VU Research Portal

Pb-isotope systematics of a fossil hydrothermal system from the Troodos ophiolite, Cyprus: Evidence for a polyphased alteration history.

Booij, E.; Bettison-Varga, L.; Farthing, D.; Staudigel, H.

published in

Geochimica et Cosmochimica Acta
2000

DOI (link to publisher)

[10.1016/S0016-7037\(00\)00449-X](https://doi.org/10.1016/S0016-7037(00)00449-X)

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

Booij, E., Bettison-Varga, L., Farthing, D., & Staudigel, H. (2000). Pb-isotope systematics of a fossil hydrothermal system from the Troodos ophiolite, Cyprus: Evidence for a polyphased alteration history. *Geochimica et Cosmochimica Acta*, 64, 3559-3569. [https://doi.org/10.1016/S0016-7037\(00\)00449-X](https://doi.org/10.1016/S0016-7037(00)00449-X)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:

vuresearchportal.ub@vu.nl

Pb-isotope systematics of a fossil hydrothermal system from the Troodos ophiolite, Cyprus: Evidence for a polyphased alteration history

ERNST BOOIJ,^{1,*} LORI BETTISON-VARGA,² DORI FARTHING,² and HUBERT STAUDIGEL³

¹Faculteit der Aardwetenschappen, Vrije Universiteit Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

²Department of Geology, The College of Wooster, Wooster OH 44691 USA

³Scripps Institution of Oceanography, University of California, La Jolla, CA 92093-0225, USA

(Received September 21, 1999; accepted in revised form May 5, 2000)

Abstract—Pb-isotopic ratios have been determined on massive sulphides from the Troodos ophiolite and their inferred source rocks: epidiosites and greenschist altered dikes. The latter have distinctly higher Pb-isotope ratios than the sulphides. The high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for the whole rocks indicate the involvement of an old (sedimentary) Pb-component. Extensive leaching of three epidiosite samples shows that the radiogenic Pb can be removed and the resulting trend for the leached samples is consistent with a Pb-Pb age of ~ 95 Ma for these rocks. Inferred initial Pb isotope ratios are similar to those of the sulphides (this study) and fresh glasses from the Akaki Canyon in Cyprus. Therefore the Pb incorporated in the massive sulphides may originate from these greenschist facies hydrothermally altered rocks.

The isotopic composition of the leachate Pb points toward a sedimentary origin. Calculation of the Pb-isotopic ratios for 90 Ma old “average” Troodos sediment shows that the “foreign” Pb in the epidiosites may very well be derived from this source. This Pb probably does not reside within the mineral lattices of these metamorphic rocks, but rather is adsorbed on mineral surfaces or is present in microscopic particulate matter that may have been filtered from the circulating seawater. Unmodified seawater is considered an unlikely Pb source because of the extremely small dissolved Pb contents of seawater. Furthermore, no seawater or sedimentary signature is evident in the sulphides. Several models of Pb transport from different sources into these rocks may be envisaged, such as dissolution of Miocene evaporites and brine formation, equilibration of pore waters to the Pb isotope ratios of host sediments, and direct infiltration of deep sea particulate matter from the nepheloid layer. With the limited amount of data presently available it is impossible to critically determine the most likely processes of Pb transport. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

High-temperature, convectively driven submarine hydrothermal systems at sea floor spreading centres are believed to be of major importance to the heat transport from the newly formed oceanic crust. These seawater-fed hydrothermal systems are also believed to have major impacts on the chemical, mineralogical, and physical properties of the oceanic lithosphere. One of the most eminent processes is the formation of sulphide deposits by precipitation of sulphides from upwelling hot hydrothermal fluids upon mixing with cold circulating seawater in the more permeable portions in the upper parts of the oceanic lithosphere.

Present-day knowledge of these submarine hydrothermal systems comes partly from their most accessible component: the hot springs that emanate hydrothermal fluids at or near the ridge axis, but also from seawater–basalt and seawater–diabase interaction experiments and petrologic and geochemical studies on both in situ oceanic crust and ophiolites. Because the inferred source rocks from these hydrothermal systems are located at depths in the oceanic crust only reached by ODP/DSDP Hole 504B, most of the petrologic and geochemical evidence on these inferred source rocks come either from fault scarps along axial valleys or from ophiolites. It has been suggested that broad recharge and discharge fluid pathways

within the oceanic crust are characterised by specific mineral assemblages (Harper et al., 1988; Gillis and Robinson, 1990; Saccoccia and Gillis, 1995). In particular, epidiosites have been identified as remnants of pathways of discharging hydrothermal fluids, and as potential reaction zone rocks. Richardson et al. (1987) and Schiffman et al. (1987) proposed that these rocks represent the source rocks for the massive sulphide deposits formed at the seafloor/seawater interface.

In contrast to the greenschist-altered diabase with which they are often closely associated, epidiosites completely lack a relict igneous texture. They are characterised by a granular texture and mainly consist of epidote + quartz + magnetite/spinel $\pm$ chlorite $\pm$ actinolite (Richardson et al., 1987; Schiffman et al., 1987). The low $\delta^{18}\text{O}$ values observed for these rocks (2.8–5‰), the fluid inclusion trapping temperatures of up to 400°C, the high Ca and low Mg contents, and the general depletions of Cu and Zn in these rocks all support the suggestion that these rocks are the reaction products of the deep-seated interactions between the oceanic crust and seawater, in a process that produced ore-forming fluids (Richardson et al., 1987; Schiffman et al., 1987; Schiffman and Smith, 1988). Seyfried et al. (1988) suggested from experimental data and thermodynamic modeling that epidiosites may form by the interaction of compositionally evolved (Ca-Na-K-Cl) fluids with diabase or gabbros. Because of the low Mg contents of both ridge crest hydrothermal fluids and fluids from basalt and diabase alteration experiments, it has been suggested that the Mg removal accompanying the epidiosite formation may require fluid/rock

* Author to whom correspondence should be addressed (booe@geo.vu.nl).

mass ratios in the order of 1000 (Seyfried et al., 1988; Bettison-Varga et al., 1995).

Although it is very likely that the epidiosites form by interaction with compositionally evolved hydrothermal fluids, they probably do not form the only source for the metals incorporated into the massive sulphides. Studies on greenschist-altered rocks (not epidiosites) from the lower sheeted dikes from ODP Hole 504B also show significant depletions in Cu, Zn, and S (Zuleger et al., 1995). Furthermore, some debate exists as to whether or not the epidiosites were axis-parallel or oblique features, and therefore either related to on-axis or off-axis hydrothermal activity (Richardson et al., 1987; Schiffman and Smith, 1988). As a consequence of this: were the fluids that were responsible for the formation of the epidiosites essential to the formation of the massive sulphides, or had the ore-forming fluid chemistries been set prior to epidiotisation?

