# Active geothermal systems with entrained seawater as modern analogs for transitional volcanic-hosted massive sulfide and continental magmato-hydrothermal mineralization: The example of Milos Island, Greece

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# ABSTRACT

Low-sulfidation epithermal mineralization on Milos (Aegean arc) records high paleofluid salinities that cannot be explained by a Broadlands-type low-salinity geothermal system. The  $\delta D$  and  $\delta^{18}O$  data do not document <sup>18</sup>O-shifted meteoric waters, one of the characteristic features in terrestrial geothermal systems. Nor is a submarine origin indicated—stable isotope data show mixing of meteoric, seawater, and volcanic-arc gases. Strontium isotope data are comparable to those of a nearby active seawater-entrained geothermal system. These are features seen in hydrothermal systems associated with emergent volcanoes. The similarities between ancient and active systems on Milos in terms of salinity,  $\delta D$  vs.  $\delta^{18}O$ , and strontium isotope systematics strongly suggest that seawater is the main source for Na and Cl. We suggest that geothermal systems containing seawater associated with emergent volcanoes are an additional analog for intrusion-centered oredeposit models. Furthermore, such systems bridge the gap between submarine and terrestrial geothermal systems—the modern analogs for volcanic-hosted massive sulfide and epithermal mineralization in the scheme of intrusion-centered hydrothermal mineralization.

Keywords: epithermal processes, seawater, Milos, isotopes.

# INTRODUCTION

Geothermal systems in convergent platemargin settings are the active equivalents of high-level (2-3 km deep) intrusion-centered hydrothermal ore deposits (e.g., Hedenquist and Lowenstern, 1994). In the terrestrial environment, volcanic emanations are the surface expressions of porphyry copper and highsulfidation epithermal gold mineralizing processes at depth (Hedenquist et al., 1993). Located farther from the magmatic source are low-sulfidation (LS) epithermal deposits (sensu White and Hedenquist, 1990). Here, geothermal systems such as Broadlands-Ohaaki are an active analog (e.g., Simmons and Browne, 2000). Generally, in LS epithermal mineralization, fluid inclusions document lowsalinity fluids (<1 wt% salts + CO<sub>2</sub>), and these are equivalent to the low-chlorinity (<1000 ppm) fluids seen in Broadlands-type geothermal systems. However, fluid inclusions in some LS epithermal deposits (e.g., Emperor; Eaton and Setterfield, 1993) also identify saline fluids (up to 15 wt% salts). The LS character of these gold ores is attributed to deposit-scale rock buffering. However, the origin of the high salinity and the nature of active analogs to these systems remain unresolved (Sillitoe and Hedenquist, 2003). To

date, the main active analog for terrestrial high-salinity ore systems is the Salton Sea geothermal system (McKibben and Hardie, 1997). However, the geotectonic environment (continental rift) is different from that of intrusion-centered ore deposits (subductioncollision), and it is not an appropriate counterpart for saline LS epithermal systems. In the submarine environment, saline geothermal systems are well known, and deep-water (>2000 m) systems, such as the Trans-Atlantic Geotraverse (e.g., You and Bickle, 1998), are exemplars for volcanic-hosted massive sulfide (VHMS) deposits. In the shallow submarine to transitional volcanic arc environment, a hybrid VHMS to epithermal transition is recognized on the basis of epithermal-style metal enrichment in shallow submarine geothermal systems and VHMS deposits (Hannington et al., 1999). In addition, the commonality between the volcano-tectonic settings of some subaerial LS epithermal and VHMS deposits suggests a link between the two (Sillitoe and Hedenquist, 2003). However, ancient examples of potential hybrid systems are commonly deformed and metamorphosed (e.g., Eskay Creek, British Columbia, Canada; Sherlock et al., 1999), making direct comparison with submarine active systems (e.g., Conical Seamount, adjacent to Lihir Island, Papua New Guinea; Petersen et al., 2002) equivocal, and it is generally recognized that there are no clearly documented active analogs for this hybrid style of mineralization.

