Hydrothermal mobilisation of Au and other metals in supra-subduction oceanic crust: insights from the Troodos ophiolite

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Abstract

The Troodos ophiolite is an ideal location to investigate the relationships between the mobilisation of metals by hydrothermal fluids from the lower oceanic crust and the formation of volcanogenic massive sulphide (VMS) deposits. The ophiolite hosts the classic “Cyprus-type” Cu-rich VMS deposits as well as abundant zones of epidosite alteration in the lower sheeted dyke section that are significantly depleted in base metals including Cu and Zn, and are considered to be the source of the metals enriched in the overlying deposits. Previous research indicates that the Troodos VMS deposits are irregularly enriched in Au and related elements As, Sb, and Se, but the behaviour of these elements during the hydrothermal alteration of the Troodos ophiolite hitherto has been poorly investigated. Low detection limit whole rock analyses of

fresh glass samples reveal that the Troodos primitive crust has a similar metal content and distribution to modern-day arc-related environments such as the Manus Basin. Compared to mid-oceanic ridge basalt (MORB), the Troodos primitive crust is enriched in As, Sb and Pb most likely due to addition from a subducting slab during crustal formation. During early stages of magmatic differentiation (9-3.5 wt.% MgO) Au, As, Sb, Se, Cu, Zn and Pb behave as incompatible elements due to the sulphide-undersaturated nature of the melt. The onset of magnetite crystallisation, however, at ~3.5 wt.% MgO leads to sulphide segregation and depletion of strongly chalcophile elements (Au, Cu and Se) during continued differentiation (<3.5 wt.% MgO) whereas poorly chalcophile elements (As, Sb, Zn and Pb) remain incompatible. These differences in metal behaviour can account for the Cu-rich, Zn-Pb-poor of the Cyprus-type VMS deposits as the source area rocks show high Cu fertility compared to Zn and Pb. Mobilisation of metals during hydrothermal alteration of the Troodos ophiolite is more extensive than observed in hydrothermally altered MORB. Mass balance calculations show that the epidosite zones are significantly depleted in Au (-88±16 %), As (-89±23 %), Sb (-60±12 %), Se (-91±20 %), Cu (-84±18 %), Zn (-63±9 %) and Pb (-60±8 %). Background altered diabase from outside epidosite zones shows similar metal depletions which suggests that the source areas of VMS are not restricted to epidosite zones but are extended to the lower sheeted dyke section. The masses of metals mobilised from a source area of 10.9 km³, (composed of a 5 km³ epidosite zone and 5.9 km³ of background altered diabase) in the Solea graben are 47 t Au, 21 kt As, 1200 t Sb, 3100 t Se, 2.4 Mt Cu, 1.8 Mt Zn and 27 kt Pb. Comparison of metal quantities mobilised from lower sheeted dike section in the Solea graben with those hosted in VMS deposits shows trapping efficiencies ranging from 4 to 37 % indicating that most of the metals is lost by other processes.

Keywords: VMS deposit, hydrothermal alteration, gold, Troodos ophiolite, magnetite crisis

Introduction

Volcanogenic massive sulphide (VMS) deposits form by focused discharge of hydrothermal fluids on or near the seafloor (e.g. Tornos et al., 2015). They are exploited primarily for the base metals Cu, Zn

and Pb (e.g. Galley et al., 2007; Mudd et al., 2013), and it is generally accepted that these metals are sourced in part from hydrothermal reaction zones in the lower sheeted dyke section of the oceanic crust (e.g. Alt, 1995). Depletions in base metals from the lower sheeted dyke section has been observed in deep drill cores in the oceanic crust, such as Ocean Drilling Program (ODP) Hole 504B and Hole 1256D (e.g. Alt et al., 1989; 2010; Alt, 1995; Bach et al., 2003; Teagle et al., 2006; Patten et al., 2015). Base metal depletions have also long been recognised from epidosite zones in ophiolites such as Troodos, Cyprus, (Richardson et al., 1987; Schiffman et al., 1987; Schiffman and Smith, 1988) where over 80% of the primary Cu and Zn has been removed (Jowitt et al., 2012). An important sub-class of VMS deposits are those enriched in Au, Ag, and a related suite of semi-metals As, Sb, Se, Te and Bi (Hannington, 1999; Huston, 2000). In certain deposits, Au contents are sufficiently high that they are classified as Au-rich VMS deposits. Mercier-Langevin et al. (2011) characterised Au-rich VMS deposits by a grade of more than 3.46 g/t Au and a tonnage of 31 t Au. Despite the economic significance, the causes of Au enrichments in these deposits are not well constrained.

Gold-rich VMS deposits occur mostly in arc-related tectonic settings and are hosted in intermediate to felsic volcanic rocks (e.g. Herzig et al., 1993; Barrie and Hannington, 1998). Arc settings display a number of characteristics that could potentially promote Au enrichment in VMS deposits. First, arc-related magmas are generally volatile-rich and undergo significant magmatic degassing which may cause direct input of metals into hydrothermal fluids (e.g. Urabe et al., 1987; Stanton, 1990; Yang and Scott, 1996; Sillitoe et al., 1996; Kamenetsky et al., 2001; Moss et al., 2001; Yang and Scott, 2002; Pertersen and Herzig, 2002; Sun et al., 2004; deRonde et al., 2011). Second, oceanic crust produced in volcanic arc settings can form in relatively shallow seawater (>2000-1500 mbsf, e.g. Monecke et al., 2014) which, due to the lower confining pressure, promotes sub-seafloor boiling of hydrothermal fluids and metal fractionation that could cause Au-enrichment during VMS formation (Urabe et al., 1987; Huston and Large, 1989; Butterfield et al., 1990; Poulsen and Hannington, 1996; Hannington, 1999; Barriga et al., 2007). Third, oceanic crustal rocks formed in arc-related settings have generally higher Au content than in MOR settings, which increases the

amount of Au available for mobilisation by hydrothermal circulation (Huston, 2000; Moss et al., 2001; Herrington et al., 2011; Pitcairn, 2011). In mid-oceanic ridge (MOR) settings significant masses of Au as well as As, Sb and Se (hereafter referred to as *related elements*) are mobilised during alteration in the lower sheeted dykes, but the degree of mobilisation is similar to that of the base metals and alone is not sufficient to generate the Au enrichment required to form Au-rich VMS deposits (Patten et al. 2015). Higher primary Au content in arc-related rocks has been previously suggested as the cause for Au enrichment in VMS deposits (e.g. Moss et al., 2001; Herrington et al., 2011). However, the behaviour of Au and related elements during hydrothermal alteration of arc-related oceanic crust has not been investigated.

The Troodos ophiolite, Cyprus, which is one of world's most well studied ophiolites, shows a full exposure of the crustal sequence from ultramafic rocks to seafloor sediments. It is supra-subduction oceanic crust (e.g. Myashiro, 1973; Rautenschlein et al., 1985; Muenow et al., 1990) that probably formed during subduction initiation (Pearce and Robinson, 2010). The Troodos ophiolite has contributed greatly to our understanding of the formation of VMS deposits as it hosts the eponymous Cyprus-type VMS deposits; structurally controlled Cu-rich sulphide deposits hosted in mafic volcanic rocks that form at or near the seafloor (Constantinou and Govett, 1973; Adamides, 2010a; 2010b). The ophiolite also exposes the hydrothermal reaction zones located at the base of the sheeted dyke complex that are considered to be the source areas for the base metals enriched in the deposits (Richardson et al., 1987; Schiffman et al., 1987; Schiffman and Smith, 1988; Richards et al., 1989; Bettison-Varga et al., 1992; Jowitt et al., 2012). The Troodos ophiolite therefore provides an ideal locality for investigation of the mobility of metals including Au during hydrothermal alteration of arc-related oceanic crust. The Au content of the VMS deposits in Troodos is poorly documented (Herzig et al., 1991) but there is evidence for significant but irregular Au enrichment. The sulphide ore from the Limni deposit for example, has 3.4 ppm Au grade (Table 1; Moiser et al., 1983). Seafloor weathering of the VMS deposits has caused supergene Au enrichment in gossans and ochres (Herzig et al., 1991) and Au-rich umbers, either primary or enriched by off-axis low temperature fluid circulation, are also common (Herzig et al., 1991; Prichard et al., 1998).

In this study we apply low detection limit analytical techniques to investigate the behaviour of Au, As, Sb and Se, as well Cu, Zn and Pb, during hydrothermal alteration of the Troodos ophiolite. The objectives are: (1) to determine the distribution of Au and related elements in the primary crust of the Troodos ophiolite for comparison with modern day supra-subduction zone analogues; and (2) to quantify the mobility of Au and related elements from the different lithological units during hydrothermal fluid circulation, with specific focus on the epidosite zones. We then discuss the implications for formation of VMS deposits, particularly those that are Au-rich.

Geological setting

The Troodos ophiolite

The Troodos ophiolite was formed in the eastern Mediterranean basin during the closure of the Tethys Ocean (Robertson, 1987; Garfunkel, 1998) and is a segment of supra-subduction oceanic crust (e.g. Miyashiro, 1973; Pearce, 1975). It is considered to have formed during subduction initiation (Pearce et al., 1984; Rautenschlein et al., 1985; Pearce and Robinson, 2010) at 90-92 Ma (Mukasa and Ludden, 1987; Osozawa et al., 2012). Boninitic volcanism extended up to 75 Ma due to ridge subduction (Osozawa et al., 2012). Regelous et al. (2014) alternatively propose formation in a fore-arc setting at a triple junction. The core of the ophiolite is characterised by partially to completely serpentinised peridotites representing the mantle sequence (e.g. Gass, 1987; Batanova and Sobolev, 2000; Nuriel et al., 2009) surrounded by the plutonic sequence composed of layered ultramafics, gabbros and plagiogranites corresponding to the lower part of the oceanic crust (e.g. Gass, 1987; Fig. 1). Higher in the sequence the extensively exposed sheeted dyke complex represents the fossilised pathways for magma migrating from the magmatic chambers to the volcanic section (Baragar et al., 1987). The dykes were produced from different magmatic chambers (Baragar, et al. 1987) with intrusion vertical, lateral and/or orthogonal to the magmatic chamber but always parallel to the spreading-axis in a near-vertical plane (Baragar et al., 1987; Staudigel et al., 1992; Staudigel et al., 1999). The upper oceanic crust at Troodos, commonly referred to as the volcanic section, has been

sub-divided, based on field evidence and analyses of fresh glass samples (e.g. Miyashiro, 1973; Robinson et al., 1983; Cameron, 1985; Rautenschlein et al., 1985; Thy et al., 1985; Bednarz and Schminke, 1994; Portnyagin et al., 1997), into the basal unit (BU), the lower lava sequence (LLS) and the upper lava sequence (ULS; Fig. 1). The basal unit is a combination of intrusive dykes and extrusive lavas that represents the transitional zone of the oceanic crust (Fig. 1). The lower and upper lava sequences have a composition that follows a basaltic andesite-andesite-dacite-rhyolite (BADR) trend but also host boninite and high magnesian andesite series (Bailey et al., 1991; Pearce and Robinson, 2010 and references therein).

Hydrothermal system of the Troodos ophiolite

The ancient hydrothermal system in the Troodos ophiolite shares many similarities with those in modern-day oceanic crust (e.g. Gillis and Robinson, 1988; Alt and Teagle, 2000). It can be simplified into two subdomains; the seawater-derived fluids domain that mainly affected the volcanic section, and the hydrothermal fluids domain that affected the sheeted dyke and plutonic complexes. The alteration in the seawater-derived fluids domain was caused by flow of low temperature fluids (50-200 °C) producing pervasive background alteration throughout the volcanic section with smectite, celadonite, zeolite and calcite being the most common secondary minerals (Gillis and Robinson, 1988; Berdnarz and Schminke, 1989; Gillis and Robinson, 1990). An increase in alteration temperatures occurred from the lower lava sequence (50-100 °C) to the basal unit (100-200 °C; Gillis and Robinson, 1988). Late stage pervasive flow of low temperature (<50 °C) oxidised seawater at high water rock ratios led to seafloor weathering in the top of the lava pile in the upper volcanic section (Gillis and Robinson, 1988). Secondary alteration minerals in this zone include Fe-hydroxide, smectite, K-feldspar and calcite (Gillis and Robinson, 1988; Berdnarz and Schminke, 1989; Gillis and Robinson, 1990). Finally localised alteration halos associated with VMS deposits, stockworks and mineralised zones developed during interaction of hydrothermal fluids with seawater-derived fluids at high temperature (~300 °C; e.g. Gillis and Robinson, 1988; Richards et al., 1989; Berdnarz and Schminke, 1989; Gillis and Robinson, 1990), with smectite, illite, chlorite, quartz, pyrite and chalcopyrite being the most abundant secondary minerals (Richards et al., 1989; Gillis and Robinson, 1990).

145 An important change in the hydrothermal system occurs between the basalt unit and the upper
146 sheeted dyke section with the hydrothermal fluid domain characterised by high temperature (>200 °C)
147 alteration dominating in the sheeted dyke and plutonic complexes. The upper section of the sheeted dyke
148 complex was altered mainly to sub-greenschist facies conditions (200-250 °C) whereas the lower section
149 was altered at greenschist-amphibolite facies conditions (>300 °C; Schiffman and Smith, 1988; Gillis and
150 Robinson, 1990). Background altered dykes (referred as diabase) were partially to completely altered to
151 amphibole, albite, and chlorite, with minor quartz, epidote, titanite and secondary sulphides (e.g. Jowitt et
152 al., 2012; Cann et al. 2015). A narrow range of elevated strontium isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}$
153 $\sim 0.7053 \pm 6$) across the Troodos sheeted dykes indicates that the downwelling of seawater-derived
154 hydrothermal recharge fluids was pervasive (Bickle and Teagle, 1992), rather than channelled by deep
155 faults.

156 In contrast to modern-day oceanic crust where the discharge of hydrothermal fluids appears to occur
157 in the same pathways as fluid recharge (e.g., Harris et al., 2015), discrete zones of intensive hydrothermal
158 fluid alteration at high temperature (350-400 °C) and high water rock ratio (Seyfried et al., 1988) are evident
159 in the Troodos ophiolite through the localised development of epidosite zones (Richardson et al. 1987;
160 Schiffman and Smith, 1988; Gillis and Robinson, 1990; Bickle and Teagle, 1992). Epidosites represent
161 zones of extensive interaction between the focused upwelling high temperature hydrothermal fluids with
162 newly intruded dykes (Cann et al., 2015). The alteration can be a dyke-by-dyke process that leads to rapid
163 porosity generation and extensive dissolution of primary mineral assemblage (Cann et al., 2015). Six main
164 epidosite zones have been recognised on Troodos: five within the sheeted dyke complex and one in
165 plagiogranites (Richardson et al., 1987; Bettison-Varga et al., 1992; Jowitt et al., 2012; Cann et al., 2015).
166 Epidosite zones are not restricted to the lower sheeted dyke section and extend into the upper plutonics.
167 They are several hundred meters wide and up to a kilometre long relative to the strike of the dykes
168 (Richardson et al., 1987; Bettison-Varga et al., 1992; Cann et al., 2015). Within the epidosite zones the
169 degree of alteration is highly variable both at outcrop and dyke scale giving the specific pistachio banded

aspect (Jowitt et al., 2012; Cann et al., 2015). Diabase is the least altered and is characterised by amphibole, plagioclase, chlorite, epidote, quartz, oxides and titanite with conservation of igneous texture (Jowitt et al., 2012). It is followed by transitional diabase-epidote which contains higher chlorite (>30 %), epidote (15-30 %) and quartz (15-20 %) abundances but lacks igneous texture (Jowitt et al., 2012). Intermediate epidosite has high epidote and quartz content (>30 %) but moderate chlorite (15-30 %), and finally end-member epidosite, which represents the most advance stage of hydrothermal alteration, is characterised by a granoblastic texture and high epidote-quartz content (>60 %) and little chlorite (<10 %, Jowitt et al., 2012). Replacement of Fe-Ti oxides by titanite increases with the degree of epidotisation (e.g. Jowitt et al., 2012). Mobilisation of Cu and Zn during epidotisation has been extensively documented (Richardson et al. 1987; Schiffman et al. 1987; Schiffman and Smith 1988; Humphris and Cann, 2000). More recently, Jowitt et al. (2012) precisely quantified base metal release with Cu (-87 % to -91 %), Zn (-63 % to -65 %), Ni (-59 % to -78 %) and Mn (-52 % to -60 %) being significantly depleted depending on the degree of epidotisation.