In order to identify the sources of the metals concentrated by submarine hydrothermal systems, Pb isotopes have been extensively used. Studies of sulphide deposits from unsedimented spreading centres indicate that the Pb-isotopic compositions of the sulphides are similar to, and in general show smaller ranges than the underlying basalts (Brévar et al., 1981; Hegner and Tatsumoto, 1987; Vidal and Clauer, 1981). This indicates that the primary source of the Pb is the crust itself, and that the mobilisation of Pb by these hydrothermal systems has an averaging effect on the variation in Pb-isotopic compositions of the ore-forming fluids. However, studies from sedimented ridge crests such as the Guyamas Basin and Escanaba Trough indicate that overlying sediments provide an additional source of Pb. In these cases the massive sulphide deposits contain a mixture of basalt-derived and sediment-derived Pb (LeHuray et al., 1988).

Pb isotopic compositions as well as other isotopic and trace element evidence indicates that Troodos crust has a significantly different composition than MORB, and carries a continental component (Spooner and Gale, 1982; Hamelin et al., 1984; Rautenschlein et al., 1985), consistent with a suprasubduction setting of formation for Troodos. Spooner and Gale (1982) suggest that massive sulphides from Troodos have slightly more radiogenic Pb isotope compositions than gabbros from the underlying crust and suggest a mixed igneous and seawater source for the sulphide-Pb. However, this suggestion was disputed by Doe (1982) on the basis of the extremely small concentrations of dissolved Pb in seawater, and the unrealistically high flow rates of seawater through the system required to supply the necessary amounts of Pb. The study of Hamelin et al. (1988) suggests that the source rocks of the individual massive sulphide deposits may be traced using Pb-isotopes. These authors found distinct but limited ranges for the Pb isotopic compositions of the individual massive sulphide deposits from Troodos.

In this paper, Pb isotopic compositions of inferred source rocks (epidiosites and greenschist-altered diabase), massive sulphides, and sulphide separates from the inferred source rocks are presented. An attempt is made to come to a better understanding of the systematics of lead in the oceanic crust during hydrothermal alteration, and to evaluate the relationship between the epidiosites and the massive sulphide deposits. Furthermore, the influence of several other possible sources of Pb such as sediments and the fluids responsible for the recent

(< ~ 2 Ma, Robertson, 1977) serpentinisation of the Troodos mantle sequence is evaluated.

2. GEOLOGIC SETTING

The Troodos ophiolite is a remnant of ~92 Ma Cretaceous seafloor, formed in the former Tethys ocean. Varga and Moores (1985) suggested that in Troodos three spreading centres and ridge jumps were preserved in the form of structurally defined grabens: Solea, Mitsero, and Larnaca (Figure 1). The inferred upflow systems of the hydrothermal fluids responsible for the formation of massive sulphide deposits in the Solea and Mitsero grabens have been studied by several authors (e.g., Schiffman et al., 1987; Richardson et al., 1987; Bettison-Varga et al., 1992). These zones of discharging compositionally evolved hydrothermal fluids are characterised by the extensive alteration of diabase to epidote + quartz $\pm$ chlorite assemblages called epidiosites, which are believed to be a primary source of metals for the overlying massive sulphide deposits.

Epidiosites have granoblastic textures of coarse to fine-grained epidote and lobate quartz that show mutually inclusive relations. Epidiotisation occurs in regions of extensive alteration surrounded by less intensely altered areas. Completely epidiotised dikes may occur adjacent to dikes with igneous textures altered to a greenschist facies assemblage of chlorite + quartz + albite + actinolite with minor epidote. From field evidence Bettison-Varga et al. (1992) suggested that in zones of intense epidiotisation flowpaths of upwelling hydrothermal solutions are mainly controlled by fracturing of the diabase. In zones of minor epidiotisation, fluid flow may have been grossly parallel to dike margins (Richardson et al., 1987).

3. SAMPLING AND EXPERIMENTAL METHODS

Samples of epidiosites, greenschist-altered diabase, and sulphides from the sheeted intrusive complex were collected from the northern, central, and detachment epidiosite zones of the Solea graben and from the Phterykhoudi zone of the Mitsero graben. Sulphides from massive sulphide deposits from the Solea, Mitsero, and Larnaca grabens were also sampled. Approximate sampling locations are given in Figure 1.

In order to identify other possible sources of Pb in the Troodos hydrothermal system, two sediment samples were also analysed. Both samples are deep-water pelagic limestones from Yerasa and represent the Paleogene Pakhna formation capping the Troodos basement. These data serve to expand the limited Pb-isotopic database for Troodos sediments from Hamelin et al. (1988). Another possible source for fluids circulating through the Troodos crust at some stage in its history may have been associated with the serpentinisation of the Troodos mantle sequence (Magaritz and Taylor, 1974), which occurred due to the underplating of a microcontinent (Erostenes seamount?) under Cyprus (Robertson, 1977). In order to test the isotopic composition of these fluids we analysed two serpentinites from Troodos. Since Pb-contents of fresh mantle rocks are generally very low, the isotopic ratios of these rocks will be very susceptible to any introduction of Pb from a different source.

Whole rock epidiosite and greenschist-altered diabase, as well as the sediment and serpentinite samples were crushed and only chips from sample interiors were ground in agate ball mills. Samples were then washed in milli-Q water. Epidotes and sulphides were separated from the whole rocks using heavy liquid and magnetic separation techniques, and subsequently ultrasonically cleaned in milli-Q water, leached in 3 N HCl, and washed again three times with milli-Q water. Pb and U were separated using conventional ion-exchange techniques.

Three samples were selected for a further investigation and were separated into a fine fraction (< ~10 μ m) and a coarse fraction (> ~10 μ m). The fine fraction was dissolved without further leaching steps. The coarse fraction was first ultrasonically leached with 0.5 N

Fig. 1. Simplified map of the Troodos ophiolite shows volcanic units and dikes, and the igneous complex (modified after Varga and Moores, 1985). Also shown are the three structural grabens (Solea, Mitsero, and Larnaca) and approximate locations of graben axes. Locations of the reaction zones sampled in this study are given in the insert maps (modified after Bettison-Varga et al., 1992 and Bickle and Teagle, 1992).

Table 1. Pb and U isotopic data from massive sulphides, epidiosites, and greenschist assemblages from the sheeted intrusive complex of Troodos.

