



Processes influencing extreme As enrichment in shallow-sea hydrothermal fluids of Milos Island, Greece

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ABSTRACT

Arsenic (As) is naturally enriched in most terrestrial and marine hydrothermal systems. Its discharge from shallow-sea hydrothermal vents into coastal marine environments can dramatically affect the surrounding ecosystems. Shallow-sea hydrothermal venting of acidic (pH~5), hot (40–116 °C), and highly sulfidic (up to 3.1 mM H₂S) fluids occurs at Palaeochori and Spathi Bays, off the southeast coast of Milos Island, Greece. Two distinct types of fluids, both extremely As enriched, were collected from the submarine vents often within a few meters of each other: (1) a high-Cl fluid (enriched in Cl by up to 47% relative to seawater) depleted in Mg and SO₄ and enriched in major (Na, Ca, K, B, Sr, and Br) and minor/trace elements (Si, Li, Rb, Cs, As, Fe, Mn, and Ba), and (2) a low-Cl fluid (depleted in Cl by up to 66% relative to seawater) also depleted in Na, Mg, SO₄, and Br. The maximum concentration of As reached 39 μM in the high-Cl fluids and up to 78 μM in the low-Cl fluids. This is approximately 3000 times the concentration of As in seawater and far exceeds the concentrations typically found in mid-ocean ridge (MOR) and back-arc basin (BAB) fluids, which are typically <0.7 and <10 μM, respectively.

We used a combination of elemental analyses and stable and radiogenic isotope data (oxygen, deuterium, and strontium) to understand the primary controls on As enrichment. Those parameters all indicated that the fluids were a mixture of seawater and a hydrothermal fluid originally derived from seawater but altered by water–rock interaction, subcritical phase separation (boiling), and vapor/brine segregation. Since As was extremely enriched in both the high-Cl and the low-Cl thermal fluids, we conclude that this element readily partitions into the vapor phase in the Milos hydrothermal system. The original source of As is most likely the leaching of the greenschist facies metamorphic basement rocks transpierced by an abundance of secondary quartz and calcite veins rich in pyrite. It is possible that these veins were deposited from As-rich magmatic fluids, similar to some epithermal Au deposits. A poorly-crystalline orpiment precipitates as hydrothermal fluids mix with overlying seawater, and removes much of the dissolved As prior to discharge.

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1. Introduction

Arsenic (As) is naturally enriched in many hydrothermal fluids, both in terrestrial and marine environments (Ballantyne and Moore, 1988; Douville et al., 1999; Pichler et al., 1999; Smedley and Kinniburgh, 2002; Webster and Nordstrom, 2003; Planer-Friedrich et al., 2007). Where high-As hydrothermal fluids discharge into coastal marine environments, ecosystems can be dramatically impacted (McCloskey et al., 2005; Karlen et al., 2010). Several studies have investigated the biogeochemical cycling of As in shallow-sea hydrothermal systems (McCloskey

et al., 2005; Price and Pichler, 2005a; Price et al., 2007; Hallock et al., 2010; Karlen et al., 2010), but the corresponding mechanisms of As enrichment remain poorly understood.

Most research suggests that the As in hydrothermal fluids is generally leached from the underlying host rocks, and therefore, the rock type may constrain or even control As levels in hydrothermal fluids (Webster and Nordstrom, 2003). Recent research demonstrates that hydrothermal fluids, particularly those associated with more continental-type (felsic) magmas produced in arc, back-arc, and continental arc settings, contain high concentrations of metals including As (Yang and Scott, 1996; Fleet and Mumin, 1997; Mehrabi et al., 1999; Fuxin et al., 2001; Kiliyas et al., 2001; Muntean et al., 2011). Where these metal-rich magmatic fluids precipitate, As-rich epithermal (Carlin-type) gold (Au) deposits can occur (Arehart, 1996; Mehrabi et al., 1999). Subsequent leaching of

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these precipitates can lead to extremely elevated concentrations of As in hydrothermal fluids.

Magmatic volatile inputs and phase separation can also influence the As concentrations of discharging hydrothermal fluids (Butterfield et al., 1990; Fouquet et al., 1991; Gamo et al., 1997; German and Von Damm, 2003; Reeves et al., 2011). Phase separation, in particular, is a ubiquitous process in seafloor hydrothermal systems (Bischoff and Rosenbauer, 1984; Butterfield et al., 1990; Ishibashi, 1995; Hannington et al., 2001; German and Von Damm, 2003; Von Damm et al., 2003; Foustoukos et al., 2007). If the fluids are heated or depressurized below the critical point of H₂O, boiling (subcritical phase separation) occurs, creating a brine and a low-salt vapor phase which may subsequently condense to a near-zero salt solution (Bischoff and Rosenbauer, 1984; German and Von Damm, 2003). Below the critical point of seawater phase separation can be equated to “subcritical” boiling producing ~3.2 wt.% NaCl liquid coexisting with a low-salinity vapor, while during “supercritical” phase separation, a high-salinity vapor (= 3.2 wt.% NaCl) is formed by condensation of a small amount of liquid (Foustoukos et al., 2007). Thus, vent fluid salinities can vary drastically, from less than 6% up to 200% of seawater values (German and Von Damm, 2003). Although evidence suggests that As may partition into the vapor phase (Berndt and Seyfried, 1990; Douville et al., 1999; Pokrovski et al., 2005; Foustoukos et al., 2007), the effect of phase separation as a controlling factor on As behavior in hydrothermal fluids remains unclear.