The VMS deposits of the Troodos ophiolite

Most of the Troodos VMS deposits occur at the lower lava sequence and the upper lava sequence boundary within the volcanic section (Constantinou and Govett, 1973; Adamides, 2010b). They are generally characterised, from top to bottom, by a sedimentary cover and an oxidised horizon, implying seafloor formation, underlain by a massive sulphide lens and a stockwork zone (e.g. Constantinou and Govett, 1973; Adamides, 2010a; 2010b; Keith et al., 2016). The Apliki VMS deposit, in the Solea graben (Fig. 1), is an exhalative structurally controlled deposit characterised by moderate tonnage and Cu grade (Table 1) and is a good example of Cyprus-type VMS deposit. Some deposits, such as Mavrovouni (Table 1, Adamides, 2010a), lack evidence for formation on the seafloor and show extensive alteration halos suggesting formation by sub-seafloor replacement (Adamides 2010a; Tornos et al. 2015). The Troodos VMS deposits are classified as mafic type (Barrie and Hannington, 1999) and range in size from 50 000 t up to 16 million t with average grade of 1.3 ± 1.1 % Cu and 0.8 ± 0.4 % Zn (Hannington et al., 1998). The Au grade is rarely reported (Table 1; Herzig et al., 1991; Hannington et al., 1998) and for most deposits it is

relatively low (Table 1). A notable exception is the Limni deposit that had 3.4 ppm Au grade (Table 1), almost classifying it as an auriferous deposit ($\text{Au} > 3.46$ ppm; Mercier Langevin et al., 2011). The Skouriotissa deposit, within the Solea graben (Fig. 1), is the largest and most recently exploited VMS deposit in Troodos (Table 1). It is subdivided into the Phoukasa and Phoenix deposits (Table 1, Adamides, 2010a). The Phoukasa deposit is a typical exhalative Cyprus-type deposit whereas the Phoenix deposit is a result of partial supergene alteration of a sulphide lens that occurs on the seafloor and probably also during later subaerial environment (Adamides, 2010a). The Au grade of Skouriotissa deposit is not clearly defined because of the extensive supergene alteration (Table 1; Hannington et al., 1998). During seafloor weathering of the massive sulphides, Au has been locally enriched in gossans and ochres which average 7 ppm Au (0.6-28.4 ppm; Herzig et al., 1991). Umbers, which are sedimented from hydrothermal vent plumes, show low initial Au content (e.g. Skouriotissa $\text{Au} = 0.08 \pm 0.07$ ppm; Herzig et al., 1991) but late Au enrichment associated with silicification of umbers during low temperature off-axis fluid circulation occurs in places (up to 2.35 ppm Au, Table 1; Prichard and Maliotis, 1998). At Skouriotissa and other VMS deposits, additional Au enrichment occurred during acid sulphate ground water leaching into the “Devil’s mud”, a siliceous horizon underlying or overlying the orebody (Wilson et al., 1959; Bear, 1963; Herzig et al., 1991). Gold was profitably mined from Skouriotissa from the early 1930s to 1942 and a total of 2.2 t of Au have been extracted (Wilson et al., 1959). Gold was also mined from the Apliki deposit (80 kg; Wilson et al., 1959).

Sampling and analytical methods

A suite of 124 samples representative of the variation in lithology and alteration have been used in this study including 89 collected during fieldwork, and 25 sheeted dyke and gabbro samples previously documented by Bickle and Teagle (1992). In addition, ten fresh glass samples representative of the BADR series (Coogan et al., 2017; Appendix 1) have been analysed to determine the primary concentration of Au and related elements in the Troodos crust. From the basal unit and volcanic section, 26 samples have been selected. Samples are mostly of pillow lava, lava flow, and hyaloclastite but also include samples of dykes,

picritic lava flows and alteration halos surrounding VMS mineralisation. Sixty-seven samples from the lower sheeted dyke section have been selected mostly from the Spilia-Kannavia, Kykko-Pedhoulas, Phterykoudi-Potamos and Lemithou epidosite zones (Fig. 1; Bickle and Teagle, 1992; Richardson et al., 1987; Jowitt et al., 2012). Sheeted dyke samples are variably altered from diabase to end-member epidosite (Richardson et al., 1987; Jowitt et al., 2012; Cann et al., 2015). From the plutonic sequence 11 gabbros and 6 plagiogranites have been selected, and from the mantle sequence 2 dunites, one hazburgite and one serpentinised pyroxenite.

Fresh glasses and altered samples have been analysed using the same methods in order to have a coherent and homogeneous database. Because fresh glasses have not been investigated by microanalytical techniques, their analyses most likely include minor microphenocrysts, and partially devitrified zones. The elements investigated in this study, however, are moderately to strongly chalcophile (e.g. Peach et al., 1990; Li and Audétat, 2012; Patten et al., 2013) and are likely to be only weakly affected by the presence of silicate microphenocrysts. Additionally, most of these elements show very limited mobility during low temperature seawater alteration (e.g. Alt et al., 2010; Patten et al., 2015) and little mobilisation associated with devitrification is expected. Magmatic sulphide droplets, that are potentially present within fresh glass samples, are important hosts for the investigated elements (e.g. Peach et al., 1990; Patten et al., 2016) and therefore whole rock analyses are preferable to in-situ analyses of thin sections that may miss these rare phases. Thus, the glass composition for the elements investigated in this study are interpreted as representative of magmatic composition. Major element concentrations were carried out by X-Ray Fluorescence (XRF), using a Rigaku ZSX Primus II Spectrometer at Stockholm University. Accuracy and precision was controlled through analyses of the reference material AGV-2, an andesite powder provided by USGS (Appendix 2). Trace element analyses were carried out by laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) of whole rock glass beads at Stockholm University using a ESI NWR-193 nm excimer laser coupled to a Thermo Fisher XSeries 2 quadrupole mass spectrometer. A spot size of 150 μm was used with a laser pulse frequency of 10 Hz and a laser energy density of 7 $\text{J}\cdot\text{cm}^{-2}$.

Calibration was carried out using NIST SRM 612 and Si as the internal standard. Accuracy and precision were verified by analyses of external reference materials BCR-2G (Appendix 2). All trace elements are reproduced to better than 10 % accuracy except for Sc, Zn, Ga, Nb, Cs, Ta, Pb and U which are reproduced to better than 15 % (Appendix 2). Data reduction and calculation of trace element concentrations were performed off-line through IOLITE software (Hellstrom et al. 2008, Paton et al. 2011).

Gold whole rock analyses have been carried out following the ultra-low detection limit technique developed by Pitcairn et al. (2006a) at Stockholm University. To minimise possible nugget effects, 3g grams of sample powder are digested with HNO₃-HF-aqua regia. Gold is extracted from the sample solution by chromatography using an inert resin saturated with di-isobutyl ketone (DIBK) and is subsequently analysed using a Thermo Fisher XSeries 2 ICP-MS. The 3 σ method detection limit calculated from blank digests is 0.027 ppb. Analytical accuracy and precision were controlled through analyses of CANMET reference material TDB-1 and USGS reference materials WMS-1 and CH-4 (Appendix 3). Arsenic, Sb and Se analyses were carried out by Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) at Stockholm University following the method described in Pitcairn et al. (2006b). Using the same acid digests from Au analyses hydride generation is achieved by mixing sample solutions with a reductant solution (0.4 % NaOH and 0.7% NaBH₄) and is analysed using a PSA 10.055 Millennium Excalibur instrument . The 3 σ method detection limits are 0.059 ppb, 0.081 ppb and 0.039 ppb for As, Sb and Se respectively. Analytical accuracy and precision were also controlled through analyses of CANMET reference material TDB-1 and USGS reference materials WMS-1 and CH-4 (Appendix 3). Gold and As are reproduced to better than 10 % accuracy for TDB-1 and better than 15 % for WMS-1 and CH-4 whilst Sb is reproduced to better than 10 % accuracy for WMS-1 and CH-4 and better than 15 % for TDB-1 (Appendix 3). Selenium is reproduced to better than 15 % for CH-4 but shows poorer accuracy for TDB-1 and WMS-1 (>15 %, Appendix 3).

Results

Based on immobile element concentrations, most volcanic, sheeted dyke and plutonic sample compositions follow the BADR series although several samples are picritic ($\text{MgO} > 30 \text{ wt.}\%$, Fig. 2, Appendix 1). Significant trace metal variation is observed between and within each rock type either due to primary magmatic variability or remobilisation during alteration. We report the average concentrations and standard deviation for each lithological unit; the range is reported when the standard deviation is higher than the average.

The fresh glasses

The 10 fresh glass samples analysed in this study have composition ranging between 2.95 wt.% and 7.91 wt.% MgO and are representative of the BADR series. The bulk of the samples have a basaltic-andesitic composition ($n=8$; 52-57 wt.% SiO_2 , Appendix 1), with one basalt (52 wt.% SiO_2), and one andesite (60 wt.% SiO_2 ; Appendix 1). The concentrations of Zn, As and Sb increase systematically from basaltic to andesitic composition ranging between 55-100 ppm, 359-1520 ppb and 25-150 ppb respectively (Appendix 1). The basaltic-andesite samples have the highest Cu, Se and Au concentrations ($96 \pm 36 \text{ ppm}$, $120 \pm 61 \text{ ppb}$ and $2.1 \pm 1.0 \text{ ppb}$ respectively) whereas the andesitic sample shows the lowest concentrations (29 ppm, 69 ppb and 0.77 ppb respectively; Appendix 1). One fresh glass sample shows anomalously high Au concentration (24 ppb) although a more realistic value of 2.2 ppb can be calculated from the Au/Se correlation ($R^2=0.62$). This latter value, however, is not used in calculations.

The volcanic section

Of the 26 whole rock samples from the volcanic section, 23 samples follow the BADR series and 3 are picritic. Significant variation occurs in the volcanic section samples due to the different styles of alteration (Table 2). Samples altered by low temperature fluid circulation show slightly lower average concentrations of Au, As, Sb, Se, Cu and Pb and higher Zn concentration than fresh glass samples (Table 2). Samples from alteration halos in the vicinity of mineralised zones, which contain variable amount of

secondary sulphides, have the highest Se, Cu, Zn and Pb concentrations (170 ± 130 ppb; 162 ppm, 4.8-1200 ppm; 120 ± 110 ppm and 5.0 ppm, 0.28-23 ppm respectively) and also high As, Sb (Table 2). Although a few samples show relative high Au content (>2 ppb, $n=3$), samples from alteration halos in the vicinity of mineralised zones are not systematically enriched in Au relative to the other alteration types (Table 2). Only one sample affected by seafloor weathering alteration has been analysed in this study (TVS-033-KA) and shows the highest CaO, K₂O, As and Sb concentrations in the volcanic section and high LOI (23.5 wt.%, 5.4 wt.%, 6.5 ppm, 230 ppb and 15.5 % respectively, Table 2 and Appendix 1). The other metals have concentrations within the range of the low temperature altered samples. Picritic samples have similar compositions to the BADR background altered samples for all metals except Au, which has significantly higher concentrations in the picrites (2.0 ± 0.2 ppb). This value is similar to Au analyses of fresh boninites reported by Hamelyn et al. (1984; 1.9 ± 1.9 ppb). Picrite Se concentrations (97 ± 72 ppb) are in the same order of magnitude than that reported by Hamelyn et al. (1985) for boninites (53 ± 55 ppb).

The lower sheeted dyke complex

The major element compositions of the sheeted dyke samples are controlled by the secondary mineral assemblages (Richardson et al., 1987; Jowitt et al., 2012). Increase of modal epidote relative to chlorite and amphibole leads to higher SiO₂ and CaO, and lower MgO, Na₂O and K₂O (Jowitt et al., 2012; Table 2). The average concentrations of Au (0.28 ppb, 0.07-3.7 ppb), As (100 ± 64 ppb), Sb (36 ± 12 ppb), Se (27 ppb, 0.8-430 ppb), Cu (24 ppm, 0.60-226 ppm), Zn (42 ± 33 ppm) and Pb (0.97 ppm, 0.10-6.9 ppm) in the sheeted dyke samples are significantly lower than in the volcanic section and fresh glass samples (Table 2). Strongly chalcophile elements (Au, Se and Cu; e.g. Peach et al., 1990; Li et al., 2012; Patten et al., 2013) and Pb show large variations (Table 2) due to a small number of samples with higher concentrations. These anomalies are likely due to the presence of specific secondary minerals such as pyrite. Concentrations of Au, related elements and base metals are generally similar in all types of alteration but subtle differences may still be observed. End-member epidosite samples show the lowest concentrations of Au (0.18 ± 0.02 ppb), Sb (27 ± 16 ppb), Se (7.8 ppb, 1.6-24 ppb), Cu (10 ppm, 2.7-36 ppm) and Zn ($19 \pm$

10 ppm; Table 2). Diabase samples from outside epidosite zones show similar metal contents to those within epidosite zones.

Plutonic complex and ultramafics

Differences in the major element compositions between the gabbros and the plagiogranites are shown in Table 2. Metal concentrations in the plutonic samples are overall higher than those in the lower sheeted dyke section but lower than in the volcanic section. Concentrations of Au, As, Se, Cu and Zn are higher in the gabbros (1.3 ± 1.3 ppb; 130 ± 45 ppb; 94 ± 73 ppb; 70 ± 37 ppm; 40 ± 8.0 ppm respectively) than in the plagiogranites (0.19 ± 0.06 ppb; 110 ± 51 ppb; 48 ± 35 ppb; 4.8 ± 2.5 ppm; 26 ppm, 0.8-57 ppm respectively). Conversely, Sb and Pb show higher concentrations in the plagiogranites (40 ± 8.0 ppb and 0.54 ± 0.30 ppm respectively) than the gabbros (23 ± 11 ppb and 0.54 ± 0.30 ppm respectively, Table 2). Gabbros and plagiogranites show variable degrees of alteration from background altered to partially epidotised with varying proportions of chlorite, epidote and quartz, which most likely caused metal mobility but insufficient samples have been analysed to determine it. Agiorgitis and Becher (1979) reported Au concentrations of 0.77 ± 0.05 ppb and 1.4 ± 0.1 ppb for a Troodos olivine gabbro and a bronzite gabbro respectively, which are in the same range than the average gabbro value from this study (1.3 ± 1.3 ppb). Ultramafic samples from the mantle sequence have lower Au (0.33 ± 0.26 ppb), As (100 ± 55 ppb), Sb (22 ± 5.0 ppb), Se (33 ± 31 ppb), Cu (13 ppm, 2.1-41 ppm) and Pb (0.39 ± 0.06 ppm) concentrations than the gabbros (Table 2). Only Zn shows higher concentrations (47 ± 6 ppb; Table 2). The average Au concentration in ultramafic rocks (0.19 ± 0.08 ppb) is of the same order of magnitude as a single data reported by Agiorgitis and Becker (1979; 0.52 ± 0.1 ppb).

Discussion

Composition of the primitive crust at Troodos

Since Myashiro (1973) highlighted the arc-related nature of the Troodos ophiolite, the primitive crustal composition has been extensively investigated using fresh glass samples (Rautenschlein et al., 1985; Hamlyn et al., 1985; Flower and Levin, 1987; Mehegan et al., 1988; Muenow et al., 1990; Bednarz et al., 1994; Portnyagin et al., 1997; Jowitt et al. 2012; Appendix 4). It is now accepted that Troodos ophiolite formed in a supra-subduction setting probably during subduction initiation (e.g. Pearce and Robinson, 2010). Subduction and release of aqueous fluids has a profound impact on geochemistry and melt generation in the mantle wedge (e.g. Pearce 1982; Pearce and Peate, 1995), and generates significantly different magma compositions compared to MORB. The Manus and Lau basins have been suggested to represent modern-day supra-subduction oceanic crust analogues to the Troodos ophiolite (Pearce and Robinson, 2010). Fresh glass compositions from different arc-related environments normalised to MORB values show that the Troodos ophiolite and the Manus basin have similar metal abundances, whereas the Lau basin shows metal contents closer to MORB composition (Fig. 3). The Troodos ophiolite and the Manus basin are significantly enriched in As, Sb and Pb relative to MORB (Fig. 3), most likely due to contamination of the mantle wedge by direct input from the subducting slab, either from the sediments or the altered crust (Pearce and Peate, 1995; Noll et al., 1996; Hattori et al., 2005; Richards, 2011; Timm et al., 2012; Hattori and Guillot, 2013; Regelous et al., 2014). Gold concentrations in the Troodos ophiolite (0.77-4.20 ppb; Appendix 1) are within the range of MORB compositions (0.2-5.8 ppb; Jenner et al., 2010) indicating that Au may not be strongly mobilised by slab contamination (Fig. 3). Copper and Zinc concentrations in the different arc settings are similar to those of MORB suggesting that these elements are not released from the slab during subduction (Fig. 3). Finally Se shows lower concentrations in the Troodos ophiolite (119 ± 53 ppb) relative to MORB range (243-723 ppb; Jenner et al., 2010) suggesting a depleted mantle source (Fig. 3).