Sample number	Lithology	Location	Non-age corrected Pb isotopic ratios			Pb (ppm)	U (ppm)	$^{238}\text{U}/^{204}\text{Pb}$
			$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$			
71294-2	massive sulphide	Troulli mine	18.55	15.54	38.53	18 ± 5^b	—	—
71394-1	massive sulphide	Kokknoyia mine	18.54 (18.54) ^a	15.59 (15.59) ^a	38.54	5 ± 3^b	0.006	0.08 ± 0.05
71394-3	massive sulphide	Agrokipia mine	18.55 (18.54)	15.58 (15.58)	38.53	5 ± 3^b	0.029	0.37 ± 0.22
71894-1	massive sulphide	Apliki mine	18.52 (18.46)	15.56 (15.56)	38.34	35 ± 6^b	2.158	3.9 ± 0.6
71394-4	epidote separate from epidosite host	Mitsero graben	18.54	15.59	38.47	—	—	—
71394-5	sulphide separate from epidosite host	Mitsero graben	18.48	15.55	38.41	—	—	—
71394-6	epidosite	Mitsero graben	18.99 (18.91)	15.67 (15.67)	38.60	1.2	0.125	6.6
71394-7	greenschist assemblage	Mitsero graben	18.93 (18.89)	15.67 (15.67)	38.56	1.7	0.066	2.4
71394-7s	sulphide from 71394-7a	Mitsero graben	18.58	15.59	38.54	—	—	—
71494-1	epidosite	Solea graben-NZ	18.94 (18.88)	15.64 (15.64)	38.47	1.1	0.077	4.4
71494-3	epidosite	Solea graben-CZ	19.24 (19.21)	15.71 (15.71)	38.64	2.8	0.107	2.4
71494-3	leached epidosite		19.80	15.64	39.21	—	—	—
71494-3	fine fraction of epidosite 71494-3		19.00	15.69	38.43	—	—	—
71494-3	0.5N HCl leachate of 71494-3		18.96	15.70	38.45	—	—	—
71494-3	HCl/HF leachate of 71494-3		19.09	15.72	38.47	—	—	—
71494-4	epidosite	Solea graben-CZ	19.15 (19.12)	15.68 (15.68)	38.58	3.3	0.094	1.8
71494-4	leached epidosite		19.13	15.61	38.83	—	—	—
71494-4	fine fraction of epidosite 71494-4		19.00	15.70	38.45	—	—	—
71494-4	0.5 N HCl leachate of 71494-4		19.04	15.71	38.50	—	—	—
71494-4	HCl/HF leachate of 71494-4		19.06	15.72	38.53	—	—	—
71494-5	epidosite	Solea graben-CZ	18.80 (18.72)	15.63 (15.63)	38.52	1.1	0.101	5.8
71594-5	epidosite	Solea graben-DZ	18.74 (18.54)	15.66 (15.66)	38.51	0.6	0.136	14.3
71594-5e	epidote separate from 71594-5	Solea graben-DZ	18.88	15.62	38.47	—	—	—
71694-2	greenschist assemblage	Solea graben-CZ	18.95 (18.88)	15.70 (15.70)	38.53	1.2	0.098	5.2
71694-2s	sulphide separate from 71694-2	Solea graben-CZ	18.56	15.59	38.44	—	—	—
71694-4	epidosite	Solea graben-CZ	18.83 (18.76)	15.65 (15.65)	38.43	1.5	0.111	4.7
71694-4	leached epidosite		18.78	15.59	38.58	—	—	—
71694-4	fine fraction of epidosite 71694-4		—	—	—	—	—	—
71694-4	0.5 N HCl leachate of 71694-4		18.73	15.66	38.28	—	—	—
71694-4	HCl/HF leachate of 71694-4		18.86	15.67	38.42	—	—	—
71694-6	sulphide from quartz vein in greenschist host	Solea graben-CZ	18.45	15.55	38.32	18 ± 6^b	—	—
71994-3	epidosite	Solea graben-CZ	18.94 (18.40)	15.63 (15.63)	38.51	0.2	0.121	38.1
71994-4	sulphide separate from epidosite host	Solea graben-CZ	18.48	15.58	38.40	—	—	—
Sediments								
YS01	pelagic sediment	Yerasa	18.80	15.70	38.71	4.62	—	—
YS44	pelagic sediment	Yerasa	18.86	15.70	38.93	4.11	—	—
Serpentinities								
S1	serpentinite	Troodos	18.32	15.67	38.09	3.45	—	—
S2	serpentinite	Troodos	18.34	15.64	38.06	0.52	—	—

NZ = northern zone, CZ = central zone, and DZ = detachment epidosite zones as defined by Schiffman et al. (1987) and Bettison-Varga et al. (1992).

^a Values in parenthesis are age-corrected assuming a formation age for Troodos of 92 Ma (Mukasa and Ludden, 1987).

^b Analysed by XRF.

HCl for 3 h, followed by a second ultrasonic leach in a 6 N HCl/4% HF mixture for 15 min. Untreated fine fractions, the two leachates of the coarse fraction, and the leached coarse fractions were all analysed for Pb isotopic ratios.

The isotopic data were collected on a Finnigan MAT 261 solid source mass spectrometer. Pb was analysed using the silica gel/H₃PO₄ method on single zone refined Re-filaments, and U was analysed as a phosphate using double filaments. Except for the leached samples and leachates, Pb isotope data for all other samples were analysed twice from the same sample dissolution, and the data given in Table 1 are averages of both runs. The reproducibility for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios was better than 1.22, 1.53, and 1.23‰, respectively. All Pb isotopic ratios were corrected to account for mass-fractionation by 1.44‰ per atomic mass unit. Repetitive runs of the NBS981 Pb standard ($n = 5$), during the course of this study indicate that the reproducibility of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios was better than 0.19, 0.24, and 0.41‰, respectively. The reproducibility of the U/Pb ratio was better than 0.25%. Total Pb-blanks varied between 70 and 150 pg.

To be able to investigate any possible contamination introduced by

chemicals used in the laboratory, Pb isotopic ratios for a number of chemicals used in the clean lab were analysed. HBr, HNO₃, and trichloromethane (used as rinsing agent in the heavy liquid separation) show only a very limited variation in their isotopic ratios, with an average composition of: $^{206}\text{Pb}/^{204}\text{Pb}$ 17.76 ± 0.06 ; $^{207}\text{Pb}/^{204}\text{Pb}$ 15.61 ± 0.04 , and $^{208}\text{Pb}/^{204}\text{Pb}$ 37.63 ± 0.07 (analyses by S. Tom-massini).

Pb concentrations for the whole rocks and epidote separates were determined by isotope dilution, Pb concentrations for the sulphides were determined by XRF using a Philips PW1404 sequential X-ray spectrometer equipped with a Rh-anode tube. U-contents were determined by isotope dilution.

4. RESULTS

Distinct differences exist between the isotopic ratios of the sulphides and the epidiosites and greenschist altered diabases (Table 1). $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of massive sulphide deposits and sulphide separates from the

Fig. 2. (a,b) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams showing data from this study. Also shown are fields for massive sulphides (Doe and Zartman, 1979; Spooner and Gale, 1982; Hamelin et al., 1988), glasses (Rautenschlein et al., 1985), Troodos sediments (Hamelin et al., 1988 and this study), and the Indian MORB array (Ito et al., 1987; Mahoney et al., 1989; Mahoney et al., 1998; Rehkämper and Hofmann, 1997). Fields for seawater were plotted using data from Mn nodules (Abouchamie and Goldstein, 1995; von Blanckenburg et al., 1996; Ling et al., 1997). The linear trend of the leached epidosite samples has a slope of 0.0479 ($R^2 = 0.994$), which is consistent with a Pb-Pb age of ~ 95 Ma.

greenschist assemblages vary between 18.45–18.58, 15.54–15.59, and 38.32–38.54, respectively. Contrasting to this, the reaction zone rocks show isotopic compositions ranging from 18.74 to 19.24, 15.63 to 15.71, and 38.47 to 38.64. The data are plotted in Figures 2a,b and it is clear that both the sulphides from the massive sulphide deposits and the sulphide separates from the epidosite and greenschist altered dikes are less radiogenic than the epidotes and greenschist-altered diabase. In general, isotopic compositions of the altered Troodos rocks differ from present-day MORB by having elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$ ratio. This is in broad accordance with the interpretation that the Troodos mantle source had a continental component, consistent with the generally accepted suprasubduction zone setting of formation for Troodos (Robinson et al., 1983; Rautenschlein et al., 1985).