We report new strontium isotope data and describe features of Cenozoic epithermal mineralization hosted by the emerging volcanic complexes of Milos Island. By comparing these findings with similar findings on wellcharacterized modern systems, we suggest that active geothermal systems recharged by both sea and meteoric waters, such as those in the Aegean volcanic arc (Aegean arc type), represent an active analog for hybrid epithermal-VHMS mineralization. Furthermore, this proposition links the submarine and terrestrial ore-forming environments in the scheme of intrusion-centered hydrothermal mineralization.

## AEGEAN ARC

The Aegean arc is a zone of Pliocene to modern volcanism related to active backarc extension caused by the subduction of the African plate beneath the Aegean microplate (e.g., Pe-Piper and Piper, 2002). It is built on continental crust, comprises seven major volcanic centers, and is located 120–250 km north of the Hellenic Trench (Fig. 1A). The volcanic rocks are calc-alkaline with localized high-K variants and range from basalt to rhyolite in composition, but are predominantly andesites and dacites. Present-day hydrothermal activity comprises both low-enthalpy (Aegina, Sousaki, Methana) and high-enthalpy systems (Milos, Nisyros, Santorini).

## **Milos Geology and Mineralization**

Late Pliocene submarine and late Pleistocene to Holocene subaerial volcanic rocks overlie Mesozoic metamorphic basement and upper Miocene–lower Pliocene marine sedimentary rocks, recording a transition from a shallow submarine (<200 m) to subaerial volcanic setting (e.g., Fytikas et al., 1986) (Fig. 1B). Emergence probably occurred in the middle to late Pleistocene (Stewart and McPhie, 2004). Plutonic rocks are not known on Milos



Figure 1. A: Main geotectonic elements of eastern Mediterranean along with volcanic centers and regions of geothermal activity. B: Main geologic features of Milos Island plus location of low-sulfidation epithermal mineralization (Profitis Ilias and Chondro Vouno) and main surface manifestations of geothermal system (Milos map adapted from Fytikas et al., 1986)—points 1 and 2 show the locations of the deep geothermal reservoir (Zephyria) and main shallow submarine geothermal system (Paleochori Bay), respectively. UPI—upper Pleistocene; LPI—lower Pleistocene; UPo—upper Pliocene; LPo—lower Pliocene; UMi—upper Miocene; M—Mesozoic.

and have only been reported as ignimbritehosted granitic xenoliths from the nearby islet of Kimolos (Pe-Piper and Piper, 2002).

The oldest submarine volcanic rocks occur on western Milos and host LS gold-silver mineralization-the Profitis Ilias (5.5 Mt at 4.4 g/t gold and 43 g/t silver) and Chondro Vouno (1.2 Mt at 1 g/t gold and 124 g/t silver) deposits (Fig. 1B), which constitute a 20 km<sup>2</sup> epithermal system with a combined resource of 0.8 Moz gold and 12.4 Moz silver. Mineralization is hosted by silicified, sericitized, and adularized rhyolitic tuffs and ignimbrites and consists of crustiform or colloform-banded quartz (or chalcedony)  $\pm$  adularia + barite + sericite veins related to quartz + adularia + sericite (or illite) wall-rock alteration. Mineralized veins extend to depths of at least 300 m below the current surface ( $\sim 600$  m above sea level [masl]). Hypogene metallic minerals include pyrite, galena, chalcopyrite, sphalerite, marcasite, tetrahedrite, native gold, and electrum. Sulfides mainly occur deep in the system (below ~300 masl) as disseminated stockwork mineralization of unknown vertical extent. Elevated gold values are concentrated above the base-metal zone and are spatially related to boiling (Kilias et al., 2001). Final ice-melting  $(T_{m-ice})$  fluid-inclusion data demonstrate that 70% of the fluid inclusions have net salinities in excess of seawater (Table 1; Data Repository Table DR1),<sup>1</sup> showing that throughout its life span, fluids in the system were saline.