After the onset of mantle melting, the composition of the magma generated is controlled by differentiation caused by fractional crystallisation in the lower crust. The fresh glass samples in the Troodos ophiolite that represent the melts which migrated upwards after differentiation, range from around 9 wt.% MgO for the most primitive compositions to < 1 wt.% MgO for the most fractionated (Fig. 4). The supra-subduction affinity of the Troodos ophiolite is highlighted by the covariation of TiO₂ and MgO, which is characteristic of the BADR series (Fig. 4; Pearce and Robinson, 2010). During magmatic differentiation the TiO₂ concentration gradually increases until around 3.5 wt.% MgO, where magnetite crystallisation occurs leading to a subsequent plateau and rapid decrease in TiO₂ as differentiation continues (Fig. 4; Pearce and Robinson, 2010; Regelous et al., 2014). The magmatic evolution of the Troodos BADR series can be divided into a first pre-magnetite crystallisation stage (9-3.5 wt.% MgO) and a second post-magnetite crystallisation stage (3.5-<1 wt.% MgO). Similar trends can be observed in the Manus Basin data that plots within the BADR field, and to some degree in the Lau Basin data although due to the higher TiO₂ contents these samples plot in the MORB field (Fig. 4). The crystallisation of magnetite has a strong effect on the behaviour of S and the other metals.

Behaviour of S in the primitive crust

Most of the base metals, Au and related elements are chalcophile elements and are affected by sulphide segregation during magmatic differentiation (e.g. Peach et al., 1990; Barnes and Lightfoot, 2005; Jowitt, 2009; Jenner et al., 2010; Patten et al, 2013). It is thus necessary to understand the behaviour of S during magmatic differentiation of the primitive crust at Troodos and the possible implications on metal distribution. Within the BADR series, S shows a similar trend to TiO₂ during differentiation with incompatible behaviour during the first stage (9-3.5 wt.% MgO) and compatible behaviour during the second stage (3.5-<1 wt.% MgO, Fig. 4; Jowitt, 2009). The average S concentration in Troodos BADR series fresh glasses (Table 3; 459 ± 311 ppm; Muenow et al., 1990; Bednarz et al., 1994; Jowitt, 2009) is within the range estimated by Alt (1994) for primary magmatic values (200-930 ppm). The incompatible behaviour of S during the first stage of magmatic differentiation suggests that most of S is preserved in the

melt. The sudden drop of S at MgO values of around 3.5 wt.% indicates that at this stage of differentiation S starts to be efficiently removed from the melt. The two most likely processes to remove S from the melt are 1) sulphide saturation and 2) magmatic degassing (Kamenetsky et al., 2001; Yang and Scott, 2002; Sun et al., 2004; Jenner et al., 2010; 2012; 2015; Park et al., 2015; Sun et al., 2015).

Arc-related magmas have high oxygen fugacity inherited from their mantle source, which has been oxidised by fluids from the subducting slab, with S present as sulphate rather than sulphide (e.g. Mungall, 2002; Wallace and Edmonds, 2011; Richards, 2011; Richards, 2015). In Troodos ophiolite the oxygen fugacity averages FMQ +1.5 compared to MORB (FMQ = 0; Coogan et al., 2003). Jugo (2009) calculated that the sulphur content at sulphide saturation (SCSS) for arc-related magmas with $\text{FMQ} + 0.5 < f\text{O}_2 < \text{FMQ} + 1.7$ should have a SCSS between 1500 and 4500 ppm S. Using Bednarz et al. (1994) fresh glass data and the Liu et al. (2007) method, the SCSS is calculated for the Troodos ophiolite (Fig. 4). The Liu et al. (2007) method is appropriate for Troodos SCSS calculation as it predicts the SCSS in melts with a large composition range, high water content (up to 9 wt.% H_2O) and high $f\text{O}_2$ (up to FMQ+2). The liquidus temperatures used for the calculation are estimated using the PELE 7.3 algorithm (Boudreau, 1999) and a pressure of 887 bar (assuming 3.5 km water depth; Keith et al., 2016; and a magmatic chamber at 2 km extrapolated from CY1, CY1A and CY4 drill cores; e.g. Vine and Smith, 1990; Alt, 1994). The SCSS calculated ranges between 437 ppm and 1071 ppm S, which is below the range estimated for arc-related magmas by Jugo (2009) but higher than most of the S concentrations in the fresh glasses (Fig. 4) and within the range estimated by Alt et al. (1994; 200-1000 ppm S). During the first stage of magmatic differentiation the S concentration is lower than the SCSS, but as S is concentrated in the melt it eventually crosses the SCSS at MgO values of ~4-3.5 wt.% MgO (Fig. 4) concomitant with magnetite crystallisation. This would cause sulphide segregation which would remove S from the melt during the second stage of magmatic differentiation (Fig. 4). Despite the generally sulphide under-saturated nature of Troodos magma, primary magmatic sulphides are reported (Alt, 1994) in the sheeted dykes and gabbros. Only one fresh gabbro sample (10.8 wt.% MgO) from this study hosts unequivocal primary magmatic sulphides characterised by partially

leached pyrrhotite with pentlandite exsolution and chalcopyrite (e.g. Peach et al., 1990; Patten et al., 2012; Fig. 5). This suggests that in general the Troodos magma was sulphide under-saturated (Jowitt, 2009), but that locally sulphide saturation was reached. This is also supported by the compositions of a few glass samples which have S contents higher than the SCSS during the first stage of magmatic differentiation (Fig. 4).

In the Manus Basin, primary magmatic S (calculated using Se as a proxy; Jenner et al. 2010) shows similar behaviour to that observed in Troodos, with incompatible behaviour until ~3 wt.% MgO, after which S concentrations significantly decrease (Fig. 4). In the Manus Basin this has been interpreted to be caused by magnetite crystallisation, which causes a significant decrease in the fO_2 of the magma, triggering sulphur reduction. Sulphur reduction leads either to sulphide saturation and segregation of a sulphide phase (Jenner et al., 2010; 2012; 2015; Park et al, 2015) or the exsolution of hydrosulphide complexes in cogenetic magmatic fluids (e.g. Sun et al., 2004; Sun et al., 2015). Similar processes are observed in the Lau Basin, albeit at higher MgO values of around 5 wt.% (Jenner et al., 2012).

Several lines of evidence suggest that magmatic fluid exsolution occurred in the Troodos ophiolite. High-temperature brines in fluid inclusions from late-stage gabbros and plagiogranites in Troodos suggest that magmatic fluids have exsolved during magmatic differentiation although they undergo limited migration within the plutonic rocks (Kelley et al., 1992). Additionally, negative $\delta^{34}S$ values of pyrite from the Skouriotissa VMS deposit have been interpreted as a possible signature of magmatic origin for some of the S trapped within the deposit (Keith et al., 2016). Volatile contents of fresh glass samples show that degassing of CO_2 occurs during differentiation at ~4 wt.% MgO, whereas H_2O and Cl are preserved in the magma (Fig. 6). The behaviour of S is suggested to be more similar to that of H_2O rather than CO_2 during degassing in a high temperature magma (Wallace and Edmonds, 2011), suggesting that S may be preserved in the magma despite CO_2 loss. This is distinct from the Manus basin where both degassing of CO_2 and H_2O is observed (Kamenetsky et al., 2001). It is likely that some S loss occurred during magmatic degassing in the Troodos ophiolite but it is not interpreted to be the main cause for the S drop observed in fresh glass samples.

Sulphide segregation is most likely to be the main mechanism for S removal from the magma at 3 wt.% MgO in the Troodos ophiolite. The sulphide under-saturated nature of Troodos magma during the first stage and subsequent sulphide segregation during the second stage of magmatic differentiation both have important effects on the distribution of metals in the oceanic crust before initiation of hydrothermal alteration.

Metal behaviour in the primitive oceanic crust

Despite the limited number of fresh glass samples analysed in this study (n=10) the composition of the primitive crust at Troodos for the elements of interest can be investigated using previously published data and modern-day analogues. Like S, the strongly chalcophile elements Cu, Au and Se show incompatible behaviour during the first stage of magmatic differentiation in the Troodos samples, followed by compatible behaviour during the second stage (Figs. 4 and 7). In the case of Cu, the change in behaviour occurs at ~4 wt.% MgO rather than 3.5 wt.% MgO, but this is assumed to be within error of magnetite crystallisation and associated to sulphide segregation. Of the samples analysed for Au and Se, only one sample has an MgO value below 3.5 wt.% but low concentrations for both Au and Se in this sample point to a decrease in concentrations of these elements after sulphide segregation. Strongly chalcophile elements (Au, Se and Cu) show strikingly similar behaviour in the Manus Basin where the drop in Cu, Au and Se concentrations match those of S and TiO₂ at 3 wt.% MgO (Fig. 7; Jenner et al., 2010). The decrease in concentrations of these elements has been attributed both to volatile loss (Kamenetsky et al., 2001; Yang and Scott, 2002; Sun et al., 2004; Sun et al., 2015) and to sulphide segregation (Jenner et al., 2010; Jenner et al., 2012; Jenner et al., 2015). The poorly chalcophile elements Zn, Pb, As and Sb are incompatible throughout magmatic differentiation in Troodos suggesting that they are not significantly affected by magnetite and sulphide segregation. Their behaviour in the Manus Basin and the Lau Basin is similar except for Zn in the Manus Basin which shows weak compatibility during the second stage of magmatic differentiation (Fig. 7).

Because of the sulphide under-saturated nature of the magma in the Troodos ophiolite, Cu, Au and Se behave as incompatible elements during the first stages of magmatic differentiation. The highest

concentrations of these metals occurs immediately prior to magnetite and sulphide segregation at 3.5-5 wt.% MgO (basalt-andesite). This is clearly distinct from MORB, where the highest concentrations of these metals occur in more mafic magma (e.g. Jenner et al., 2010; Jenner et al., 2012). During the second stage of magmatic differentiation (andesite-dacite), Troodos magmas have lower Cu concentrations, and also most likely lower Au and Se concentrations, but higher Zn, As, Sb and Pb concentrations (Fig. 4 and 7). The metal behaviour during magmatic differentiation described above shows that the quantities of different metals available for hydrothermal fluid mobilisation is strongly controlled by the primary magmatic composition.

Mass variation

The systematic changes in metal concentrations in the different rock types and alteration zones of the Troodos ophiolite indicates that significant metal mobilisation has occurred. To quantify mobilisation, whole rock values are compared to the primitive crustal compositions determined from fresh glass samples. Mass variations between samples from the volcanic section and the sheeted dyke complex are calculated. The plutonic complex cannot be included in the mass balance as these samples are the crystallised residue of magmatic differentiation and are thus not directly comparable to the fresh glass samples that represent the extracted melt. To observe the primary magmatic composition of the samples, Y is used rather than MgO and TiO₂, as Y has been shown to be immobile during hydrothermal alteration and unaffected by magnetite crystallisation during magmatic differentiation (Figure 7; Jowitt et al., 2012; Patten et al., 2015). A series of differentiation curves have been determined for each element during magmatic differentiation (Jowitt et al., 2012):

$$E_e = AY^B \quad [1]$$

where E_e is the estimated element concentration for a given Y concentration and A and B are regression coefficients (Appendix 5). For elements showing a change in behaviour during magmatic

differentiation (Ti, S, Cu, Zn, Au and Se) two differentiation curves are determined (Appendix 5). Due to lack of fresh glass samples below 3.5 wt.% MgO, Au and Se differentiation trends below this value are extrapolated from the Manus Basin samples (Appendix 5). The error associated between the fresh glass data and the differentiation curves is determined using the root mean square deviation (RMSD, Appendix 5; Jowitt et al., 2012):

$$RMSD = \sqrt{\Sigma(Ec - Em)^2/n} \quad [2]$$

with E_c the calculated element concentration, E_m the measured element concentration and n the number of values used to calculate the differentiation curves. Mass variations are estimated from the deviation of a sample from the differentiation curves (Jowitt et al., 2012):

$$\% \text{ Variation} = (E_s - E_e) / E_e * 100 \quad [3]$$

where E_s is the measured value and E_e the estimated primary crust composition from equation [1]. Mass variations assume minor absolute mass change during the different styles of hydrothermal alteration that occurred in the Troodos ophiolite and that the primary Y concentrations have remained constant during alteration. This assumption can be evaluated using the method described in Jowitt et al. (2012), where Al_2O_3 , which is immobile during alteration but compatible during magmatic differentiation, is used as a proxy for bulk mass change. A discrepancy between the calculated Al_2O_3 concentrations and the measured ones would indicate bulk mass change. Average mass variation of Al_2O_3 is -0.02 ± 1.55 wt.% for samples from the volcanic section and the sheeted dyke complex which suggests that little absolute mass variation occurred in these units during the different alteration stages and it has minimal effect on the metal budget (Appendix 5; Jowitt et al., 2012). The variation in the mass change value for Al_2O_3 is caused mainly by a small number of extensively silicified samples ($n=3$; Appendix 1) in the basal unit of the volcanic section.

Mass variation in the volcanic section

The volcanic section has been affected by multiple styles and generations of alteration (e.g. Gillis and Robinson, 1990). The mobility of metals relative to each type of alteration can be estimated, but accuracy is limited by low sample numbers in some alteration types. The only sample altered by seafloor weathering has the highest As, K₂O and Rb concentrations of the volcanic section (6.47 ppm, 5.4 wt.% and 35.6 ppm respectively) and shows high Sb and Cs concentrations (236 ppb and 385 ppb respectively). These values are significantly higher than those of fresh glasses (Table 2). This is comparable to the modern day oceanic crust where K₂O, Rb and Cs (Berdnarz and Schminke, 1989; Gills and Robinson, 1990; Staudigel, 2003) as well as As and Sb (Patten et al. 2015) are known to be enriched in the volcanic section during seafloor weathering. In the low temperature altered samples, concentrations of Au and related elements are of the same order of magnitude as that of fresh glass (Table 2), suggesting little bulk mobilisation although the larger range in concentrations indicates local remobilisation has occurred. Within altered samples proximal to mineralisation, significant enrichment of metals occurs. Variations in the metal contents in these samples are most likely due to variations in the extent and conditions of alteration within this group of samples. In summary, the mobilisation of metals in the bulk of the volcanic section is relatively limited. Exceptions include enrichments in As and Sb during seafloor weathering and metal enrichment in alteration halos proximal to mineralised zones.

Mass variation in the lower sheeted dyke section

Epidosite zones

Mobility of metals from the lower sheeted dyke section is significant in both epidosite zones and background altered diabase (Fig. 8). From the Spilia epidosite zone, Jowitt et al. (2012) estimated relative proportions of each sub-class of epidosite alteration with 24 % diabase, 24 % transitional diabase-epidosite, 39 % intermediate epidosite and 13 % end-member epidosite. Assuming the same proportions for a hypothetical epidosite zone, the metal depletions are -88±16 % Au, -89±23 % As, -60±12 % Sb, -91±20 % Se, -84±18 % Cu, -63±9 % Zn and -60±8 % Pb (Table 4). These degrees of depletion are significantly higher

than those from modern-day fast-spreading ridge oceanic crust where epidosite zones are not encountered and depletions do not exceed 50 % (ODP Hole 1256D, Patten et al., 2015). Although mass variation calculation for altered plutonic rocks cannot be properly constrained, three epidotised plagiogranites show significant depletions of over 60 % for all the elements of interest. The metals show differences in degrees of mobility between the different alteration sub-groups within the epidosite zones. Strongly chalcophile elements (Au, Cu and Se) are overall more strongly depleted (>85 %) than poorly chalcophile elements (Sb, Zn and Pb; e.g. Peach et al., 1990; Li et al., 2012; Patten et al., 2013) that show less than 70% depletion. These differences are a function of the different host minerals and the effects of secondary mineralogy. Because of the sulphide under-saturated nature of the magma during the first stage of magmatic differentiation, the strongly chalcophile elements in fresh dykes are likely distributed within rare sulphide blebs and in the silicate matrix (see below). The highly reactive response of these phases to high temperature alteration, leads to efficient metal mobilisation and depletions of over 85 %. Rare secondary sulphides are observed in sheeted dykes within epidosite zones indicating sulphide precipitation during the waning stage of hydrothermal fluid circulation possibly explaining why some samples are less depleted in metals. The poorly chalcophile elements, Sb, Zn and Pb are most likely hosted by silicate or oxide minerals (e.g. Doe, 1994; Jowitt et al., 2012; Patten et al., sub), which are less reactive to alteration than the rare sulphide blebs and silicate matrix, possibly explaining the lower depletions of these elements. The degree of metal depletion is also partly controlled by the extent to which metals can be incorporated into the secondary minerals. For example Zn, Ni and Mn that are less strongly mobilised have been shown to be hosted in chlorite and amphibole (Jowitt et al., 2012). Where these two minerals are more abundant, such as in the diabase and transitional diabase-epidosites, Zn and also Sb depletions are less strong (Table 4; Jowitt et al., 2012). Arsenic is also poorly chalcophile but it is very strongly depleted possibly due to its highly mobile nature during rock alteration (see previously; Noll et al., 1996; Hattori et al., 2005; Hattori and Guillot, 2013; Patten et al., 2015) and limited incorporation into secondary minerals.