The Pb concentrations of the epidotes and the greenschist diabases range from 0.2 to 3.3 ppm. Many samples have concentrations exceeding 1 ppm, which is high for typical MORB (Hofmann, 1988), but may be normal for Back Arc Basin Basalt (BABB) (Cohen and O'Nions, 1982; Gribble et al., 1998). U concentrations vary between 0.07 and 0.14 ppm, which is within the ranges reported for both MORB and BABB (Hofmann, 1988; Cohen and O'Nions, 1982). Pb and U concentrations for the sulphides range from 5 to 35 ppm and from 0.007 to 2.16 ppm, respectively. The two serpentinites have Pb concentrations of 3.45 and 0.52 ppm, which are very high when compared to fresh mantle rocks.

From Figures 2a,b it is clear that the Pb-isotopic ratios for the massive sulphides and the sulphide separates from the epidotes show only limited variations and are very similar to those of fresh Troodos glasses as reported by Rautenschlein (1985). This similarity suggests that the Pb incorporated in the sulphides is derived from the Troodos basement. Samples from the epidosite zone show much more variation and show a positive correlation between $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. Since most

of the samples are from the Solea graben, the trend of the isotopic compositions for epidotes and greenschist altered diabase is defined by the hydrothermal system operating in that part of the Troodos crust. However, the altered diabase samples from the Mitsero graben have isotopic ratios that fall within the range of the Solea graben samples and also show the elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. An epidote separate and epidosite host rock (samples 71594-5 and 71594-5e) have nearly identical $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, whereas the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of the epidosite host rock is slightly higher. This epidote separate has distinctly higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, but a similar $^{208}\text{Pb}/^{204}\text{Pb}$ ratio to the epidote separate from the Mitsero graben (71394-4).

In Figures 2a,b our sulphide data are compared with published analyses from Troodos massive sulphide deposits (Doe and Zartman, 1979; Hamelin et al., 1988; Spooner and Gale, 1982), and glass compositions (Rautenschlein et al., 1985). Data for Moussolos massive sulphides from Spooner and Gale (1982) have been excluded, because this deposit is located within the very complex southeastern region of the ophiolite. Its close proximity to the Arakapas Transform fault introduces tectonic and mantle source complexities that are not a factor in the northern portion of the ophiolite. It is clear that the sulphide data from our study are very similar to those of previous studies. Data for the Troodos sulphides as well as the glasses seem to fall on the radiogenic end of the Indian MORB array. If the Tethyan mantle from which Troodos had formed had a composition similar to that of the present-day Indian Ocean, this would limit the requirement for a subducted sediment component to explain the high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$ ratio for Troodos.

As stated earlier, isotopic compositions of the inferred source rocks are more radiogenic than the sulphides and glasses. In general, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for the epidotes and greenschist-altered dikes show a broad positive relation-

ship, trending away from the sulphide and glass fields toward more radiogenic values. $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for these samples show a positive trend, which has a much shallower slope than the Indian MORB array, indicating either radiogenic growth at low κ ($^{232}\text{Th}/^{238}\text{U}$) values or mixing of magmatic Pb with an unknown component, or both.

The high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of the epidiosites and greenschist-altered dikes are especially puzzling because this ratio is nearly independent of any age correction. Therefore, it is clear that either these rocks are not the source rocks for the massive sulphides, or the supposed source rocks underwent a second "alteration event" that apparently did not influence the Pb isotopic composition of the sulphides enclosed in them.

The two pelagic sediments analysed here have isotopic ratios very similar to those of the sediment values reported by Hamelin et al. (1988), and are also plotted in Figures 2a,b. The two serpentinites have high Pb-contents compared to fresh mantle rocks. Since these rocks are clearly metasomatised, a large fraction of their Pb inventory may have been added during the serpentinitisation of these mantle rocks. The serpentinites also possess elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, but their $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are lower than any of the other analysed rocks from this study. Therefore, the fluids responsible for the serpentinitisation were probably not responsible for the inferred "second alteration event" that influenced the Pb isotopic ratios of the epidiosite and greenschist-altered dikes.

The fine fractions and both leachates (0.5N HCl and HCl/HF) from the three epidiosite samples that were further investigated have a similar $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ relationship to the untreated epidiosites and greenschist-altered diabase. In the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, leachates and fines show a linear trend almost parallel to the untreated samples, but offset to slightly lower $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. Their isotopic ratios differ significantly from the leached epidiosite samples. The three extensively leached epidiosite samples define linear trends in both $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic space. The least radiogenic sample of these (71694-4) has a composition very similar to that of the glasses and the sulphides.

From Figures 2a,b it can be constructed that two out of three samples that were used for the extensive leaching study (71494-3 and 71694-4) fall within the mixing arrays defined by the leachates, fine fractions, and leached samples. One sample, however (71494-4), falls outside the mixing array, mainly because the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of the unleached sample is higher than that of the sample used for the leaching experiment. Because different sample splits were used for the leached and unleached samples, we attribute this to sample heterogeneity.

Although only three samples were chosen for the extensive leaching experiment, the slope of these samples in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram has a slope of 0.0479. If it is assumed that this trend is solely due to radiogenic in-growth from the decay of U, the data yield a Pb-Pb age of about 95 Ma for the leached samples. This age is indistinguishable from the 92 Ma U/Pb zircon age for the formation of Troodos (Mukasa and Ludden, 1987). On-axis high-temperature alteration occurs during the formation of the crust and is generally considered to be short-lived. Therefore, the ~95 Ma Pb-Pb age for the leached epidiosites either records the formation age of the

ophiolite itself or the age of the hydrothermal event that caused the formation of the epidiosites.

5. DISCUSSION

Several features of the Pb-isotopic compositions for the epidiosites and greenschist-altered diabase from this study need to be explained:

- 1) the characteristic high $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of these extensively altered rocks. The high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios exclude radiogenic growth as the sole explanation of the observed trends;
- 2) the linearity of the data and the trend away from the sulphide and glass isotopic compositions;
- 3) the different isotopic signatures between greenschist altered host rocks and sulphide separates.

Analytical errors are considered unlikely explanations for the array of data given the non-mass fractionation trend of the array and the fact that none of the tested chemicals used in the laboratory have isotopic ratios that would provide suitable endmembers for the trends in Figures 2a,b to be explained by two-component mixing. Geologic sampling errors are considered unlikely because of the similarity in behaviour of isotopic compositions for sulphide separate/host rock pairs from the different grabens.

