ Cyprus UNSW staff contact: Cohen	Geochemical analysis 1 trip Aust-Cyprus	1 year	EUR 30,000
<b>Mineral exploration methods development - 2</b>	Follow-up soil geochemical studies of selected Cu deposits, to provide stronger links between mineralisation and soil geochemistry for previously untested element associations (specifically In and Re)	GSD, UNSW and other universities Mineral companies UNSW staff contacts: Graham, Cohen and Rutherford	Geochemical analysis 6 trip Aust-Cyprus	3 years	EUR 150,000
<b>Extended soil geochemical orientation studies</b>	Additional detailed transects from with analysis of rocks to fine tune the main dataset and extend lithgeochemical database for CTSS lithologies	GSD, UNSW UNSW staff contact: Cohen and Rutherford	Geochemical analysis 2 trips Aust-Cyprus	6 months	EUR 25,000
<b>Soil salinity mapping of the Cyprus coastal agricultural areas</b>	Detailed follow up of soil geochemistry involving EM mapping of various coastal and inland areas. Assistance with developing salinity management plans.	UNSW, GSD, Univ Lisbon UNSW staff contacts: Triantafilis and Kelly	Geochemical analysis 4 trips Aust-Cyprus Transport of EM devices	2 years	EUR 30,000
<b>Investigating the Polis mercury soil anomaly</b>	Detailed geochemical profiling and speciation of Hg in the northern Polis Valley and links to the Troodos margins. Follow up the large Hg anomaly detected in the Atlas project.	GSD, UNSW, Univ Cyprus UNSW staff contact: Cohen	Geochemical analysis Shallow drilling 2 trips Aust-Cyprus	1 year	EUR 25,000

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