Shallow-sea hydrothermal vents can provide valuable insights into As enrichment and behavior during these processes. They exhibit a wide range of geological, chemical, and biological phenomena similar to those at deep-sea vents (Pichler and Dix, 1996; Dando et al., 1999; Tarasov et al., 2005). Owing to differences in pressure, subcritical phase separation is likely much more prevalent in shallow-sea hydrothermal systems than in their deep-sea counterparts. Furthermore, recent evidence suggests that shallow-sea vents are often more enriched in potentially toxic elements, such as As (Varnavas and Cronan, 1988; Pichler et al., 1999; McCarthy et al., 2005; Price and Pichler, 2005b), relative to their deep-sea counterparts (Douville et al., 1999). This is most likely due to the occurrence of As-rich magmatic fluid precipitates associated with more felsic (andesitic) magmas, differing significantly from hydrothermal systems found at basalt-hosted mid-ocean ridges.

Here, we report extremely elevated concentrations of As in both high- and low-Cl fluids in shallow-sea hydrothermal fluids of Palaeochori Bay and Spathi Bay, off Milos Island, Aegean Arc, east Mediterranean Sea. We link the fluid sources and sub-seafloor processes (e.g., host rock leaching, phase separation) to the observed enrichments in As using a combination of elemental analyses and stable and radiogenic isotope data (oxygen, deuterium, and strontium).

2. Site characteristics

Submarine hydrothermal venting was previously reported for the shallow coastal waters off several of the Aegean island arc volcanoes, including Milos (Fig. 1a and b; Dando et al., 1999). The most intense submarine venting off Milos Island occurs in Palaeochori Bay, where abundant CO₂-rich gasses discharge through sand concomitant with diffusive discharges of hydrothermal fluids (Figs. 1b and 2). Echo sounder mapping of the abundant gas discharge indicated that hydrothermal venting around the island occurs over an area of approximately 35 km², making this one of the largest shallow-sea hydrothermal systems described to date (Dando et al., 1995a). Nearby – but little explored – Spathi Bay, just to the east of Palaeochori Bay, also has abundant hydrothermal venting. In places of diffuse venting, white microbial mats and hydrothermal precipitates form, which can be easily observed from aerial photographs (Fig. 2; Dando,

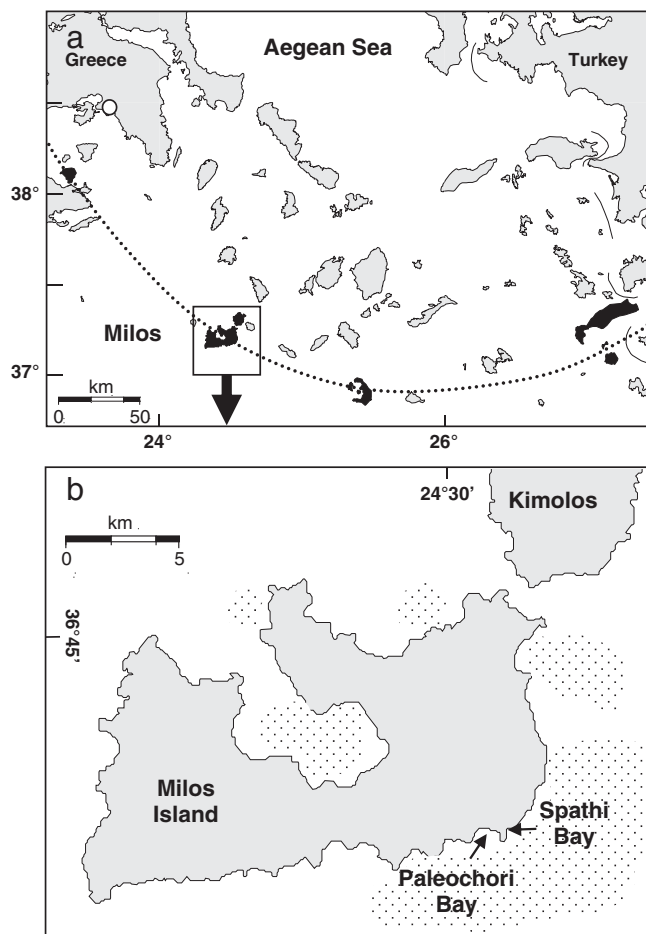


Fig. 1. (a) Location of Milos Island and other calc-alkaline volcanoes (shaded) along the Aegean Island Arc (dotted line). (b) Milos Island and the location of Palaeochori and Spathi Bays. Stippled offshore areas around the island are mapped gas emissions by echo sounding (Dando et al., 1995a). [Figures are created with the Generic Mapping Tool (<http://www.aquarius.geomar.de/>)].

2010). Abundant yellow- to orange-colored patches composed predominantly of native S and As-sulfides also occur, mostly at the higher temperature sites (Dando et al., 1999).

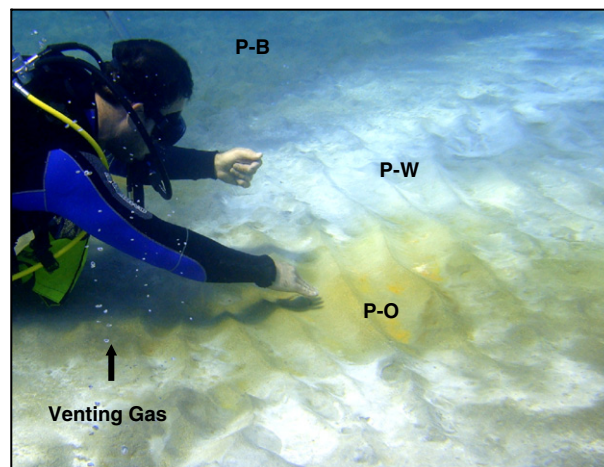


Fig. 2. Photograph of white and orange patches investigated in this study. P-O (Palaeochori–orange), P-W (Palaeochori–white), and P-B (Palaeochori–background) indicate areas where pore fluids and sediments were sampled.

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