5.1. Troodos Mantle Source

The investigation of hydrothermal ore-forming processes requires knowledge of the rocks that host the deposits. This especially holds true for ophiolites because these ancient pieces of oceanic crust often have been formed in areas of "contaminated mantle sources" such as back arc-basins, immature island arcs, or initial stages of rifting. In many cases, such as Samail (Chen and Pallister, 1981) and the many massifs studied by Hamelin et al. (1984), initial intra-massif isotopic variations have been influenced by U and Th decay since the formation of the ophiolites. Accurate determination of initial compositions, and therefore also of the initial intra-massif heterogeneities may be hampered by perturbations in the U-Th-Pb system by alteration.

Total ranges of previously reported Pb-isotopic ratios for whole rocks from Troodos are: $^{206}\text{Pb}/^{204}\text{Pb} = 16.62\text{--}18.82$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.37\text{--}15.61$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.51\text{--}38.44$ (Hamelin et al., 1984; Hamelin et al., 1988; Spooner and Gale, 1982). Data from one dolerite dike from the study of Hamelin et al. (1984) were excluded because this sample was extremely radiogenic, and falls well outside the fields defined by the other data. These large ranges in isotopic ratios were derived from a wide variety of rocks, including harzburgites, peridotites, gabbros, dikes, and lavas. These variations are almost similar to the ranges reported for Indian MORB, and appear to reflect the extreme Pb-isotopic heterogeneity within this ancient piece of oceanic crust. In contrast to these findings are the results from Rautenschlein et al. (1985) who found a relatively limited array of Pb-isotopic values for fresh hand-picked glass separates from the Akaki river section from the eastern margin of the Mitsero graben. This graben also hosts the Agropikia deposits.

The main Pb isotopic characteristic of the Troodos rocks

(including glasses and sulphides) is their high $^{207}\text{Pb}/^{204}\text{Pb}$ ratio relative to that of typical Pacific and Atlantic MORB. However, Pb-isotopic ratios of glasses and sulphides for Troodos fall at the radiogenic end of the Indian MORB array. Epidiosites and greenschist-altered dikes have even more elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, and clearly plot outside the Indian MORB-array. The high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for the Troodos rocks are virtually independent of any age correction because of the present-day near extinction of ^{235}U . This high $^{207}\text{Pb}/^{204}\text{Pb}$ ratio has been interpreted as reflecting the involvement of a continental component in the generation of the Troodos crust, and therefore an origin relating to a supra-subduction zone environment (Hamelin et al., 1984; Rautenschlein et al., 1985). Alternatively, the Troodos mantle source may have already had somewhat elevated $^{207}\text{Pb}/^{204}\text{Pb}$ isotopic ratios similar to the present-day mantle underlying the Indian Ocean.

The large range of isotopic compositions found for the Troodos extrusives and igneous rocks may have been caused by the introduction of varying amounts of subducted sediments to the mantle source or insufficient mixing to homogenise the isotopic signatures. In addition, many of the Troodos rocks have undergone extensive alteration and may therefore not record the initial Pb isotopic systematics. Radiogenic growth after the disturbance of the U-Th-Pb system would complicate the isotopic systematics even further. However, the limited range of Pb-isotopic ratios for the glasses suggests that alteration and radiogenic growth may have caused much of the variation observed in the other samples.

5.2. Sources of Massive Sulphide Pb

The isotopic ratios for the sulphides from both the massive sulphides deposits and the sulphide separates from the greenschist-altered diabases are very similar to those of the glasses. This indicates that the Troodos basement supplied most of the Pb incorporated in the massive sulphides. This is in accordance with previous findings for in situ sulphide deposits from sediment starved ridges, for which generally no other source of Pb such as sediment or seawater is identified (Brévar et al., 1981; Hegner and Tatsumoto, 1987; Vidal and Clauer, 1981).

With the exception of the leached epidiosites and one epidote separate, all epidiosites and greenschist-altered diabases have $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ isotopic ratios higher than the sulphides or the glasses. A 92 Ma age correction for the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios (see Table 1) does not bring the Pb isotopic ratios for these rocks back into the fields for the glasses and sulphides. For any reasonable value of μ ($^{238}\text{U}/^{204}\text{Pb}$), the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio is almost insensitive to any age correction, and therefore suggests that these rocks contain an additional Pb component that has been mixed with the magmatic Pb. Because geochemical, spatial, and geologic relationships support the assumption that the epidiosites and greenschist-altered dikes are related to the formation of the massive sulphide deposits, it is probable that initial isotopic ratios for these rocks were close to those of the glasses. In this case, a second alteration event must have occurred that significantly changed the initial isotopic ratios of these rocks.

As stated before, the linear trend of the three extensively leached epidiosites (that show the largest range in $^{206}\text{Pb}/^{204}\text{Pb}$ ratios) may be consistent with a Pb-Pb age of ~ 95 Ma, which

is indistinguishable from the age of Troodos. This suggests that age-correcting these three leached epidiosites would translate them back into the glass and sulphide fields. Unfortunately no U, Th, and Pb concentrations for the leached samples were determined, and hence this can not be directly checked. However, the excellent linearity of the data in both $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ space, and the fact that extrapolation of both trends passes through the glass and sulphide fields are taken as strong evidence supporting the conclusion that (after age correction) the leached epidiosites have isotopic ratios similar to the sulphides.

A later alteration event must have changed the isotopic ratios of the epidiosites and greenschist-altered dikes, while leaving the ratios of the sulphides in the greenschist hosts unchanged. Low-temperature alteration phases such as clays and zeolites are absent from these rocks; therefore, this later alteration event was probably of very low grade, and may involve only Pb adsorption to mineral surfaces. The much higher Pb contents of the sulphides will make their isotopic ratios less susceptible to Pb addition than the epidiosites and greenschists.

5.3. Sources of Epidiosite and Greenschist-Altered Diabase Pb

The three extensively leached epidiosites clearly show the effects of radiogenic Pb growth. If the ~ 95 Ma Pb-Pb age defined by these three samples has age significance, then age correction of these samples would take their ratios back to the glass and sulphide fields. From the linear trends in the Pb-isotopic diagrams, approximate μ ($^{238}\text{U}/^{204}\text{Pb}$) and ω ($^{232}\text{Th}/^{204}\text{Pb}$) values for these leached samples can be determined. If it is assumed that the two most radiogenic samples had initial ratios close to the least radiogenic sample (which is close to the glass and sulphide field), μ -values would be 69 and 23, and ω -values would be 134 and 53. κ -values ($^{232}\text{Th}/^{238}\text{U}$) determined from the linear trend of these samples in the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram would be close to 2.0. This is low for a normal depleted upper mantle (MORB) source, which has a κ -value of 3.7–3.8 (Galer and O'Nions, 1985). During high-temperature water/rock interaction Pb is removed while seawater U is added to the crust. Th seems to behave largely immobile (Michard et al., 1983; Michard and Albarède, 1985; Chen et al., 1986; 1987). This will lead to high μ and ω values and low κ -values for altered oceanic crust, and hence is consistent with the trends observed for the leached epidiosites.

Leachates and fine fractions from the three epidiosites all show high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, which are within the same range as the untreated epidiosites and greenschist-altered diabases, indicating that the $^{207}\text{Pb}/^{204}\text{Pb}$ signal of the untreated rocks is overwhelmed by the “foreign” Pb. The most likely explanation seems to be Pb and U mobility during low-temperature alteration. Th seems to be almost immobile under these conditions.