Background altered diabase

Mass variations of Au and related elements in background altered diabase from outside the epidosite zones is similar to those in the diabase within epidosite zones (Table 4). This indicates that mobilisation of Au and related elements is not restricted to epidosite zones but occurs throughout the lower sheeted dyke section. Significant loss of S (Alt, 1994) and Cu (Baragar et al. 1989) from the lower sheeted dyke complex of Hole CY-4, which recovers background altered diabases, are in agreement with the mobilisation of metals throughout the lower sheeted dyke section. Significant metal mobility has also been reported from the lower sheeted dyke section in the modern-day oceanic crust where significant epidosite alteration has not been observed (e.g. ODP Hole 504B, Alt et al., 1989; ODP Hole 1256D, Alt et al., 2010; Patten et al., 2015). Jowitt (2009) argues that unlike the epidosite zones, metal depletion in background altered diabase is not systematic as localised metal redistribution occurs within the sheeted dyke complex. Metals are locally enriched in the upper sheeted dykes and transitional zone in Troodos (Alt, 1994), as is observed in the modern-day oceanic crust (e.g. Alt et al., 1989; Teagle et al., 2006; Alt et al., 2010; Patten et al., 2015), but the extent of this mineralisation is minor in comparison to the degree of depletions from the lower sheeted dyke complex. We suggest that due to the large volume of these rocks and the degree to which they are depleted in metals, the background altered diabase represents an equally important source of metals as the epidosite zones.

Formation of VMS deposits in the Solea Graben

The Solea graben is an extensively studied locality that provides a unique overview of the link between source areas and associated ore deposits (Varga and Moores, 1985; Richardson et al., 1987; Schiffman et al., 1987; Schiffman and Smith, 1988; Bettison-Varga et al., 1992). It is characterised by a north-northwest trending graben axis and is bounded by sedimentary cover to the north and by the plutonic section to the south (Fig. 1; e.g. Granot et al., 2006; Adamides, 2010a). The Solea graben hosts some of the largest VMS deposits of Troodos ophiolite such as the Skourioatissa, Apliki and Mavrovouni deposits (Table 1; e.g. Adamides, 2010a). Within the sheeted dyke complex, three epidosite zones are recognised

with the largest in the lower to middle part of the sheeted dyke complex covering an area of 25 km² (Schiffman et al., 1987; Richardson et al., 1987; Schiffman and Smith, 1988; Bettison-Varga et al., 1992). Within this central epidosite zone two areas of 8 km² are pervasively altered to epidosite (Bettison-Varga et al., 1992). The two others epidosite zones are smaller, occurring at the base of the sheeted dyke complex in contact with the plutonic complex and at the top of the sheeted dyke complex (Bettison-Varga et al. 1992). Both the ore deposits and the epidosite zones occur to the west of the Solea graben axis (Schiffman and Smith, 1985). Ore deposits within the Solea graben occur within a surface area of ~17.5 km² (5 x 3.5 km²; Adamides, 2010a). Assuming a section of the oceanic crust of similar surface area and 2 km depth for the volcanic section and the sheeted dyke complex (extrapolated from CY-1, CY-1A and CY-4; Malpas and Williams, 1991), a simplified hydrothermal cell system within the Solea graben can be modelled and the metal mobility quantified (Fig. 9). The source area of the Solea graben VMS deposits is interpreted as both the epidosite zone and the background altered diabase within the lower sheeted dyke section. Assuming a thickness of 625 m for the lower sheeted dyke section (half of the sheeted dyke complex estimated at ~1250 m thick; Alt, 1994; Vine and Smith, 1990) the total volume of the source area in the Solea graben is 10.9 km³. Using a surface area of 8 km² for the epidosite zones (Bettison-Varga et al., 1992) and a thickness of 625 m, the volume of the epidosite zone is 5 km³. The volume of the background altered diabase is calculated to be the total volume of the lower sheeted dyke section minus the volume of the epidosite zone, which is 5.9 km³ (Fig. 9). Quantities of metals mobilised from these volumes are calculated using the metal depletions shown in Table 4. The mass balance shows that 47±9 t Au, 21±5 kt As, 1200±200 t Sb, 3100±700 t Se, 2.3±0.5 Mt Cu, 1.8±0.25 Mt Zn and 27±4 kt Pb has been removed from the 10.9 km³ altered source area in the Solea graben (Table 5). It should be emphasised that these calculations are made for a simplified hydrothermal cell system and they are an estimate of the actual mass of metal mobilised.

Comparing available data for tonnages of Au and related elements in the Solea graben VMS deposits (Table 1), with the quantity of metal mobilised from the lower sheeted dyke complex allows estimation of metal trapping efficiencies (Table 5). However, the accuracy of these trapping efficiencies, is poor due to

the limited constraints on the Au and related element concentrations in the VMS deposits (Table 1). Gold, As, Se and Cu show moderate trapping efficiencies within VMS deposits (~10-35 %) whereas <10 % of Zn and Sb are trapped. These trapping efficiencies are higher than those determined for fast spreading mid-oceanic ridge VMS deposits for which <1 % of the metals mobilised from the lower oceanic crust are trapped as VMS deposits (Patten et al., 2015). These differences in trapping efficiency are either due to better trapping mechanisms or to an underestimation of the source area size. Ohmoto (1996) estimated a source area for Kuroko-type VMS deposits of 40 km³ which is significantly larger than the one estimated in this study (10.9 km³). It is important to emphasise that the majority of the mobilised metal is lost from the system. Several mechanisms can lead to poor metal trapping in VMS deposits, such as early metal precipitation as fluids rise, unfocused fluid discharge, off-axis metal mobilisation, poor trapping efficiency during mineralisation and metal mobilisation during VMS seafloor weathering. The bulk of metal that is not trapped in VMS deposits is likely vented in the hydrothermal plume either then precipitating as fine grained sediments such as umber, or being released into seawater. Metal bearing umbers are common in the Troodos ophiolite (Herzig et al., 1991; Prichard and Maliotis, 1998), some of have been enriched in Au during late-stage off axis silicification (Prichard and Maliotis, 1998). Zone refining and seafloor weathering of VMS deposits has an important impact on metal redistribution within VMS deposits (e.g. Phoenix deposits; Herzig et al., 1991; Adamides et al., 2010a; Keith et al., 2016). The Cu grade of the Phoenix deposit (0.5 wt.% Cu), which formed by seafloor weathering, is lower than that of the parent Skouriotissa deposit (Adamides et al., 2010a), suggesting that Cu might have been lost during zone refining and/or seafloor weathering (Table 1). Finally, loss of metals during transport from the source area to the surface can occur by formation of mineralised zones as observed mostly in the volcanic section but also in the upper sheeted dyke section (Fig. 8, e.g. Gillis and Robinson, 1988). The main implication from the mass balance of metal mobilisation in the Solea graben is that large masses of metal are mobilised in the lower sheeted section from both epidosite zones and background altered diabase, and although a significant portion of the metals mobilised at depth is trapped as VMS deposits, most is lost by several other processes.

The role of primitive crustal composition in the formation of VMS deposits

The quantity of metal available for mobilisation during hydrothermal alteration of a supra-subduction oceanic crust is strongly controlled by its primary composition. Strongly chalcophile metal concentrations (Au, Cu and Se) in the primary crust are at their maximum at around 3-5 wt.% MgO just before magnetite crystallisation and S reduction, and therefore crust of this composition has high fertility for these metals (Fig. 10). Crust with compositions below 3-3.5 wt.% MgO, however, has much lower fertility for these metals but high fertility for poorly chalcophile metals (As, Sb, Zn and Pb; Fig. 10). In the Troodos ophiolite, fresh glass compositions (median MgO = 4.3 wt.%) indicate good potential metal fertility, especially for strongly chalcophile metals (Fig. 10). The source areas in the altered lower sheeted dyke section shows slightly more mafic composition (median = 4.9 wt.% MgO) but similar metal fertility (Fig. 10). The masses of metals mobilised from the lower sheeted dykes in Troodos are significantly higher than the extent of metal mobilisation in the modern day oceanic crust such as at ODP Hole 1256D (e.g. Patten et al. 2015). This is likely a combination of high metal fertility in the source area, the sulphur undersaturated nature of the Troodos crust as the bulk of chalcophile metals most likely sit in rare sulphides and the glassy matrix which can be efficiently recrystallised, and also the larger time-integrated hydrothermal fluid fluxes (Bickle and Teagle, 1992; Alt and Teagle, 2000).

The composition of the Troodos VMS deposits is a function of the composition of the source area and the water depth at the time of formation. In Troodos, the VMS deposits are Cu-rich but Zn-Pb poor (Table 1, Hannington et al., 1998) which can be explained by the composition of the source area which has higher fertility for strongly chalcophile elements Cu, Se and Au compared to poorly chalcophile elements As, Sb, Zn and Pb. The source area compositional control is highlighted through comparison with the Manus basin where the VMS deposits are Zn-Pb-As rich but Cu poor (Herzig et al., 1993; Herzig and Hannington et al., 1995; Beaudoin et al., 2007), and the hypothetical lower sheeted dyke reaction zones likely have MgO concentrations below 3-3.5 wt.% indicating poor fertility for strongly chalcophile metals but high fertility for poorly chalcophile metals (Fig. 10). Deep water depth is has also been suggested to promote

development of Cu-rich VMS deposits (Monecke et al. 2014). Based on sediment records the water depth during formation of the Troodos deposits is suggested to be ~3500 m (Keith et al., 2016), which would enhance the development of Cu-rich affinity.

Gold enrichment during formation of VMS deposits has been suggested to occur through three main processes; 1) addition of magmatic volatiles (Urabe et al., 1987; Stanton, 1990; Yang and Scott, 1996; Sillitoe et al., 1996; Kamenetsky et al., 2001; Moss et al., 2001; Yang and Scott, 2002), 2) vapour separation by sub-seafloor boiling (Urabe et al., 1987; Huston and Large, 1989; Butterfield et al., 1990; Poulsen and Hannington, 1996; Hannington, 1999), and 3) higher Au budget in source area rocks in arc related settings (Huston, 2000; Moss et al., 2001; Herrington et al., 2011; Pitcairn, 2011). This study shows that the Troodos crust has high Au budget as the Au content of the source area rocks and the mass of Au mobilised during alteration is significantly higher than those of MORB settings (Patten et al., 2015). However, the mass of base metals mobilised is also higher and therefore the Au : base metal ratio of mobilised metals in Troodos is similar to that observed in MORB. Additional processes such as addition of magmatic volatiles and or sub-seafloor boiling would be required to enrich Au by an order of magnitude relative to the base metals to reach the Au grade of Au-rich VMS deposits (Fig. 11). The relatively limited Au enrichment in the Troodos VMS deposits suggests that these additional processes were irregularly active if not absent. Sub-seafloor boiling and phase separation of hydrothermal fluids have occurred in Troodos ophiolite (Cowan and Cann, 1988; Jowitt et al., 2005) but the water depth (~3.5 km; Keith et al., 2016) most likely limited the extent and therefore the impact on VMS deposits formation. Comparison with the Manus Basin also indicates that the composition of the source rock is not the major control on development of Au-rich VMS deposits. Gold-rich deposits are common in the Manus basin (PACMANUS hydrothermal field; e.g. Herzig et al., 1993; Herzig and Hannington et al., 1995; Moss et al., 2001; Ihle et al., 2005) despite the assumed poor Au fertility of the hypothetical lower sheeted dyke section (Fig. 9). The Au : base metal ratio in the hypothetical source area of the Manus Basin is in fact even lower than in the Troodos ophiolite (Fig. 10), yet Au-rich VMS mineralisation is far more common. Although there is evidence for boiling of hydrothermal fluids at vent

sites in the Manus Basin (PACMANUS; Barriga et al., 2007) the Au enrichment in this area is most likely a product of addition of magmatic volatiles to the hydrothermal system (Moss et al., 2001; Kamenetsky et al., 2001; Yang and Scott, 2002; Sun et al., 2004; Sun et al., 2015). Mungall et al. (2015) suggested that gas bubbles can act as carriers for sulphide droplets in degassing arc magmas. Such process would enable efficient metal mobilisation from the magma to the hydrothermal system during degassing despite possible sulphide segregation in the Manus Basin (Jenner et al., 2010; 2012; 2015; Park et al, 2015).

Conclusions

The major outcomes of this study are:

- The Troodos ophiolite shows clear subduction affinity with strong enrichments of As, Sb and Pb relative to MORB due to slab contamination. Gold contents in the Troodos ophiolitic fresh glasses (1.9 ± 1.0 ppb Au) are slightly higher but within the range of MORB values (1.2 ppb, Arevalo and MacDonough, 2010; 1.52 ± 1.21 , Jenner et al., 2012).
- The Troodos primitive crust is sulphide-undersaturated during the first stage of magmatic differentiation (9-3.5 wt.% MgO) until magnetite crystallisation occurs. In Troodos, magnetite crystallisation is interpreted to trigger sulphide saturation rather than exsolution of hydrosulphide complexes in magmatic fluids. Strongly chalcophile elements, such as Cu, Se and Au, therefore behave as incompatible elements during the first stages of magmatic differentiation and have their maximum concentrations just prior to magnetite crystallisation. Their concentrations in the melt decrease drastically after sulphide segregation. Poorly chalcophile elements, such as Zn, As, Sb and Pb are not affected by magnetite crystallisation and sulphide segregation, and behave as incompatible elements throughout whole magmatic differentiation.
- Mobilisation of metals during hydrothermal alteration of the Troodos ophiolite is extremely extensive. Percentage depletions of metals from epidosite zones range from 60% for Pb up to 90% for Se. These

depletions are considerably higher than depletion observed in hydrothermally altered MORB (Patten et al., 2015), albeit with the proviso that the mid-ocean ridge equivalents of epidiosites have not yet been sampled.

- Element mobility in Troodos is not limited to epidiosite zones and strong metal depletions also occur in background altered diabase (from -58 % for Pb to -90 % for Se) outside epidiosite zones in the lower sheeted dyke section. This implies that source areas of Troodos VMS deposits are most likely not solely restricted to the epidiosite zones but could be enlarged to the lower sheeted dyke section.
- The masses of metals mobilised from a source area of 10.9 km³, (composed of a 5 km³ epidiosite zone and 5.9 km³ of background altered diabase) in the Solea graben are 47 t Au, 21 kt As, 1220 t Sb, 3080 t Se, 2.4 Mt Cu, 1.8 Mt Zn and 27 kt Pb. The proportions of these metals trapped in the VMS deposits in the Solea Graben are estimated to range from 4 % for Zn up to 37% for Cu, indicating that most of the metals mobilised by hydrothermal circulation are not trapped in the large VMS deposits but are lost by several other processes.
- The composition of the source area exerts strong control on the composition of the VMS deposits. In Troodos, the high source area fertility for Cu is most likely a major control on the Cu-rich affinity of these deposits. However, the source area composition does not appear to control the development of Au-rich VMS deposits as a significant increase in the Au to base metal ratio would be required to produce an Au-rich VMS deposit. The most likely causes of Au enrichment are sub-seafloor boiling or addition of Au enriched magmatic volatiles.

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Figure captions

Figure 1: Geological map of the Troodos ophiolite. The main epidosite zones, Au-bearing VMS deposits and Au-rich umbers are displayed. Modified from Cyprus Geological Survey Mineral Resources Map of Cyprus (2007), Bickle and Teagle (1992), Bettison-Varga et al. (1992), Prichard and Maliotis (1998), Adamides (2010), Jowitt (2009) and Osozawa et al. (2012).

Figure 2: Immobile element diagram of the samples investigated in this study. Most of the samples plot in the island arc tholeiite field except for the picritic samples and the extensively silicified samples from the basal unit. Diagram from Dilek et al. (2007) and Pearce (2003). IAT=island arc tholeiites, WPB=withinplate basalts, Bon=boninites.

Figure 3. a) Median concentration of Troodos ophiolite, Manus Basin and Lau Basin fresh glass data normalised to median MORB values from Jenner et al. (2012). The solid black line corresponds to the average MORB values determined by Arevalo and MacDonough (2010) and the grey shaded area corresponds to the MORB range determined by the upper and lower quartile of Jenner et al. (2012) database. b) Discriminant diagrams for As, Sb and Pb subduction contamination of volcanic arc mantle wedge. Modified from Pearce and Peate (1995). Troodos data are from this study and Regelous et al. (2014); MORB data are from mid-oceanic ridges and seamounts samples from Jenner et al. (2012); Manus Basin data are from Jenner et al. (2012), Sun et al. (2004, 2007); and Lau Basin data are from Jenner et al. (2012).

