The geochemistry of hydrothermal vent waters from Milos Island, Hellenic volcanic arc

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The Hellenic Volcanic Arc is a tectonically and volcanically active part of the earth's crust, situated above the subduction zone of the African plate under the Aegean. The arc extends from the Methana peninsula (NE Peloponese) through the greek islands Milos, Santorini, Kos, Nisiros and Yali to the Bodrum peninsula, Turkey (e.g. Fytikas *et al.*, 1986). Hydrothermal venting has been reported from Nisiros, Yali (Varnavas and Cronan, 1988) and Milos (Fytikas, 1989).

The island of Milos, at the central west part of the volcanic arc, is dominated by volcanic and volcaniclastic rocks, with the exception of minor occurrences of metamorphic basement rocks and Neogene sediments outcropping at the south part of the island, underneath the volcanics (Fytikas *et al.*, 1986). Submarine and, later, sub-aerial extrusive sequences formed during a prolonged period of volcanic activity (3.5 to 0.1 Ma, Fytikas, 1989). Geochemically, the Milos volcanics show a calcalkaline character and comprise andesites, dacites and ryolites (Fytikas *et al.*, 1986). Hot water springs and fumaroles occur at several localities around the island.

In submarine settings, hot fluids exit through the sandy seafloor, often in the form of a mixed liquid/ gas phase; as a result, venting can be located due to the visually impressive presence of streams of gas bubbles. In the most hydrothermally active south-east part of the island (Palaeohori bay), extensive areas of bacteria mats are associated with submarine hydrothermal brine seeps (Fitzsimons *et al.*, 1997).

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Field observations and sampling

Hot waters were sampled from several localities, mainly shallow off-shore (up to 10 m) over two summer field seasons. A small number of on-shore hot water vents were also located and sampled. The highest fluid temperatures recorded, were around 115°C; the lowest pH was 1.7 (at 25°C). The majority of sampling took place in Palaeohori bay, where local geology indicates that fluids have mostly reacted with metamorphic basement rocks. In Milos, the metamorphic basement comprises a flysch sequence, regionally metamorphosed to greenschist facies (Fytikas, 1989).

Occasionally, venting is associated with the formation of silicious chimney structures (up to 0.5 tall and 1m wide), often brecciated and cemented by a sulphide (pyrite) matrix. Based on observations over the two field seasons, it is proposed that these structures are annual features, which grow during the summer, and collapse in the winter as a result of rough weather. Sulphide/quartz mounds often not directly associated with venting, and therefore representing either precipitates from extinct vents or from present diffuse flow, have also been recognised. These features are always mostly covered by sand and their actual size or frequency of occurrence cannot be evaluated at this stage.

Results and discussion

Exiting fluid temperatures measured during sampling, indicate that conductive cooling and/or



FIG. 1. Metal concentration of Milos hydrothermal fluids as a function of chlorinity for A: cobalt, which is enriched in the low chlorinity fluids and B: cadmium, which shows a preference for high chlorinity fluids. No correction for seawater mixing has been applied.

sub-surface mixing with seawater may have occurred. Note also that deep reservoir temperatures measured in geothermal boreholes further north (Zephyria) were 300–320°C (Fytikas, 1989).

Fluid chlorinity ranged from 0.1 to 3 times that of seawater. The low chlorinity fluids (type A) also showed low concentrations of alkalis (potassium, lithium, sodium) and calcium, high silica and total sulphur. The high chlorinity fluids (type B) contained high alkalis and calcium, lower silica and total sulphur. Both types had low magnesium and high metal concentrations, albeit consistently different from each other. Type A had the highest cobalt (1.5 µmol/kg), nickel (3.5 µmol/kg), aluminium (1.1 mmol/kg), iron (0.9 mmol/kg) and chromium (1.7 µmol/kg), and type B had the highest zinc (3.1 µmol/kg), cadmium (1.0 µmol/kg), manganese (0.2 mmol/kg) and lead (0.2 µmol/kg). Examples of the distribution of metals in the two fluid types are shown in Fig. 1, below. A probable cause of the different metal content between the two fluid types is a difference in the main fluid ligand. Metals may have been transported as chlorides in fluid type B, whereas the most likely ligand in fluid type A is sulphur, perhaps in the form of sulphide.

The Cl/Br ratios of both fluid types were constant, regardless of salinity, and same as that of seawater. This suggests a common derivation from seawater for the two fluid types by subsurface phase separation. The phase separation scenario is further supported by the mode of occurrence of the two fluid types. The high chlorinity fluids have higher density and they appear as diffuse flows, identified by their shimmering or the formation of dense brine pools. The low salinity fluids are in general associated with high gas content and vigorous bubbling at discharge. Two neighbouring low-chlorinity on-shore springs, both venting at temperatures $85-90^{\circ}$ C, were monitored over three years. The two springs show a remarkably uniform composition for most chemical species over this period of time, both individually as well as relatively to each other. This suggests that fluids from the two springs have reached equilibrium at depth with the surrounding rocks, and that each taps a distinct reservoir, despite their proximity (3 metres).

The Milos hydrothermal vents share many common characteristics with mid-ocean ridge vents, despite the difference in tectonic setting and their shallow depth of discharge. They therefore represent an ideal setting to test ideas of hydrothermal fluid formation and evolution, due to the relatively easy access to the hydrothermal sites.

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