From Figure 2b it is clear that the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the “foreign” Pb for a given $^{206}\text{Pb}/^{204}\text{Pb}$ ratio differ significantly from the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio of the sediments. If the “foreign” Pb was added in recent times from postobduction groundwaters then the leachate Pb is expected to fall in a mixing array between the sediment and the altered diabase fields, which is clearly not the case. Other possible sources of the “foreign” Pb include anthropogenic aerosols. However, European anthropo-

Fig. 3. Schematic representation of the direction of change of the Troodos sediment field upon age correction using $\mu = 8.0$ and $\kappa = 5.9$ (solid arrow) and 8.0 (dashed arrow). The length of the arrow represents a 92 Ma age correction.

genic pollutant Pb is characterised by distinctive unradiogenic compositions (Hamelin et al., 1990), and does not seem to be a significant contributor in this system.

The $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for the untreated whole rock samples and the "foreign" Pb as recorded in the leachates and fine fractions is very similar to that of Troodos sediments (this study and Hamelin et al., 1988), but also to that of seawater (see Figure 2a). Present-day $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for the leachates and fine fractions are slightly lower than those of Troodos sediments. If a sediment component is responsible for the "foreign" Pb in the epidiosites and greenschist-altered dikes, we may attempt to roughly calculate the average isotopic composition of the Troodos sediments at any time in the past. The average κ and μ values of present-day deep-sea sediments are close to 5.9 and 7.2, respectively (White et al., 1985; Ben Othman et al., 1989). Assuming similar κ and μ ratios for the Troodos sediment component responsible for the foreign Pb in the epidiosites and greenschists would move the sediment field back in the direction of the "foreign" (= leachate) Pb, but an age correction of 95 Ma would not be sufficient to make the two fields overlap. Longer and therefore unrealistic times (since they exceed the age of the ophiolite) would be required for sufficient radiogenic growth. A simple model calculation reveals that higher $^{232}\text{Th}/^{238}\text{U}$ ratios in the order of 8.0 would be required for the sediments to make both fields overlap within about 95 Ma. This procedure is illustrated in Figure 3. This required κ value is slightly high for deep-sea sediments, but not unusual (White et al., 1985; Ben Othman et al., 1989).

Dissolved Pb contents of deep seawater are in the order of 1–80 pg/g (Schaule and Patterson, 1981; Chen et al., 1986). From the trends in Figures 2a,b it may be concluded that at least

half of the Pb inventory of the epidiosites and greenschist-altered dikes is made up of "foreign" Pb. For the samples with the highest Pb contents (71494-3 and 71494-4) this implies that at least about 1.5 ppm of seawater Pb would have been added. In order to add these amounts of Pb from seawater to the rocks, alteration at minimum water/rock mass ratios in the order of 2×10^4 – 1.5×10^6 (assuming 100% scavenging efficiency) would be required. Such extreme minimum W/R ratios seem unlikely, and therefore dissolved Pb from unmodified seawater is considered an unlikely source for the "foreign" Pb component. Furthermore, no high $^{207}\text{Pb}/^{204}\text{Pb}$ seawater signal is evident from the sulphides analysed, which also argues for a limited influence of dissolved seawater Pb during the ore-forming phase of these systems.

5.4. Nature of the Alteration Event

The Pb-isotopic data appear to require a process that has affected the Pb-isotope systematics of the epidiosites and greenschist-altered dikes without apparently affecting the sulphides included within them. No petrographic evidence exists for a low-grade metamorphic overprint of the epidiosites and greenschists. With the possible exception of some of the chlorites, all minerals in the epidiosites and greenschists look very fresh in thin section. In addition, no low-temperature mineral phases such as clay minerals or zeolites were identified.

The very similar isotopic ratios of the individual samples for the $<10\text{-}\mu\text{m}$ fractions and the 0.5 N HCl and HCl/HF leachates combined with the apparent success in removing the "foreign" Pb by the leaching procedure, suggests that the bulk of the "foreign" Pb does not reside within mineral lattices of the

Fig. 4. Age-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $1/\text{Pb}$ and Pb content for epidiosites and greenschist dikes. For simple two-component mixing $^{206}\text{Pb}/^{204}\text{Pb}_i$ is predicted to correlate linearly with $1/\text{Pb}$, opposite to what is observed.

mineral phases of the epidiosites and greenschist dikes. It seems more likely that a readily dissolvable mineral phase such as carbonate, or an adsorption or electrostatic charge balancing process is responsible for the uptake of the foreign Pb in these samples. Because carbonates have not been identified in these rocks in any significant amounts, this possibility is discarded.

An alternative process that may explain the introduction of a sedimentary component into these rocks is the infiltration of suspended deep-sea particulate matter, that mainly consists of terrigenous sediments into the epidiosites and greenschist-altered dikes. A similar process was also proposed by Snow et al. (1993) to explain the extremely radiogenic nature of altered abyssal peridotites.

If the sediment component were introduced mechanically, the epidiosites and greenschist dikes would act as filters for the sediment-bearing bottom water circulating at low temperatures. From the differences in Pb isotopic compositions between sulphides and epidiosites and greenschist dikes, it is clear that the infiltration of the particulate matter postdates the formation of the epidiosites (and sulphides). Formation of epidiosites involves significant mass transfer and is accompanied by a volume decrease. Many of the epidiosite samples show some porosity, but it is in general less than ~ 2 vol%. These pores may have acted as loci for localised downwelling of seawater.

In Figure 4 the correlation between age-corrected $^{206}\text{Pb}/^{204}\text{Pb}$, $1/\text{Pb}$, and Pb content for epidiosites and greenschist dikes is depicted. From this figure it is clear that the alteration process did not involve simple binary mixing between an "uncontaminated" Troodos crust and a homogeneous sedimentary component. More complex mixing of three or more components may accommodate the data, but attempts to quantify the actual members are very difficult.

Although the actual number of "foreign" components remains unclear, Pb isotope relationships imply that at least half of the Pb inventory of the untreated epidiosites and greenschist dikes is made up of the "foreign" sediment-derived Pb. For the samples with the highest Pb contents this means that at least about 1.5 ppm of sediment-derived Pb was added to these

samples. Typical particulate matter concentrations from the deep-sea nepheloid layer are in the order of 0.2 to 0.5 g/L (Open University Course Team, 1989). Given that the Pb concentrations of deep-sea sediments average about 25 ppm (White et al., 1985; Ben Othman et al., 1989) and assuming 100% removal of the suspended material by the infiltration into the epidiosites, we can calculate approximate water/rock ratios required to explain the observed trends. Assuming an average density of 2.85 g/cm^3 for Troodos diorite (Smith and Vine, 1989) it appears that W/R volume ratios in the order of 300–800 would be required. These numbers only serve as an estimate because the efficiency of the implied infiltration process is difficult to assess, but is certainly less than 100%. On the other hand, during the submarine attenuation of the ophiolite (Bettison-Varga et al., 1992) "large" quantities of particulate matter may be introduced along faults and fissures in one dramatic event.