Figure 4. Fresh glass TiO₂, S, Cu, Zn and Pb vs MgO plots showing the magmatic differentiation trends in the Troodos ophiolite, Manus Basin and Lau Basin. The sulphur content at sulphide saturation

(SCSS) is calculated for each sample from Bednarz et al. (1994) using the Liu et al. (2007) method. Dashed red curves are the SCSS $\pm$ the root mean square deviation (RMSD). Sulphur in the Manus Basin (*S) is recalculated using Se as a proxy (Jenner et al., 2010). See text for details. Troodos data are from this study, Rautenschlein et al. (1985); Flower and Levin (1987); Mehegan (1988); Muenow et al. (1990); Bednarz et al. (1994); Portnyagin et al. (1997); Jowitt et al. (2009), Jowitt et al. (2012) and Regelous et al. (2014). Manus Basin data are from Moss et al. (2001); Sun et al. (2003); Park et al. (2010); Jenner et al. (2010); Jenner et al. (2012). Lau Basin data are from Cawood and Fryer (1994) and Jenner et al. (2012). See Appendix 4 for details about the database.

Figure 5. Primary magmatic sulphides in gabbroic sample TM-14-LE. Only one sample from this study hosts indubitably magmatic sulphide. Po = pyrrhotite, Pn = pentlandite, Cpy = chalcopyrite, Py = pyrite. The spherical shape and the pentlandite exsolutions within the pyrrhotite are characteristic features of magmatic sulphides (e.g. Patten et al., 2012). Primary magmatic sulphides are partially leached and initial limits are represented by white dashed lines. Chalcopyrite and pentlandite are more resistant to leaching than pyrrhotite. Pyrite is secondary.

Figure 6. Volatile element concentrations in Troodos fresh glass. a) CO₂ vs MgO, degassing of CO₂ at ~4 % MgO. b) and c) H₂O and Cl vs MgO, no apparent degassing of H₂O and Cl seems to occur during differentiation. Blues crosses are from Bednarz et al. (1994) and blue squares are from Regelous et al. (2014).

Figure 7. Behaviour of Au and related elements during magmatic differentiation in the Troodos ophiolite, the Manus Basin and the Lau Basin. A drop in Au and Se is observed for the Troodos ophiolite and the Manus Basin after magnetite crystallisation. Arsenic shows the lowest R² value (<2) which could be due to partial devitrification as it is a highly mobile element during low temperature seawater alteration (Patten et al., 2015). This could increase the normalised root mean square of deviation (NRMSD=21.2 %, Appendix 5). Manus Basin data are from Jenner et al. (2012) and Sun et al. (2007). Each value of Sun et al. (2007) data is the median value of three replicates instead of the average (Appendix 4). Lau Basin data from

Jenner et al. (2012). Differentiation curves for Au and Se in the Troodos ophiolite below 3.5 wt.% MgO are extrapolated from the Manus Basin data. Regression coefficients and NRMSD are given in Appendix 5. Gold value marked by * is recalculated based on Au/Se relationship, see text for details.

Figure 8. Whole rock concentrations of Au, As, Sb, Se, Cu, Zn, and Pb vs. Y. Solid black lines are calculated differentiation curves from fresh glass data shown in Figure 3 and 6 represented by the blues shaded areas; regression coefficients are given in Appendix 5. Magnetite crystallisation occurs at ~35 ppm Y. Dashed differentiation curves for Au and Se above 35 ppm Y are extrapolated from the Manus Basin dataset. Dashed differentiation curves for Cu and Zn are from Jowitt et al. (2012). Mass variation corresponds to the difference between sample whole rock values and the calculated differentiation curve. See text for details.

Figure 9. Hydrothermal system of the Solea graben. a) The source areas of the Solea graben VMS deposits are the epidosite zone and the background altered diabase. They are constrained in the lower sheeted dyke complex. Extension of the epidosite zone and of the end-member epidosites is an assumption. *For more clarity the graphical expression of depth is exaggerated by a factor 2. Upward arrows represent discharging fluids whereas downward pointing arrows represent recharge fluids. Their distribution is schematic. b) Quantity of mobilised metals from the lower sheeted dykes and percentages of metals trapped within VMS deposits or lost during mobilisation. Errors on the quantity of metal mobilised are from the mass balance calculations in Appendix 6. Errors on the percentages of metal trapped or lost are minimum estimates as the actual metal tonnage of the VMS deposits is not precisely constrained. LSDC = lower sheeted dyke complex; USDC = upper sheeted dyke complex. See text for details.

Figure 10. Cumulative frequency plots of the Troodos fresh glass, Manus Basin fresh glass and Troodos source area databases. Hypothetical cumulative frequency of the Manus Basin source area is calculated assuming as similar variation between fresh glass samples and source area samples than in Troodos ophiolite. Median values are shown and light shaded boxes represent the upper and lower quartile. Cumulative frequency plots are compared to primitive crust metal composition, the Troodos area has high

fertility for Cu, Se and Au whereas the Manus Basin hypothetical source area has high metal fertility for Zn, As, Sb and Pb. Data are referenced in Appendix 4. Troodos source area data are from this study and Jowitt (2009) and primary MgO is recalculated from Y concentration using the equation $MgO = -4.54 * Y + 49.39$. Mag cryst.= magnetite crystallisation.

Figure 11. Gold to base metal ratio of fresh glass samples from the Troodos ophiolite and the Manus Basin; Au in ppm and base metals in weight percent. Troodos data are from this study and fresh glass values of Manus Basin are from Jenner et al. (2012). Manus basin hypothetical source area has a lower Au to base metal ratio than Troodos ophiolite. Both in Troodos ophiolite and Manus Basin the Au : base metal ratio is $<<1$ and is not high enough for Au-rich VMS grade.

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Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Table 1. Gold and related elements content in Troodos VMS deposits, gossans, ochers and umbers.

	References	Tonnage (Mt)	S (%)	Cu (%)	Zn (%)	Pb (ppm)	Au (ppm)	As (ppm)	Sb (ppm)	Se (ppm)
Deposit										
Limni massive body	1	0.42		1.4			3.4			
Mavrovouni	1	15	49	3.8	0.5		0.3			
Kavalasos/Mousoulos	1	6.9	35	1	0.5	100	1.7			
Skouriotissa (Phoukasa)	1	5.4	48	2.3	0.06		0.5*			
Skouriotissa (Phoenix)	1	15		0.5						
Apliki	1	1.65	40	1.8	0.2					
West Apliki	2	3.6		0.34						
Limni	2	16	14	1	0.2					
Three Hills	2	6.2		0.37						
Memi	2	1.5	26	0.1						
Mathiatis	2	2.8	33	0.2	1					
	2									
Pyritic massive ore material										
		(n)								
Skouriotissa	1	8		2.78	0.02		0.5**	74**	3**	296**
Mathiati	1	45	48	0.17	0.26	97	0.8	160	11	20
Sha	1	1	36.7	1.9	1.2	94	1	657	20	26
Memi	1	2	49.8		0.02	2	0.02	23		35
Kambia	1	1					0.04	70	3	
Kinousa-Uncle Charles	1	1	51.5	0.18	0.02	19	0.3	105	17	5
Agrokipia	1	2	46.9	0.07	0.03	30	0.14	201	3	144
Mavrovouni	1	1		3.69	0.8		1.05	170		330
VMS related										
		(n)								
Gossan/Ocher/Umber										
Ochers Skouriotissa	3	6		0.1	0.1		7.0	276	17.50	106.3
Umbers Skouriotissa	3	4		0.3	0.1		0.08	265	3.5	
Meteoric gossan	3	1		0.1	0.0		0.23	18.0	1.0	4.0
Silicified umber Skouriotissa	4	13					2.35			
Umber										
		(n)								
Perapedhi	4	13					0.08			
Asgata	4	9					0.11			
Pyrga	4	7					1.42			
Kokkinovounaro	4	7					0.91			
Typical Unsilicified Umber	4	10					0.01	303		
Typical Silicified Umber	4	6					1.87	50		

n = number of samples. *Estimated Au grade ** One sample MH-16 (Hannington et al., 1998; Herzig et al., 1991). 1 = Hannington et al. (1998); 2 = Adamides et al. (2010b); 3 = Herzig et al. (1991); 4 = Prichard and Maliotis (1998).

Table 2. Whole rock data of the different lithological units and alteration fascies in the Troodos ophiolite.

			SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	P2O5	K2O	Au	As	Sb	Se	Cu	Zn	Pb	Y
			%	%	%	%	%	%	%	%	%	%	ppb	ppb	ppb	ppb	ppm	ppm	ppm	ppm
Volcanic section	Fresh glass	average (n=10)	54.8	0.99	15.1	12.3	0.20	5.33	8.68	2.15	0.04	0.47	1.9	850	78	120	86	79	1.9	26
		σ	2.1	0.23	0.6	1.7	0.03	1.53	1.88	0.46	0.02	0.20	1.0	370	34	54	37	11	0.56	7.6
		median	54.0	1.03	15.0	12.8	0.20	5.45	8.41	2.02	0.03	0.41	1.5	910	64	120	82	81	2.1	25
	Seafloor weathering	n=1	43.8	0.46	13.5	8.5	0.12	3.46	23.5	1.21	0.04	5.41	1.2	6500	240	b.d.l.	47	58	1.9	12
	Low temperature zone	average (n=10)	53.8	0.87	15.5	10.6	0.22	6.78	8.70	2.70	0.04	0.86	1.0	450	71	50	46	100	1.2	20
		σ	5.9	0.27	1.3	1.9	0.08	2.68	6.28	1.76	0.04	0.79	0.62	450	84	53	23	39	0.35	8.8
		median	55.1	0.86	15.8	10.2	0.22	6.86	6.46	2.37	0.04	0.76	0.95	260	35	20	41	89	1.3	17
	Mineralisation zone halo	average (n=12)	62.5	1.13	14.1	10.7	0.26	4.05	3.31	3.15	0.06	0.66	1.0	2300	140	170	160	120	5.0	15
		σ	8.7	0.28	2.3	3.9	0.16	2.64	1.00	1.26	0.01	0.59	1.10	2400	150	130	340	110	6.4	2.5
		median	60.8	1.16	14.7	12.5	0.20	4.03	3.51	3.00	0.07	0.45	0.36	1000	87	170	22	110	2.0	15
	Picrites	average (n=3)	47.2	0.20	6.3	9.3	0.15	32.2	4.16	0.32	b.d.l	0.07	2.0	320	33	97	56	59	1.1	5.0
		σ	0.5	0.02	0.6	0.1	0.00	1.74	0.46	0.10		0.00	0.17	81	3.3	72	5.4	3.0	0.78	0.51
		median	47.5	0.21	6.6	9.4	0.15	31.2	4.37	0.35		0.07	2.10	310	31	55	56	59	0.63	5.3
	Diabase	average (n=25)	58.0	0.94	15.4	10.4	0.14	5.14	6.55	3.16	0.05	0.30	0.24	110	37	54	29	45	1.1	25
		σ	5.2	0.28	0.9	1.8	0.07	1.88	2.10	1.10	0.05	0.21	0.11	89	25	110	49	36	1.80	9.2
		median	55.7	0.96	15.6	10.6	0.15	5.44	6.36	3.15	0.05	0.30	0.21	86	30	10	8.4	30	0.43	24
	Transitional diabase-epidosite	average (n=18)	56.8	1.04	15.2	12.0	0.17	5.01	8.15	1.53	0.05	0.09	0.43	86	35	10	24	52	0.63	24
		σ	4.4	0.29	1.5	2.3	0.06	1.76	2.46	1.65	0.03	0.14	0.83	35	21	9.1	28	32	0.38	6.9
		median	56.3	0.98	15.6	11.4	0.18	5.30	7.79	0.23	0.04	0.03	0.19	91	27	6.5	12	58	0.58	23
Sheeted dyke complex	Intermediate epidosite	average (n=18)	61.3	0.96	14.7	9.0	0.12	2.06	10.48	1.22	0.07	0.08	0.23	86	38	22	23	34	1.10	31
		σ	6.6	0.35	1.7	3.2	0.08	1.40	4.31	1.49	0.03	0.13	0.12	47	17	25	22	29	1.50	9.5
		median	59.5	0.97	14.6	9.9	0.15	1.90	11.03	0.27	0.07	0.02	0.21	72	36	12	14	27	0.57	30
	End-member epidosite	average (n=6)	55.3	1.08	15.6	11.1	0.09	2.53	14.26	0.01	0.04	0.02	0.18	110	27	7.8	10	19	0.89	24
		σ	1.6	0.23	0.6	1.6	0.04	1.27	2.71	0.01	0.02	0.01	0.02	24	16	10	12	10	0.60	5.3
		median	55.1	1.08	15.7	10.5	0.09	2.29	15.98	0.00	0.04	0.02	0.17	120	20	2.5	5.2	14	0.63	24
	All dykes	average (n=67)	58.3	0.98	15.2	10.5	0.14	4.04	8.73	1.92	0.06	0.16	0.28	97	36	27	24	42	0.97	26
		σ	5.6	0.31	1.3	2.6	0.07	2.19	3.79	1.69	0.04	0.20	0.44	64	21	68	35	33	1.4	9.0
		median	57.0	0.97	15.4	10.9	0.15	3.90	7.87	2.29	0.04	0.04	0.19	88	31	8.7	11	27	0.57	24
	Plutonic complex	Plagiogranites	average (n=6)	69.0	0.58	14.0	5.0	0.04	1.30	6.60	3.03	0.07	0.41	0.19	110	40	47	4.8	26	0.40
σ			3.9	0.15	1.4	2.9	0.04	0.52	4.05	1.38	0.04	0.24	0.06	51	25	35	2.5	29	0.24	9.5
median			69.8	0.63	14.7	4.2	0.02	1.52	6.30	3.33	0.08	0.37	0.21	120	34	47	5.6	15	0.37	40
Gabbros		average (n=11)	50.4	0.25	16.3	8.1	0.16	10.1	13.65	1.01	b.d.l	0.07	1.30	130	23	94	69	40	0.54	6.7
		σ	0.8	0.07	1.7	0.6	0.02	0.98	0.95	0.22		0.04	1.30	44	11	74	37	7.9	0.30	2.5
median		50.3	0.26	16.4	8.1	0.16	10.3	13.94	1.06		0.05	0.88	140	23	62	72	40	0.47	6.3	
average (n=4)		43.8	0.08	3.4	10.3	0.15	39.5	2.53	0.14	b.d.l	0.04	0.33	100	22	33	14	47	0.39	1.7	
Mantle sequence	σ	1.9	0.10	4.4	1.8	0.04	11.5	3.80	0.25		0.03	0.26	55	5.0	31	16	6.0	0.07	2.3	
	median	44.6	0.03	1.1	9.9	0.14	44.4	0.41	0.00		0.03	0.23	110	22	12	5.5	45	0.36	0.5	

All data are in Appendix 1. b.d.l. = below detection limit

Table 3. Average composition of Troodos ophiolite and MORB fresh glass.

		SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Au	As	Sb	Se	Cu	Zn	Pb	References
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)	(ppm)	(ppm)	
	Average	55.5	0.90	14.8	9.21	0.17	4.70	8.92	2.26	0.09	0.30	498	1.9	850	78	120	62	101	1.93	
Troodos	σ	3.5	0.38	1.0	1.73	0.03	2.35	2.47	0.82	0.06	0.31	303	0.97	370	34	54	51	90	0.56	1-8
	Median	55.0	0.83	14.7	9.07	0.17	3.95	8.56	2.28	0.08	0.22	445	1.5	910	64	120	57	82	2.15	
	Average	62.8	0.68	14.5	6.56	0.15	2.84	5.53	3.86	1.31	0.20	690	3.1	2500	87	230	72	83	5.10	
Manus Basin	σ	6.9	0.20	1.1	2.18	0.10	2.82	3.25	1.04	0.59	0.14	194	2.2	890	35	65	88	16	5.98	9-13
	Median	65.1	0.65	14.5	6.21	0.14	1.77	4.60	4.35	1.34	0.15	666	3.4	2300	80	220	32	80	4.38	
	Average	50.2	1.31	15.6	10.4	0.18	7.53	11.6	2.55	0.16	0.12	685	4.3	290	20	390	134	95	0.64	
Lau Basin	σ	2.4	0.39	1.3	1.46	0.04	1.56	1.57	0.55	0.13	0.07	826	3.5	140	10	69	43	34	0.43	9,14
	Median	49.8	1.21	15.7	10.1	0.18	7.96	11.7	2.57	0.12	0.11	346	3.1	240	17	370	136	94	0.50	
	Average	50.5	1.46	15.3	10.2	0.19	7.52	11.6	2.53	0.18	0.15	1110	1.5	230	16	360	88	104	0.55	
MORB	σ	0.9	0.44	1.1	1.40	0.02	0.97	0.87	0.45	0.26	0.10	194	1.2	290	13	67	26	20	0.45	9
	Median	50.6	1.43	15.2	9.9	0.19	7.59	11.6	2.51	0.12	0.14	1120	1.1	170	14	350	79	100	0.47	
MORB		50.5	1.42	15.5	9.4	0.17	7.84	11.5	2.71	0.18	0.13	1100	1.2	110	14	210	70	80	0.57	15

References: 1-this study; 2- Rautenschlein et al., 1985; 3- Mehegan, 1988; 4-Jowitt et al., 2012; 5-Muenow et al., 1990; 6-Bednarz and Schminke, 1994; 7-Portnyagin et al., 1997; 8-Flower and Levin 1987; 9-Jenner et al., 2012; 10-Moss et al., 2001; 11-Park et al., 2010; 12-Sun et al. 2004; 13-Sun et al., 2007; 14-Cawood and Fryer, 1994; 15- Arevalo and McDonough, 2010. See Appendix 1 and 4.

Table 4. Mass variation of samples from the lower sheeted dyke section of the Troodos ophiolite.

			Au	As	Sb	Se	Cu	Zn	Pb	Au	As	Sb	Se	Cu	Zn	Pb	
			%	%	%	%	%	%	%	ppb	ppb	ppb	ppb	ppm	ppm	ppm	
Lower Sheeted Dyke Complex	All dykes	average (n=63)	-80	-87	-45	-75	-66	-50	-33	-1.3	-680	-40	-81	-57	-46	-0.46	
		σ	31	9	54	61	46	41	81	0.70	210	34	68	42	38	1.37	
		median	-88	-88	-59	-92	-87	-71	-59	-1.5	-628	-37	-95	-74	-57	-0.83	
	Diabase	average (n=20)	-84	-85	-49	-47	-62	-45	-21	-1.4	-663	-40	-51	-54	-42	-0.16	
		σ	7	14	26	104	64	47	106	0.48	225	28	116	55	45	1.90	
		median	-86	-89	-57	-85	-90	-68	-58	-1.4	-614	-36	-92	-74	-52	-0.86	
	Transitional diabase-epidosite	average (n=17)	-71	-88	-41	-90	-63	-38	-50	-1.2	-635	-32	-95	-55	-34	-0.70	
		σ	56	5	50	8	42	39	34	1.0	163	31	19	37	36	0.52	
		median	-88	-87	-50	-95	-85	-32	-59	-1.3	-581	-29	-92	-71	-29	-0.71	
	Intermediate epidosite	average (n=18)	-79	-90	-54	-79	-64	-62	-24	-1.3	-795	-51	-86	-52	-59	-0.47	
		σ	19	6	23	22	36	37	98	0.68	210	32	29	36	36	1.6	
		median	-87	-91	-65	-89	-77	-72	-64	-1.6	-804	-47	-99	-72	-68	-1.0	
	End-member epidosite	average (n=6)	-90	-83	-57	-92	-88	-77	-26	-1.6	-606	-40	-97	-75	-67	-0.41	
		σ	2	5	30	11	13	13	53	0.37	141	26	18	21	14	0.73	
		median	-90	-82	-71	-98	-93	-84	-55	-1.7	-607	-42	-103	-83	-70	-0.63	
	Greenschist diabase	Diabase (n=5)	average	-76	-83	14	-90	-57	-42	-48	-1.3	-679	-40	-79	-55	-46	-0.45
		Transntional diabase- epidosite (n=1)	σ	18	6	137	7	44	35	31	0.71	218	35	70	43	39	1.4
		median	-87	-86	-66	-90	-86	-64	-58	-1.4	-622	-37	-94	-73	-56	-0.81	
Calculated depletion of epidosite zone		Median	-88	-89	-60	-91	-84	-63	-60	-1.5	-679	-39	-96	-74	-55	-0.85	
		Error	16	23	12	20	18	9	8	0.27	178	7.5	21	16	7.7	0.12	

Errors are propagated as detailed in Appendix 6

Table 5. Mass variation from the Solea graben source areas and comparison with VMS deposits.

		Volume (km ³)	Density (kg.m- 3)	Mass (Mt)		Au (t)	As (kt)	Sb (t)	Se (t)*	Cu (kt)	Zn (kt)	Pb (kt)
Solea graben source area	Epidosite zone	5	3095	15475	Δ	23	11	610	1500	1100	850	13
					σ	4.2	2.8	120	330	240	120	1.8
	Greenschists diabase	5.9	2847	16904	Δ	24	11	620	1600	1200	950	14
					σ	4.5	2.8	120	350	260	130	1.9
	Total source area	10.9	2961	32379	Δ	47	21	1200	3100	2400	1800	27
					σ	8.7	5.5	240	680	510	250	3.7
Solea Graben VMS deposit	Phoukasa			5		0.59	0.40	16.2	221.4	124.2	3.24	
	Phoenix			15		1.65				75		
	Mavrovrouni			15		4.5	2.55		615	570	75	
	Apliki			2		0.1				29.7		
	Total VMS			37		6.8	2.95	16.2	836.4	798.9	78.2	n.d.
Percentage metal trapped in VMS						15	14	1.4	27	33	4.3	
Percentage metal lost						85	86	99	73	67	96	

*Se values of the Phoukasa and Mavrovrouni deposits in Table 1 appear excessively high relative to other Troodos VMS deposits and an average of 41 ppm is used for calculation from the average of other VMS deposits (Table 1). Δ= mass variation; σ= propagated error (Appendix 6); n.d.= not determined.

Appendix I. Whole rock data summary

Sample	Unit	Rock type	Aluminum type	As ^a technique	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As ^a BG-FA5	As
 

Appendix 2. Major and trace elements reference materials and internal standard for whole rock analyses.

		Method	Reference Material	n	Average	σ (%)	RSD	Working values	Recovery rate	References
SiO ₂	wt. %	XRF	AGV-2	30	60	0.027	0.04	60.2	100	
Al ₂ O ₃	wt. %	XRF	AGV-2	30	17	0.015	0.09	17.2	99	
CaO	wt. %	XRF	AGV-2	30	5.2	0.004	0.07	5.3	99	
MgO	wt. %	XRF	AGV-2	30	1.8	0.005	0.29	1.8	99	
MnO	wt. %	XRF	AGV-2	30	0.10	0.001	0.50	0.1	100	
P ₂ O ₅	wt. %	XRF	AGV-2	30	0.59	0.068	11.5	0.5	120	
Fe ₂ O ₃	wt. %	XRF	AGV-2	30	6.8	0.020	0.30	6.8	100	
Na ₂ O	wt. %	XRF	AGV-2	30	4.2	0.015	0.35	4.3	99	
K ₂ O	wt. %	XRF	AGV-2	30	2.9	0.003	0.09	2.9	99	
TiO ₂	wt. %	XRF	AGV-2	30	1.1	0.002	0.18	1.1	103	
Sc	ppm	LA-ICP-MS	NIST612	50	41	1.17	2.9	40	103	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	37	0.76	2.1	33	112	Jochum et al., 2008
V	ppm	LA-ICP-MS	NIST612	50	39	1.09	2.8	39	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	400	7.94	2.0	416	96	Jochum et al., 2008
Cr	ppm	LA-ICP-MS	NIST612	50	36	1.05	2.9	36	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	18	0.28	1.5	18	100	Jochum et al., 2008
Ni	ppm	LA-ICP-MS	NIST612	50	39	1.12	2.9	39	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	17	0.38	2.3	17	100	Jochum et al., 2014
Ga	ppm	LA-ICP-MS	NIST612	50	36	0.97	2.7	37	98	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	19	0.37	1.9	23	83	Jochum et al., 2008
Rb	ppm	LA-ICP-MS	NIST612	50	31	0.97	3.1	31	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	42	1.11	2.6	47	90	Jochum et al., 2008
Sr	ppm	LA-ICP-MS	NIST612	50	78	2.38	3.0	78	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	350	7.06	2.0	340	103	Jochum et al., 2008
Y	ppm	LA-ICP-MS	NIST612	50	38	1.28	3.4	38	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	34	1.17	3.4	37	92	Jochum et al., 2008
Zr	ppm	LA-ICP-MS	NIST612	50	38	1.07	2.8	38	100	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	180	5.01	2.8	184	98	Jochum et al., 2008
Nb	ppm	LA-ICP-MS	NIST612	50	40	1.33	3.3	39	103	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	14	0.29	2.1	13	111	Jochum et al., 2008
Cs	ppm	LA-ICP-MS	NIST612	50	42	1.18	2.8	43	98	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	1.0	0.03	3.4	1.1	88	Jochum et al., 2008
Ba	ppm	LA-ICP-MS	NIST612	50	40	1.31	3.3	39	102	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	710	13.36	1.9	677	105	Jochum et al., 2008
La	ppm	LA-ICP-MS	NIST612	50	36	1.21	3.4	36	100	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	26	0.67	2.6	25	104	Jochum et al., 2008
Ce	ppm	LA-ICP-MS	NIST612	50	39	1.07	2.7	38	102	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	50	1.12	2.2	53	95	Jochum et al., 2008
Pr	ppm	LA-ICP-MS	NIST612	50	37	1.26	3.4	38	98	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	6.5	0.20	3.1	6.7	97	Jochum et al., 2008
Nd	ppm	LA-ICP-MS	NIST612	50	36	1.08	3.0	36	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	28	0.83	3.0	29	98	Jochum et al., 2008
Sm	ppm	LA-ICP-MS	NIST612	50	38	1.30	3.4	38	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	6.9	0.27	3.9	6.6	105	Jochum et al., 2008
Eu	ppm	LA-ICP-MS	NIST612	50	35	1.18	3.4	36	98	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	2.0	0.05	2.4	2.0	102	Jochum et al., 2008
Gd	ppm	LA-ICP-MS	NIST612	50	37	1.30	3.5	37	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	6.5	0.16	2.5	6.8	96	Jochum et al., 2008
Tb	ppm	LA-ICP-MS	NIST612	50	36	1.24	3.5	38	96	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	1.0	0.06	6.0	1.1	91	Jochum et al., 2008
Dy	ppm	LA-ICP-MS	NIST612	50	36	1.06	3.0	36	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	6.3	0.20	3.1	6.4	98	Jochum et al., 2008
Ho	ppm	LA-ICP-MS	NIST612	50	38	1.34	3.5	38	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	1.3	0.05	4.0	1.3	102	Jochum et al., 2008
Er	ppm	LA-ICP-MS	NIST612	50	38	1.38	3.6	38	100	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	3.7	0.09	2.5	3.7	101	Jochum et al., 2008
Tm	ppm	LA-ICP-MS	NIST612	50	38	1.41	3.7	37	103	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	0.5	0.03	6.5	0.5	96	Jochum et al., 2008
Yb	ppm	LA-ICP-MS	NIST612	50	39	1.40	3.6	39	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	3.6	0.16	4.3	3.4	107	Jochum et al., 2008
Lu	ppm	LA-ICP-MS	NIST612	50	37	1.15	3.1	37	100	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	0.5	0.02	3.2	0.5	97	Jochum et al., 2008
Hf	ppm	LA-ICP-MS	NIST612	50	35	1.11	3.2	37	95	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	4.6	0.13	2.8	4.9	94	Jochum et al., 2008
Ta	ppm	LA-ICP-MS	NIST612	50	40	1.47	3.7	38	106	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	0.9	0.03	3.8	0.7	115	Jochum et al., 2008
Th	ppm	LA-ICP-MS	NIST612	50	38	1.24	3.3	38	101	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	5.9	0.19	3.2	5.7	104	Jochum et al., 2008
U	ppm	LA-ICP-MS	NIST612	50	37	1.30	3.5	37	99	Jochum et al., 2011
	ppm	LA-ICP-MS	BCR-2G	6	1.5	0.04	2.7	1.7	89	Jochum et al., 2008

Appendix 3. Reference materials and internal standard for whole rock analysis.*Au values in ppb. **not certified values.

Element	Method	Reference Material	n	Average (ppm)	σ (ppm)	RSD	Published values (ppm)	σ (ppm)	RSD	Recovery rate	References Method	References
Au*	Au-technique	TDB-1	14	6.4	0.5	7.9	6.3	1.3	21.3	101	ICP-MS	Bédard and Barnes, 2002a
		WMS-1	10	218	64	29.4	246	44	17.9	89	INAA	Constantin, 2009
		CH-4	14	586	141	24.0	713	62	8.7	82	INAA	Constantin, 2009
As	HG-AFS	TDB-1	20	2.1	0.4	16.4	2.2	0.3	13.6	98	INAA	Bédard and Barnes, 2002b
		WMS-1	18	21	6	28.1	19	1	3.7	112	INAA	Bédard and Barnes, 2002b
		CH-4	20	7.7	0.7	8.6	8.8	0.5	5.7	87		Shalley and Leaver, NRCan**
Sb	HG-AFS	TDB-1	20	0.63	0.24	38.6	0.72	0.03	4.2	87	INAA	Bédard and Barnes, 2002b
		WMS-1	17	6.9	1.1	15.4	6.9	1.0	14.5	99		Shalley and Leaver, NRCan**
		CH-4	13	0.77	0.32	41.8	0.77	0.4	51.9	100		Shalley and Leaver, NRCan**
Se	HG-AFS	TDB-1	20	0.37	0.10	26.8	0.7			53		Shalley and Leaver, NRCan**
		WMS-1	10	68	12	18.3	87			78		Shalley and Leaver, NRCan**
		CH-4	18	1.9	0.2	10.6	2.1	0.2	9.5	89		Shalley and Leaver, NRCan**
Cu	LA-ICP-MS	NIST 612	50	37	1	2.9	38	2	4.0	98	Compiled	Jochum et al., 2011
		BCR-2G	6	16	0.5	2.9	16	5		105	LA-ICPMS	Jocum et al., 2005
Zn	LA-ICP-MS	NIST 612	50	38	1.1	3.0	39	1.7	4.3	97	Compiled	Jochum et al., 2011
		BCR-2G	6	107	2	1.9	125			85	Compiled	Jocum et al., 2008
Pb	LA-ICP-MS	NIST 612	50	39	1.3	3.4	39	0.2	0.5	100	Compiled	Jochum et al., 2011
		BCR-2G	6	9.4	0.4	3.8	11			86	Compiled	Jocum et al., 2008