Other possible mechanisms of the introduction of sediment-derived Pb into the epidiosites may include seawater that had previously undergone isotopic exchange with deep-sea sediments covering the ophiolite, or brines formed by dissolution of the Miocene evaporites (mainly gypsum) by seawater. Both types of fluids could carry a sedimentary Pb signal into the epidiosite and greenschist-altered dikes. Later by changing physicochemical conditions such as solution pH, Eh, $f\text{O}_2$, etc., Pb may be immobilised by adsorption on mineral surfaces (Morel, 1983; Honeyman and Santchi, 1988), or precipitate from solution as salts, oxides, or hydroxides. So far, no Pb isotopic ratios of either deep-sea sediment porewaters or Troodos evaporites have been determined and therefore these possibilities cannot further be evaluated.

6. CONCLUSIONS

Overall, Pb-isotope systematics from this fossil hydrothermal system record a complex polyphased alteration history involving multiple sources. Source rocks (epidiosites and greenschist-altered dikes) and massive sulphides and sulphide sepa-

rates from the epidiosites are not in isotopic equilibrium. Isotopic ratios for leached epidiosites are consistent with a Pb-Pb age of ~95 Ma, which is indistinguishable from the ~92 Ma crystallisation age of the igneous complex. The excellent linearity of the data for the leached epidiosites in the $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ diagram, and the fact that the extrapolated trend passes through the glass and sulphide fields strongly suggest that age-corrected Pb isotopic ratios of leached epidiosites may be similar to those of massive sulphide deposits and sulphide separates from the epidiosites. Given the similarity of the isotopic trends for the epidiosites and greenschist-altered dikes, Pb-isotopic ratios for these rocks and the sulphides were probably very similar directly after the greenschist facies hydrothermal event responsible for their formation.

Postdating this high-temperature alteration event, epidiosites and greenschist dikes underwent a second alteration event, which involved the transport of Pb with a sedimentary isotopic signature into these rocks. Neither the method of transport nor the exact sources of the "foreign" Pb are completely understood.

The results from this study do not contradict the interpretation from previous studies that the epidiosites are reaction zone rocks for discharging hot hydrothermal fluids, of which the axial hot springs may be the present-day analogues.

Acknowledgments—Constructive discussions with and reviews by J. Alt, G. R. Davies, T. Elliott, and B. Peucker-Ehrenbrink significantly improved this manuscript. This project was supported in part by undergraduate research grants from the North Central Section of the Geological Society of America and the Council on Undergraduate Research (to D.F.) and by NSF EAR 9458418 (to LBV). This is the Netherlands School of Sedimentary Geology contribution number: 20000601.

REFERENCES

- Abouchamie W. and Goldstein S. L. (1995) A lead isotopic study of Circum-Antarctic manganese nodules. *Geochim. Cosmochim. Acta* **59**, 1809–1820.
- Ben Othman D., White W. M., and Patchett J. (1989) The geochemistry of marine sediments, island arc magma genesis and crust-mantle recycling. *Earth Planet. Sci. Lett.* **94**, 1–21.
- Bettison-Varga L., Schiffman P., and Janecky D. R. (1995) Fluid-rock interaction in the hydrothermal upflow zone of the Solea graben, Troodos ophiolite, Cyprus. In *Low-Grade Metamorphism of Mafic Rocks*, Vol. 296 (ed. P. Schiffman and H. W. Day), pp. 81–100. Geological Society of America spec. pub.
- Bettison-Varga L., Varga R. J., and Schiffman P. (1992) Relation between ore-forming hydrothermal systems and extensional deformation in the Solea graben spreading center, Troodos ophiolite, Cyprus. *Geology* **20**, 987–990.
- Bickle M. J. and Teagle D. A. H. (1992) Strontium alteration in the Troodos ophiolite: Implications for fluid fluxes and geochemical transport in mid ocean ridge hydrothermal systems. *Earth Planet. Sci. Lett.* **113**, 219–237.
- Brévar O., Dupré B., and Allègre C. J. (1981) Metallogenesis at spreading centers: Lead isotope systematics for sulphides, manganese crusts, basalts and sediments from the Cyamex and Alvin areas (East Pacific Rise). *Econo. Geol.* **76**, 1205–1210.
- Chen J. H. (1987) U, Th and Pb isotopes in hot springs on the Juan de Fuca Ridge. *J. Geophys. Res.* **92**, 11,411–11,415.
- Chen J. H. and Pallister J. S. (1981) Lead isotopic studies of the Samail ophiolite, Oman. *J. Geophys. Res.* **86**, 2699–2708.
- Chen J. H., Wasserburg G. J., von Damm K. L., and Edmond J. M. (1986) The U-Th-Pb systematics in hot springs on the East Pacific Rise at 21°N and Guaymas basin. *Geochim. Cosmochim. Acta* **50**, 2467–2479.
- Cohen R. S. and O'Nions R. K. (1982) Identification of recycled continental material in the mantle from Sr, Nd and Pb isotopic investigations. *Earth Planet. Sci. Lett.* **61**, 73–84.
- Doe B. R. (1982) The lead and strontium isotope geochemistry of metalliferous sediments associated with Upper Cretaceous ophiolitic rocks in Cyprus, Syria and the sultanate of Oman: Discussion. *Canadian J. Earth Sci.* **19**, 1720–1723.
- Doe B. R. and Zartman R. E. (1979) Plumbotectonics I, The Phanerozoic. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. Barnes), pp. 22–70. Wiley-Interscience.
- Galer S. J. G. and O'Nions R. K. (1985) Residence time of thorium, uranium and lead in the mantle with implications for mantle convection. *Nature* **316**, 778–782.
- Gillis K. M. and Robinson P. T. (1990) Patterns and processes of alteration in the lavas and dykes of the Troodos ophiolite, Cyprus. *J. Geophys. Res.* **95**, 21,523–21,548.
- Gribble R. F., Stern R. J., Newman S., Bloomer S. H., and O'Hearn T. (1998) Chemical and isotopic composition of lavas from the Northern Mariana Trough: Implications for magmatogenesis in Back-arc basins. *J. Petrology* **39**, 125–154.
- Hamelin B., Dupré B., and Allègre C. J. (1984) The lead isotope systematics of ophiolite complexes. *Earth Planet. Sci. Lett.* **67**, 351–366.
- Hamelin B., Dupré B., Brévar O., and Allègre C. J. (1988) Metallogenesis at paleo-spreading centers: Lead isotopes in sulphides, rocks and sediments from the Troodos ophiolite (Cyprus). *Chem. Geol.* **68**, 229–238.
- Hamelin B., Grousset F., and Sholkovitz E. R. (1990) Pb isotopes in surficial pelagic sediments from the North Atlantic. *Geochim. Cosmochim. Acta* **54**, 37–47.
- Harper G. D., Bowman J. R., and Kuhns R. (1988) Field, chemical, and isotopic study of submarine hydrothermal metamorphism of the Josephine ophiolite, north western California. *J. Geophys. Res.* **93**, 4625–4657.
- Hegner E. and Tatsumoto M. (1987) Pb, Sr and Nd isotopes in basalts and sulphides from the Juan de Fuca Ridge. *J. Geophys. Res.* **92**, 11,380–11,386.
- Hofmann A. W. (1988) Chemical differentiation of the Earth: The relationship between mantle, continental crust and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314.
- Honeyman B. D. and Santchi P. H. (1988) Metals in aquatic systems. *Environ. Sci. Technol.* **22**(8), 862–871.
- Ito E., White W. M., and Göpel C. (1987) The O, Sr, Nd and Pb isotope geochemistry of MORB. *Chem. Geol.* **62**, 157–176.
- LeHuray A. P., Church S. E., Koski R. A., and Bouse R. M. (1988) Pb isotopes in sulphides from mid-ocean ridge hydrothermal sites. *Geology* **16**, 362–365.
- Ling H. F., Burton K. W., O'Nions R. K., Kamber B. S., von Blanckenburg F., Gibb A. J., and Hein J. R. (1997) Evolution of Nd and Pb isotopes in Central Pacific seawater from ferromanganese crusts. *Earth Planet. Sci. Lett.* **146**, 1–12.
- Magaritz M. and Taylor H. P. (1974) Oxygen and hydrogen isotope studies of serpentinization in the Troodos ophiolite complex, Cyprus. *Earth Planet. Sci. Lett.* **23**, 8–14.
- Mahoney J. J., Frei R., Tejada M. L. G., Mo X. X., Leat P. T., and Nägler T. F. (1998) Tracing the Indian ocean mantle domain through time: Isotopic results from old west Indian, east Tethyan and south Pacific seafloor. *J. Petrology* **39**(7), 1285–1306.
- Mahoney J. J., Natland J. H., White W. M., Poreda R., Bloomer S. H., Fisher R. L., and Baxter A. N. (1989) Isotopic and geochemical provinces of the Indian Ocean spreading centers. *J. Geophys. Res.* **94**, 4033–4052.
- Michard A. and Albarède F. (1985) Hydrothermal uranium uptake at ridge crests. *Nature* **317**(6034), 244–246.
- Michard A., Albarède F., Michard G., Minster J. F., and Charlou J. L. (1983) Rare-earth elements and uranium in high temperature solutions from East Pacific Rise hydrothermal vent field (13°N). *Nature* **303**, 795–797.
- Morel F. M. M. (1983) *Principles of Aquatic Chemistry*. John Wiley & Sons.
- Mukasa S. B. and Ludden J. N. (1987) Uranium-lead isotopic ages of plagiogranites from the Troodos ophiolite, Cyprus and their tectonic significance. *Geology* **15**, 825–828.

- Open University Course Team. (1989) *Ocean Chemistry and Deep Sea Sediments*. Open University (Pergamon Press).
- Rautenschlein M., Jenner G. A., Hertogen J., Hofmann A. W., Kerrich R., Schmincke H.-U., and White W. M. (1985) Isotopic and trace element composition of volcanic glasses from the Akaki Canyon, Cyprus: Implications for the origin of the Troodos ophiolite. *Earth Planet. Sci. Lett.* **75**, 369–383.
- Rehkämper M. and Hofmann A. W. (1997) Recycled oceanic crust and sediment in Indian Ocean MORB. *Earth Planet. Sci. Lett.* **147**, 93–106.
- Richardson C. J., Cann J. R., Richards H. G., and Cowan J. G. (1987) Metal depleted root zones of the Troodos ore-forming hydrothermal systems, Cyprus. *Earth Planet. Sci. Lett.* **84**, 243–253.
- Robertson A. H. F. (1977) Tertiary uplift history of the Troodos massif, Cyprus. *Geol. Soc. Amer. Bull.* **88**, 1763–1772.
- Robinson P. T., Melson W. G., O'Hearn T., and Schmincke H.-U. (1983) Volcanic glass compositions of the Troodos ophiolite, Cyprus. *Geology* **11**, 400–404.
- Saccocia P. J. and Gillis K. M. (1995) Hydrothermal upflow zones in the oceanic crust. *Earth Planet. Sci. Lett.* **136**, 1–16.
- Schaule B. K. and Patterson C. C. (1981) Lead concentrations in the northern Pacific: Evidence for global anthropogenic perturbations. *Earth Planet. Sci. Lett.* **54**, 97–116.
- Schiffman P. and Smith B. M. (1988) Petrology and oxygen isotope geochemistry of a fossil seawater hydrothermal system within the Solea Graben, northern Troodos ophiolite, Cyprus. *J. Geophys. Res.* **93**(B5), 4612–4624.
- Schiffman P., Smith B. M., Varga R. J., and Moores E. M. (1987) Geometry, conditions and timing of off-axis hydrothermal metamorphism and ore-deposition in the Solea graben. *Nature* **325**, 423–424.
- Seyfried W. E., Berndt M. E., and Seewald J. S. (1988) Hydrothermal alteration processes at mid-ocean ridges: Constraints from diabase alteration experiments, hot-spring fluids and composition of the oceanic crust. *Canadian Mineralogist* **26**, 787–804.
- Smith G. C. and Vine F. J. (1989) The physical properties of diabases, gabbros and ultramafic rocks from C.C.S.P. project drill hole CY-4 at Palkhori, Cyprus. In *Cyprus Crustal Study Project: Initial Report, Hole CY-4*, Geological Survey of Canada Paper 88-9 (ed. I. L. Gibson, J. Malpas, P. T. Robinson, and C. Xenophontos), pp. 295–314.
- Snow J. E., Hart S. R., and Dick H. J. (1993) Orphan Strontium-87 in abyssal peridotites: Daddy was a granite. *Science* **262**, 1861–1863.
- Spooner E. T. C. and Gale N. H. (1982) Pb isotopic composition of ophiolitic volcanogenic sulphide deposits, Troodos Complex, Cyprus. *Nature* **296**, 239–242.
- Varga R. J. and Moores E. M. (1985) Spreading structure of the Troodos ophiolite, Cyprus. *Geology* **13**, 846–850.
- Vidal P. and Clauer N. (1981) Pb and Sr isotopic systematics of some basalts and sulphides from the East Pacific Rise at 21°N (project RITA). *Earth Planet. Sci. Lett.* **55**, 237–246.
- von Blanckenburg F., O'Nions R. K., and Hein J. R. (1996) Distribution of pre-anthropogenic lead isotopes in deep ocean water from Fe-Mn crusts. *Geochim. Cosmochim. Acta* **60**, 4957–4963.
- White W. M., Dupré B., and Vidal P. (1985) Isotope and trace element geochemistry from the Barbados Ridge–Demera Plain region, Atlantic Ocean. *Geochim. Cosmochim. Acta* **49**, 1875–1886.
- Zuleger E., Alt J. C., and Erzinger J. (1995) Primary and secondary variations in major and trace element geochemistry of the lower sheeted dike complex: Hole 504B, Leg 140. *Proceedings of the Ocean Drilling Program, Scientific Results*. (ed. J. Erzinger, K. Becker, H. J. B. Dick, and L. B. Stokking). **137/140**, 65–80.