Appendix 4. Literature compilation of the fresh glass data used in this study

Sample	SiO2 (%)	Al2O3 (%)	TiO2 (%)	MgO (%)	CaO (%)	MnO (%)	Na2O (%)	FeO (%)	P2O5 (%)	K2O (%)	S (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	Au (ppb)	As (ppb)	Sb (ppb)	Se (ppb)	Y (ppm)	References
Troodos BADR serie																				
316-00	51.9	16.4	0.66	6.96	11.99		2.00	7.78		0.16	500									Mucnow et al., 1990
86-09	54.3	15.8	0.54	6.05	10.50		1.84	7.78		0.22	1000									Mucnow et al., 1990
87-46	52.4	15.9	0.67	6.58	11.15		2.03	8.29		0.26	1000									Mucnow et al., 1990
86-6	54.6	14.6	1.30	3.35	7.75		10.54	7.75		0.29	1200									Mucnow et al., 1990
86-34	53.5	14.3	1.32	3.44	7.95		2.08	11.48		0.68	400									Mucnow et al., 1990
86-9	55.4	15.5	0.49	7.27	11.04	0.16	1.67	8.26	0.04	0.22	400	121	292						13.0	Bednarz and Schminke, 1994
87-3	55.3	15.8	0.69	6.43	10.34	0.15	2.20	8.11	0.06	0.20	100	130	79						19.0	Bednarz and Schminke, 1994
84-43	54.0	16.1	0.69	8.15	9.65	0.13	2.01	8.67	0.07	0.53		37	71						17.0	Bednarz and Schminke, 1994
87-46	55.9	0.73	7.62	10.69	0.17	1.62	8.97	0.06	0.37	300	186	88							24.0	Bednarz and Schminke, 1994
CY-2a 113.2	59.5	15.4	1.13	3.44	7.25	0.20	2.79	9.90	0.11	0.30	200	319	202						38.0	Bednarz and Schminke, 1994
CY-2a 123.15	62.7	14.6	1.15	2.43	6.07	0.19	3.00	9.30	0.14	0.34	200	91	128						48.0	Bednarz and Schminke, 1994
CY-2a 124.75	62.6	14.7	1.16	2.39	6.10	0.20	3.05	9.33	0.12	0.35	200	64	112						38.0	Bednarz and Schminke, 1994
CY-2a 136.29	60.8	14.9	1.22	2.77	6.79	0.20	2.88	10.11	0.14	0.29	200	67	123						40.0	Bednarz and Schminke, 1994
CY-2a 141.6	60.7	13.4	1.23	2.89	6.68	0.21	2.78	10.29	0.12	0.30	200	65	116						36.0	Bednarz and Schminke, 1994
84-04a	58.0	14.8	1.35	3.94	6.00	0.10	2.77	11.68	0.12	1.23		32	89						32.0	Bednarz and Schminke, 1994
84-64	58.0	15.1	1.25	3.53	5.17	0.18	3.06	11.77	0.12	1.19		300	41	104					34.0	Bednarz and Schminke, 1994
86-6	56.9	14.7	1.36	3.91	7.74	0.20	2.84	11.95	0.12	0.27	700	73	141						33.0	Bednarz and Schminke, 1994
86-7	56.9	15.9	1.21	4.45	7.49	0.17	2.78	10.72	0.10	0.24	600	78	120						34.0	Bednarz and Schminke, 1994
86-10	60.7	15.0	1.49	2.74	6.12	0.19	3.21	10.02	0.10	0.20	500	29	747						48.0	Bednarz and Schminke, 1994
86-17	59.7	15.6	1.36	3.53	5.80	0.16	2.94	10.40	0.15	0.37	600	23	109						41.0	Bednarz and Schminke, 1994
86-26	58.7	15.1	1.27	3.45	4.91	0.16	3.91	11.52	0.12	0.80	900	42	109						37.0	Bednarz and Schminke, 1994
86-34	55.4	15.1	1.32	4.29	8.09	0.20	2.64	12.40	0.10	0.46	700	68	113						30.0	Bednarz and Schminke, 1994
87.25	60.6	15.0	1.38	2.77	6.05	0.20	2.98	10.46	0.15	0.37	200	13	112						40.0	Bednarz and Schminke, 1994
87.26	69.4	13.6	0.62	0.84	6.43		3.33	6.15	0.13	0.45	100	15	97						55.0	Bednarz and Schminke, 1994
87-37	64.1	14.1	0.88	2.50	5.22	0.23	2.96	8.61	0.40	0.53	100	10	105						78.0	Bednarz and Schminke, 1994
JOW1-24B	59.5	12.5	1.08	1.14	4.85	0.22	3.60	8.10	0.00	0.33	156	12	77						47.4	Jowitt et al., 2012
JOW1-27B	54.7	12.8	1.29	1.33	3.88	0.19	2.46	8.97	0.27	0.93	248	10	82						47.9	Jowitt et al., 2012
JOW1-2A	60.0	13.6	1.09	1.35	5.31	0.15	3.56	7.26	0.14	0.49	206	7	68						38.9	Jowitt et al., 2012
JOW1-3A	58.8	13.3	1.04	1.57	5.42	0.16	3.20	7.66	0.16	0.30	215	11	72						38.5	Jowitt et al., 2012
JOW2-6A	58.7	13.4	1.10	1.59	5.36	0.15	3.36	7.72	0.14	0.73	199	12	81						47.7	Jowitt et al., 2012
JOW1-19B	58.5	13.1	1.40	1.64	5.56	0.18	4.07	9.80	0.00	0.32	236	18	135						79.6	Jowitt et al., 2012
JOW2-9A	57.6	13.9	1.20	1.89	6.30	0.12	3.42	9.03	0.00	0.25	356	14	92						40.3	Jowitt et al., 2012
JOW1-7A	56.1	13.4	1.23	2.04	6.20	0.19	3.23	9.04	0.15	0.27	461	19	97						47.0	Jowitt et al., 2012
JOW1 8B	55.4	13.7	1.46	2.48	6.60	0.19	3.38	9.56	0.15	0.26	425	18	87						43.5	Jowitt et al., 2012
JOW2-8A	55.7	13.7	1.19	2.50	6.58	0.19	3.43	9.25	0.00	0.29	288	19	78						36.2	Jowitt et al., 2012
JOW1-5A	54.6	13.5	1.33	2.54	6.51	0.17	3.29	9.17	0.15	0.24	485	15	79						41.9	Jowitt et al., 2012
JOW2-10A	53.5	13.8	1.25	3.09	7.49	0.17	2.50	10.49	0.00	0.64	589	47	87						34.5	Jowitt et al., 2012
JOW2-4A	52.1	13.7	1.58	3.40	7.60	0.19	3.15	10.48	0.11	0.20	725	30	79						36.2	Jowitt et al., 2012
JOW2-3A	53.6	14.0	1.58	3.51	7.90	0.19	3.31	11.29	0.00	0.24	753	32	79						38.4	Jowitt et al., 2012
JOW2-14A	51.7	13.6	1.47	3.70	8.00	0.15	2.75	11.21	0.00	0.67	1053	45	125						37.2	Jowitt et al., 2012
JOW1-1A	51.9	13.9	1.55	3.74	8.21	0.19	3.20	11.34	0.12	0.20	949	43	77						35.6	Jowitt et al., 2012
JOW2-1A	52.5	13.7	1.39	3.80	7.25	0.14	2.38	8.49	0.00	0.62	853	41	86						32.6	Jowitt et al., 2012
JOW2-13A	52.4	13.7	1.47	3.83	8.05	0.13	2.68	11.08	0.00	0.68	989	37	111						35.1	Jowitt et al., 2012
JOW1-30B	50.8	15.0	0.50	6.95	11.29	0.12	1.70	6.40	0.04	0.12	445	57	36						14.3	Jowitt et al., 2012
JOW2-7A	50.8	15.5	0.65	6.08	11.93	0.14	1.07	7.35	0.04	0.10	643	53	37						15.0	Jowitt et al., 2012
JOW2-2A	50.8	15.4	0.53	7.68	12.47	0.11	1.95	7.24	0.00	0.08	785	71	57						16.9	Jowitt et al., 2012
JOW2-11A	51.0	15.5	0.59	7.70	12.50	0.15	1.93	7.08	0.00	0.09	769	52	34						15.4	Jowitt et al., 2012
TRD-148	42.8	12.5	0.40	9.74	17.91	0.15	0.80	6.29	0.04	0.18		63	55							Portnyagin et al., 1997
TRD-147	51.4	15.9	0.49	8.40	13.90	0.14	1.55	6.81	0.05	0.12										Portnyagin et al., 1997
TRD-149	51.1	15.5	1.03	5.72	7.69	0.14	2.55	8.70	0.15	0.11		95	96							Portnyagin et al., 1997
TRD-149	55.5	15.2	1.05	3.83	8.73	0.18	2.18	10.41	0.09	0.20										Portnyagin et al., 1997
TRD-152	46.4	15.7	0.66	7.03	7.82	0.15	1.32	10.32	0.13	2.79		83	84							Portnyagin et al., 1997
TRD-151	50.4	15.1	0.61	6.08	9.78	0.15	1.55	7.50	0.07	2.97		161	52							Portnyagin et al., 1997
TRV-48	50.8	16.2	0.41	8.34	13.69	0.14	1.37	7.36	0.04	0.09										Portnyagin et al., 1997
TRV-49	51.2	16.0	0.59	6.76	11.27	0.17	1.98	7.88	0.07	0.17										Portnyagin et al., 1997
TRV-53	54.6	15.8	0.63	6.02	10.23	0.19	1.80	8.40	0.06	0.19										Portnyagin et al., 1997
AM-9	53.5	14.5	0.30	8.91	12.69		0.80	7.64	0.05	0.01		72	67						8.0	Flower and Levin 1987
AM-11	53.4	14.0	0.30	9.42	12.28		0.84	7.60	0.05			67	63						7.0	Flower and Levin 1987
AM-13	54.0	13.3	0.26	9.70	12.21		0.58	7.98	0.04											Flower and Levin 1987
AM-14	53.5	13.2	0.25	9.86	12.50		0.54	7.90	0.05	0.07										Flower and Levin 1987
AM-15	53.3	14.7	0.33	8.16	12.52		0.70	7.73	0.05											Flower and Levin 1987
AM-16	54.2	14.6	0.40	7.51	11.51		1.33	7.35	0.06	0.13		68	61						10.0	Flower and Levin 1987
AM-19	52.9	15.1	0.41	9.02	10.86		1.54	7.52	0.05	0.14		80	67						7.0	Flower and Levin 1987
AM-31	53.5	13.9	0.32	8.97	12.18		0.67	7.69	0.04	0.11		72	66						9.0	Flower and Levin 1987
AM-35	53.7	14.1	0.30	8.83	11.91		0.64	7.97	0.06	0.10		70	67						7.0	Flower and Levin 1987
AM-36	54.7	15.0	0.40	7.32	11.59		1.24	7.48	0.06	0.13		72	64						10.0	Flower and Levin 1987
ET-4-1	54.3	15.8	0.48	6.42	10.90	0.14	1.78	7.73	0.03	0.18		81	66	0.90					10.8	Regelous et al., 2014
ET-4-3	51.8	16.0	0.63	7.59	12.50	0.14	1.85	7.49	0.04	0.09										Regelous et al., 2014
ET-4-4	51.9	16.1	0.63	7.64	12.54	0.15	1.87	7.54	0.05	0.09										Regelous et al., 2014
ET-4-5	52.5	15.5	0.82	5.68	10.25	0.18	2.06	8.86	0.05	0.15		84	82	0.98					20.7	Regelous et al., 2014
ET-4-6	51.9	16.2	0.65	7.70	12.62	0.13	1.85	7.48	0.04	0.10		75	61	0.62					13.8	Regelous et al., 2014
ET-4-7	55.7	14.0	1.42	3.24	7.95	0														

Appendix 4. Literature compilation of the fresh glass data used in this study.

	SiO ₂ (%)	Al ₂ O ₃ (%)	TiO ₂ (%)	MgO (%)	CaO (%)	MnO (%)	Na ₂ O (%)	FeO (%)	P ₂ O ₅ (%)	K ₂ O (%)	S (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	Au (ppb)	As (ppb)	Sb (ppb)	Se (ppb)	Y (ppm)	References
HS-12-12	54.6	14.1	1.30	3.18	7.85	0.18	2.47	11.55	0.11	0.46	72	106	1.37							Regelous et al., 2014
HS-12-13	56.0	14.7	1.12	2.73	7.79	0.15	2.45	10.36	0.08	0.23	67	115	1.85							29.1 Regelous et al., 2014
HS-12-14	60.2	14.0	1.26	1.99	6.22	0.17	3.18	9.71	0.15	0.30	11	113	1.74							40.3 Regelous et al., 2014
HS-12-15	58.3	14.3	1.17	1.78	5.95	0.18	3.07	8.99	0.15	0.28	9	107	1.76							38.5 Regelous et al., 2014
HS-12-16	59.4	14.1	1.12	1.78	5.90	0.16	2.94	8.50	0.15	0.27	10	105	1.63							41.2 Regelous et al., 2014
HS-14-4	58.0	13.1	1.30	2.05	6.09	0.14	1.83	9.61	0.13	0.26	17	105	1.61							38.2 Regelous et al., 2014
HS-14-5	54.6	15.7	0.48	6.51	10.77	0.10	1.79	7.67	0.04	0.21	86	71	1.05							51.9 Regelous et al., 2014
HS-14-6	61.5	13.8	0.96	1.11	4.91	0.17	3.02	7.42	0.16	0.53	81	122	1.62							32.9 Regelous et al., 2014
HS-25-2	55.2	14.0	1.34	2.80	7.05	0.14	2.47	10.65	0.10	0.22	44	100	1.46							30.5 Regelous et al., 2014
HS-25-3	55.0	14.8	1.26	3.09	7.70	0.19	2.69	10.87	0.10	0.22	37	112	1.50							33.3 Regelous et al., 2014
Boninites																				
TRD-150	44.4	10.3	0.34	22.23	7.96	0.16	0.51	8.16	0.05	0.07	55	59								Portnyagin et al. 1997
TRV-57	43.8	9.3	0.30	22.97	7.19	0.14	0.42	8.05	0.05	0.11										Portnyagin et al. 1997
95	50.2	12.4	0.46	11.20	9.20	0.14	1.67	5.37	0.05	0.35	80	48			1.30					Hamlyn et al. 1985
201	53.8	11.4	0.31	12.54	8.73	0.16	1.30	6.06	0.02	0.15	160	36								Hamlyn et al. 1985
92	51.7	12.5	0.19	12.74	9.88	0.14	1.10	6.10	0.01	0.39	50	43			2.60					56 Hamlyn et al. 1985
106	49.8	11.2	0.19	13.92	10.12	0.15	0.66	5.71	0.02	0.21	20	51			2.10					Hamlyn et al. 1985
Cy7	41.6	5.1	0.11	2.25	31.00	2.68	0.14	0.29	4.94	0.01	0.10		56							Hamlyn et al. 1985
116	51.4	12.1	0.27	11.24	10.78	0.16	0.74	6.51	0.02	0.12	210	12			3.10					95 Hamlyn et al. 1985
Manus Basin																				
MD3	52.0	13.0	0.38	9.19	14.37	0.13	1.59	6.67	0.09	0.25	392	87	81	1.24	3.78	1121	37.5	131	10.1	Jenner et al., 2012
MD101	51.5	15.3	0.45	6.86	11.81	0.16	1.89	7.71	0.18	0.32	413	102	80	1.37	3.70	1185	37.6	138	11.4	Jenner et al., 2012
DR86	55.5	14.9	0.83	4.24	0.89	0.18	3.11	11.09	0.35	0.68	755	184	99	2.50	5.50	1596	60.2	252	19.9	Jenner et al., 2012
MD7A	58.4	15.3	1.17	3.22	7.15	0.19	3.59	8.95	0.67	0.84	1109	279	100	2.47	4.05	1927	54.5	370	17.4	Jenner et al., 2012
MD7b	59.8	14.9	1.23	3.07	6.79	0.21	3.77	9.18	0.81	0.92	1051	282	109	3.07	7.06	1709	62.2	350	24.1	Jenner et al., 2012
MD8	60.8	15.6	1.06	2.39	5.84	0.17	4.16	7.47	0.63	1.08	600	28	121	3.71	1.14	2230	80.3	200	30.0	Jenner et al., 2012
MD5	60.5	15.7	1.06	2.43	5.89	0.17	4.08	7.29	0.43	1.07	643	37	106	3.26	1.38	2307	76.8	214	25.4	Jenner et al., 2012
MD65	67.4	14.8	0.70	1.50	3.65	0.15	4.59	4.73	0.20	1.56	639	18	105	5.06	0.66	3071	111.0	213	30.7	Jenner et al., 2012
MD28	66.3	14.6	0.67	1.41	3.56	0.14	0.51	4.88	0.21	1.57	651	19	104	4.86	0.82	2965	112.0	217	30.8	Jenner et al., 2012
MD36	69.4	14.4	0.66	1.04	3.41	0.15	4.68	5.06	0.28	1.55	681	22	113	5.53	0.72	3203	104.8	227	32.7	Jenner et al., 2012
MD114	65.5	14.4	0.76	1.13	3.58	0.15	4.75	6.06	0.39	1.34	694	34	116	4.99	1.04	2882	101.2	231	33.6	Jenner et al., 2012
DR87	72.9	12.8	0.43	0.26	1.79	0.11	4.73	3.50	0.15	1.69	666	17	81	5.44	3597	133.6	222	35.1	Jenner et al., 2012	
MD6	76.1	11.9	0.35	0.15	1.11	0.09	4.58	2.89	0.05	2.49	682	17	85	6.38	0.85	4090	155.5	227	36.5	Jenner et al., 2012
297-1	69.2	14.4	0.64	0.83	3.00	0.13	4.82	4.87	0.14	1.77	100	19	86							Moss et al., 2001
297-4	66.4	14.2	0.68	1.61	3.74	0.15	4.56	5.66	0.16	1.49	100	21	79							Moss et al., 2001
297-C	66.9	14.4	0.68	1.61	3.72	0.15	4.62	5.65	0.17	1.51	200	23	83							Moss et al., 2001
299-1	55.2	15.7	0.95	4.15	8.05	0.19	3.31	11.48	0.25	0.76	100	406	84							Moss et al., 2001
299-2	67.8	14.4	0.72	0.91	3.25	0.14	4.78	5.29	0.17	1.73	200	16	83							Moss et al., 2001
299-3	67.6	14.3	0.71	0.87	3.20	0.14	4.71	5.23	0.17	1.69	200	19	87							Moss et al., 2001
299-4	67.8	14.5	0.72	0.88	3.16	0.14	4.78	5.26	0.17	1.69	200	26	88							Moss et al., 2001
299-5	67.8	14.3	0.72	0.88	3.21	0.14	4.71	5.30	0.17	1.70	100	8	88							Moss et al., 2001
299-6	65.5	14.2	0.67	1.54	3.65	0.14	4.54	5.59	0.17	1.52	200	20	79							Moss et al., 2001
305-2	66.8	14.3	0.65	1.16	3.45	0.13	4.59	5.32	0.17	1.68	400	8	85							Moss et al., 2001
305-3	66.9	14.6	0.74	0.94	3.30	0.15	4.74	5.37	0.18	1.61	100	23	83							Moss et al., 2001
305-4	66.5	14.3	0.71	1.19	3.42	0.14	4.63	5.46	0.19	1.55	100	20	81							Moss et al., 2001
87DR1	72.5	12.8	0.45	0.47	2.09	0.11	4.96	3.53	0.07	1.85	200	18	67							Moss et al., 2001
88DR	70.6	13.4	0.44	0.52	2.15	0.11	5.04	3.85	0.07	2.08		21	78							Moss et al., 2001
100DR	54.4	15.9	0.56	5.77	10.14	0.15	2.72	8.29	0.15	0.75	400	93	72							Moss et al., 2001
MD-1	52.1	15.4	0.44	7.97	12.44	0.14	1.98	8.64	0.07	0.27	400	87	107							Moss et al., 2001
MD-2	52.5	17.4	0.47	6.06	11.63	0.17	2.03	9.28	0.10	0.49	300	112	71							Moss et al., 2001
MD-3	50.8	13.0	0.40	11.52	12.06	0.14	1.77	8.44	0.07	0.25	400	77	54							Moss et al., 2001
MD-4	67.0	14.0	0.69	1.35	3.51	0.14	4.91	5.35	0.16	1.62	100	23	79							Moss et al., 2001
MD-7	56.3	15.1	1.04	3.26	6.97	0.17	3.81	10.38	0.41	0.89	100	239	83							Moss et al., 2001
MD-8	59.1	15.0	1.02	2.17	5.27	0.18	4.14	9.90	0.55	0.94	800	87	107							Moss et al., 2001
MD-13	61.6	15.2	0.94	2.02	5.33	0.18	4.51	7.89	0.44	1.15	400	13	na							Moss et al., 2001
MD-20	65.9	14.7	0.79	1.01	3.49	0.16	4.76	5.71	0.23	1.44	100	72	73							Moss et al., 2001
M20A	66.3	14.6	0.75	1.03	3.26	0.14	4.85	6.10	0.20	1.56	100	20	85							Moss et al., 2001
MD-22	66.7	13.5	0.58	1.45	2.79	0.12	4.52	5.80	0.12	1.51	200	37	80							Moss et al., 2001
MD-223	66.9	13.6	0.58	1.60	3.19	0.12	4.47	5.57	0.13	1.66	200	38	77							Moss et al., 2001
MD-24	65.9	13.8	0.70	1.15	3.17	0.15	4.49	6.64	0.18	1.56	200	21	87							Moss et al., 2001
MD-24	67.1	13.6	0.55	0.99	2.64	0.13	4.74	4.84	0.13	2.05	200	40	76							Moss et al., 2001
MD																				

Appendix 4. Literature compilation of the fresh glass data used in this study.

Appendix 4. Literature compilation of the fresh glass data used in this study																					
Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	FeO (%)	MgO (%)	CaO (%)	MnO (%)	Na ₂ O (%)	FeO (%)	P ₂ O ₅ (%)	K ₂ O (%)	S (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	Au (ppb)	As (ppb)	Sb (ppb)	Se (ppb)	Y (ppm)	References	
MD6	74.8	11.1	0.34	0.14	0.98	0.06	2.44	2.84	0.04	2.19	17	17	45	6.96	1.43					Sun et al., 2004; Sun et al., 2007	
MD65	67.0	14.3	0.65	1.50	3.60	0.13	3.24	5.02	0.14	1.40	19	19	45	5.40	0.87					Sun et al., 2004; Sun et al., 2007	
MD7	56.8	14.2	1.07	2.99	6.21	0.19	3.00	10.00	0.42	0.84	249	249	45	3.18	7.42					Sun et al., 2004; Sun et al., 2007	
Lau Basin																					
834B RR-1	50.7	16.2	1.33	7.19	11.04	0.13	3.09	10.12	0.13	0.18	74	57			1.98	1			27	Cawood and Fryer, 1994	
834B 108R-1	50.3	17.0	1.10	8.50	11.66	0.15	2.65	9.22	0.10	0.12	75	42			2.12	1			23	Cawood and Fryer, 1994	
834B	50.0	17.2	1.05	8.99	11.54	0.13	2.57	8.90	0.10	0.12	82	38			1.88	1			21	Cawood and Fryer, 1994	
834B	50.6	17.0	1.41	5.91	11.40	0.16	3.31	9.56	0.31	0.31	62	71			9.96	1			36	Cawood and Fryer, 1994	
834B	49.9	17.9	1.20	7.46	12.44	0.12	2.52	8.44	0.11	0.02	65	45			4.84	1			25	Cawood and Fryer, 1994	
834B	49.5	18.0	1.19	7.58	12.33	0.12	2.67	8.58	0.11	0.04	72	47			1.03	1			25	Cawood and Fryer, 1994	
835B	50.4	16.2	1.14	7.98	12.16	0.12	2.11	9.43	0.11	0.12	81	63			2.44	1			22	Cawood and Fryer, 1994	
836A	57.0	14.5	1.16	3.53	8.06	0.23	2.91	12.43	0.14	0.26	135	102			5.22	0			34	Cawood and Fryer, 1994	
836B	48.4	16.6	0.75	7.98	14.46	0.15	1.98	9.29	0.13	0.11	114	35			11.37	1			18	Cawood and Fryer, 1994	
836B	48.5	16.3	0.75	9.52	13.06	0.15	1.81	9.37	0.05	0.04	110	57			10.02	1			17	Cawood and Fryer, 1994	
839B	53.3	15.0	0.65	9.40	11.52	0.19	1.37	10.16	0.07	0.30	131	58			6.82	1			15.0	Cawood and Fryer, 1994	
NLD13-1	48.3	17.0	1.45	8.60	12.12	0.18	2.72	10.17	0.11	0.09	989	163	91	0.63	2.32	393	11.7	385	23.9	Jenner et al., 2012	
NLD18-2	48.1	16.2	1.75	7.58	11.59	0.23	2.98	11.10	0.17	0.30	1222	154	109	-	244	19.2	401	28.1	24	Jenner et al., 2012	
NLD23-1	49.0	15.5	1.63	7.28	11.65	0.18	2.94	11.39	0.14	0.20	1066	147	108	1.00	439	19.8	339	27.1		Jenner et al., 2012	
NLD25-1	49.3	15.1	1.81	7.39	11.26	0.20	3.12	11.37	0.16	0.21	1110	144	113	0.99	1.54	493	21.9	349	30.9		Jenner et al., 2012
NLD27-1	49.2	16.4	1.30	8.51	11.59	0.20	2.57	10.23	0.13	0.17	915	138	99	0.74	382	21.6	341	24.6		Jenner et al., 2012	
NLD31-1	48.4	17.3	1.31	8.77	11.79	0.16	2.49	9.06	0.14	0.21	809	154	89	0.67	1.84	296	19.8	340	19.3		Jenner et al., 2012
NLD14-2	49.1	16.5	1.49	8.25	11.54	0.19	2.61	10.11	0.14	0.20	959	117	101	1.04	531	13.1	314	26.6		Jenner et al., 2012	
NLD30	49.5	15.7	1.54	7.93	10.43	0.16	2.87	11.11	0.09	0.27	1166	101	125	0.68	390	20.7	308	19.9		Jenner et al., 2012	
NLD11-1	50.1	15.8	1.56	7.12	11.78	0.18	2.77	10.05	0.21	0.40	1001	108	90	1.56	1.32	659	26.1	358	23.0		Jenner et al., 2012
NLD20	49.0	15.9	1.52	8.75	10.99	0.17	2.57	10.52	0.12	0.15	1106	102	125	0.73	1.84	327	28.6	315	15.7		Jenner et al., 2012
NLD35-2	50.8	14.6	1.78	6.50	10.59	0.21	3.12	10.03	0.15	0.24	1171	83	117	1.03	0.95	343	14.2	335	34.5		Jenner et al., 2012
NLD38	49.2	15.4	1.58	7.67	11.64	0.19	2.53	10.06	0.16	0.14	1078	148	108	0.47	17.77	206	43.9	369	31.6		Jenner et al., 2012
NLD41	62.0	14.1	1.22	2.00	5.05	0.18	4.71	8.28	0.32	0.77	423	49	145	2.14	0.84	682	50.0	436	118.8		Jenner et al., 2012
NLD43	50.1	14.1	1.66	6.82	11.10	0.21	2.73	10.86	0.12	0.12	1256	188	122	0.48	1.88	233	17.3	431	36.5		Jenner et al., 2012
NLD44	49.7	13.1	2.22	5.34	9.99	0.28	2.77	14.00	0.19	0.19	1672	173	163	0.67	24.9	257	24.9	528	52.6		Jenner et al., 2012
NLD45	50.1	13.2	1.99	5.79	10.54	0.26	2.58	13.91	0.14	0.13	1532	195	151	0.60	236	25.0	522	46.6		Jenner et al., 2012	
NLD40	49.9	15.7	1.19	8.24	12.48	0.19	2.35	9.83	0.08	0.10	898	183	98	0.34	3.02	206	16.8	410	26.7		Jenner et al., 2012
NLD39	52.3	12.5	2.40	3.79	7.97	0.30	3.40	15.55	0.43	0.26	1704	93	207	1.23	1.28	422	33.4	616	93.8		Jenner et al., 2012
NLD47	50.0	14.0	1.60	6.72	11.09	0.23	2.66	11.01	0.14	0.14	1247	211	125	0.52	2.56	222	16.4	434	35.5		Jenner et al., 2012
NLD42	49.7	15.6	1.07	8.51	12.50	0.19	2.28	9.18	0.07	0.04	856	194	90	0.20	3.69	177	8.0	364	25.8		Jenner et al., 2012
NLD48	49.3	15.3	1.08	8.36	12.68	0.19	2.14	10.47	0.05	0.04	879	176	94	0.27	3.79	139		353	25.0		Jenner et al., 2012
NLD51	48.6	16.2	1.10	8.73	13.06	0.16	1.97	9.62	0.11	0.10	854	170	83	0.48	3.50	211		331	23.3		Jenner et al., 2012
NLD50	49.7	15.3	1.19	8.07	12.27	0.16	2.34	10.04	0.11	0.12	831	169	85	0.46	3.14	237	15.8	374	31.6		Jenner et al., 2012
NLD49	49.7	14.4	1.35	7.52	12.57	0.21	2.32	11.90	0.09	0.06	1064	205	111	0.32	4.37	198	11.1	416	31.2		Jenner et al., 2012
0.00	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0								0.0		Jenner et al., 2012
NLD63	48.7	17.4	0.78	9.83	12.66	0.15	1.91	9.16	0.04	0.02	813	151	83	0.16	4.87	165	8.8	330	17.9		Jenner et al., 2012
NLD61	51.0	15.1	0.68	8.55	13.81	0.18	1.79	9.20	0.02	0.03	812	176	85	0.18	4.65	176	10.1	378	19.6		Jenner et al., 2012
NLD64	49.9	14.7	0.84	8.14	12.62	0.18	2.04	10.66	0.04	0.04	914	166	92	0.27	4.71	180		410	21.1		Jenner et al., 2012
NLD65	51.0	14.8	0.86	8.09	12.82	0.20	2.02	10.31	0.06	0.04	957	173	94	0.28	2.91	174	14.8	456	21.3		Jenner et al., 2012
NLD66	50.5	15.0	1.14	7.77	12.01	0.21	2.18	10.90	0.07	0.07	1052	130	108	0.42	14.8	201	14.8	453	26.0		Jenner et al., 2012
NLD58	49.9	14.3	1.12	7.53	12.05	0.19	2.39	11.22	0.06	0.04	1120	135	99	0.28	167	13.9	344	27.6			Jenner et al., 2012
NLD59	48.5	15.9	1.03	8.05	12.11	0.19	2.25	10.40	0.04	0.05	1092	121	85	0.37	138	7.8	339	26.3			Jenner et al., 2012

Sulphur data from Jenner et al. (2012) are the primary S values recalculated using Se as a proxy. Gold data from Moss et al. (2001) are close to detection limit and are not used. Sun et al. (2007) Au data are the median values of three replicate analyses.

Appendix 5. Regression coefficients and correlation coefficients of magmatic differentiation curves.

Appendix 5. Regression coefficients and correlation coefficients of magmatic differentiation curves.

Element		Troodos					Manus Basin			
		A	B	R ²	RMSD	NRMSD	A	B	R ²	
	MgO						MgO			
Au	>3.5 %	19.64	-1.395	0.53	0.28	17.63	>3 %	12.50	-0.575	0.92
	<3.5 %	0.89	-0.129				<3 %	1.23	-0.129	0.05
As		2584.00	-0.755	0.19	234.90	21.22		2737.30	-0.326	0.85
Sb		448.09	-1.141	0.57	8.63	10.31		97.09	-0.36	0.85
Se	>3.5 %	455.48	-0.828	0.22	26.89	19.23	>3 %	1118.90	-1.016	0.96
	<3.5 %	71.04	-0.027				<3 %	218.43	-0.027	0.34
S	>3.6 %	2448.90	-0.813	0.18	137.66	10.20	>3 %	3356.80	-1.016	0.96
	<3.6 %	137.09	0.9442	0.33			<3 %	655.30	-0.027	0.34
Cu	>4 %	214.40	-0.516	0.12	73.39	23.93	>3 %	1197.70	-1.232	0.56
	<4 %	8.62	1.3885	0.40			<3 %	27.95	0.3152	0.11
Zn		129.48	-0.281	0.21	83.18	11.87	>3 %	134.64	-0.3	0.48
							<3 %	85.88	0.099	0.13
Pb		2.65	-0.498	0.44	0.45	18.70		4.54	-0.358	0.80
Ti	>3.5 %	5.19	-1.179	0.74	0.19	17.00	>3 %	1.98	-0.672	0.61
	<3.5 %	0.81	0.4937	0.84			<3 %	0.65	0.3401	0.76
	Y						Y			
Au	>36 ppm	92.81	-1.313		0.42	16.66	<24 ppm	84.10	-1.313	0.31
	<36 ppm	0.109	0.8885	0.28			>24 ppm	0.64	0.7502	0.92
As		65.567	0.759	0.21	232.49	20.42		123.88	0.9137	0.87
Sb		2.3128	1.0635	0.53	9.98	11.57		3.04	1.0236	0.90
Se	>36 ppm	28.10729574	0.2456		31.40	19.24	>24 ppm	93.65	0.2456	0.35
	<36 ppm	22.179	0.5128	0.10			<24 ppm	7.86	1.2183	0.82
Cu	>25 ppm	708047	-2.779	0.29	38.40	5.74	>24 ppm	44.60	-0.217	0.02
	<25 ppm	31.925	0.3478	0.11			<24 ppm	2.84	1.4252	0.37
Zn		26.608	0.3744	0.27	73.75	10.94		37.71	0.2506	0.31
Pb		0.1468	0.6982	0.49	0.29	16.01		0.22	0.9242	0.73
Al ₂ O ₃	>15 ppm	21.072	-0.108	0.42	0.17	2.79				
	<15 ppm	10.184	0.1706	0.62						

RMSD root mean square of deviations (RMSD in ppb for Au, As, Sb and Se and in ppm for S, Cu, Zn and Pb), NRMSD normalised RMSD in per cent (Patten et al., 2015).

Appendix 6. Error propagations table

			Au	As	Sb	Se	Cu	Zn	Pb
Analysis error	$\sigma 1$	%	1.2	2.5	1.0	11.2	4.9	14.7	14.3
		Preferred Reference Materials	TDB-1	TDB-1	WMS-1	CH-4	BCR-2G	BCR-2G	BCR-2G
Dif. curve error	$\sigma 2$	%	16.7	20.4	11.6	19.2	5.7	10.9	16.0
Mass balance error	$\sigma \text{ tot}$	%	16.7	20.6	11.6	22.3	7.5	18.3	21.5

$\sigma 1$ corresponds to the errors of the elemental analyses from the preferred reference materials in Appendix 3; $\sigma 2$ corresponds to the errors of the differentiation curves from the NRMSD in Appendix 5. Errors are propagated as follow: $\sigma \text{ tot} = \sqrt{(\sigma 1^2 + \sigma 2^2)}$.