# Active Geothermal System

Data indicate a two-component reservoir in the active geothermal system (Liakopoulos, 1987; Pflumio et al., 1991). (1) A highenthalpy system is located 1–2 km below sea level (Fig. 1, Zephyria), with seawater recharge. Reservoir temperatures are in the range 250–350 °C, and estimated salinities are consistently higher than seawater (average 9 wt% salts). This high salinity results from Rayleigh distillation as seawater percolates, through progressively hotter rocks, into the reservoir. Owing to its high salinity, venting of the geothermal fluid is accompanied by boiling close to the top of a local two-phase

TABLE 1. SUMMARY OF SALINITY DATA FOR PROFITIS ILIAS (PI)–CHONDRO VOUNO (CV) EPITHERMAL Au-Ag MINERALIZATION

Deposit	Salinity (wt% NaCl equivalent)					Fluid inclusions with $T_{m-ice}$
	п	Min.	Max.	Mean	S	>4 wt% Naci eq. (%)
CV*	132	0.5	14.7	6.1	3.0	86
PI <sup>†</sup>	139	0.0	11.3	5.2	2.1	71

reservoir. (2) A shallow reservoir (100-175 °C) overlies the high-enthalpy system. It is located close to sea level (Fig. 1, Paleochori Bay) and is recharged by meteoric water and seawater intrusion. It is commonly saline (up to 5 wt% salts) and heated by gas escaping from the underlying deep reservoir. Seawater, as a major component of both the deep and shallow reservoirs, is documented on the basis of <sup>87</sup>Sr/86Sr ratios and δD, δ<sup>18</sup>O, and Cl systematics (Pflumio et al., 1991). In the shallow (<100 m) submarine environment, venting geothermal fluids contain suspended particulate matter strongly enriched in Fe, Mn, Si, and Ba, and locally deposited aluminumphosphate-sulfate minerals, pyrite, marcasite, barite, gypsum, and calcite (Baltatzis et al., 2001; Cronan and Varnavas, 1999; Stueben and Glasby, 1999). In addition, the deep reservoir is metalliferous (Pb: 180 ppb; Zn: 1458 ppb) (Christanis and Seymour, 1995) and has gold concentrations of ~0.3 ppb (Liakopoulos, 1987).

#### Seawater as a Fluid Component on Milos

Comparison of  $\delta D$  vs.  $\delta^{18}O$  data of inclusion fluids from the Profitis Ilias epithermal mineralization with fluids of active geothermal systems associated with emergent volcanoes reveals remarkable similarities (Fig. 2). In the active systems the geothermal fluids have a three-component source (sea, meteoric, and magmatic), and the waters fall in a zone projecting from the meteoric water line to values intermediate to seawater and volcanic-arc gases (Fig. 2). The fluid-inclusion data for the Profitis Ilias LS mineralization show an analogous trend and lie in a similar zone; this is in sharp contrast to typical low-salinity LS

<sup>&</sup>lt;sup>1</sup>GSA Data Repository item 2005111, Table DR1, fluid inclusion data for the Chondro Vouno epithermal Au-Ag mineralization, and Table DR2, strontium isotope data, is available online at www.geosociety.org/pubs/ft2005.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.



Figure 2. Fluid-inclusion  $\delta D$  vs.  $\delta^{18}O$  data for Profitis Ilias, comparing epithermal mineralization with active systems on Aegean arc with reference points for eastern Mediterranean seawater (crossed squares labeled S) and estimated present-day geothermal liquids (filled triangles: M-Milos and N-Nisyros). Milos epithermal mineralization data are from Naden et al. (2003); geothermal data are from Brombach et al. (2003), Kavouridis et al. (1999), and Liakopoulos (1987); fields for volcanic arc gases and Broadlands and volcanic-hosted massive sulfide (VHMS) mineralization are from Giggenbach (1992), Field and Fifarek (1985), and Huston (1999). VSMOW-Vienna standard mean ocean water.

mineralization in which stable isotope data show <sup>18</sup>O-shifted fluids at constant  $\delta$ D values (see Broadlands field in Fig. 2). It is also different from the isotopic composition typical of VHMS ore-forming fluids (Fig. 2), which is explained by incorporation of magmatic fluids into a hydrothermal system dominated by evolved seawater (Huston, 1999).

In terms of strontium isotope data (Fig. 3; Table DR2 [see footnote 1]), the basement metamorphic sequence has 87Sr/86Sr ratios (0.7033-0.7137) that encompass the entire range of values. This range permits a variety of interpretations of fluid and rock interactions. However, we think that the clustering of measured <sup>87</sup>Sr/<sup>86</sup>Sr ratios for the modern geothermal fluids (0.7092-0.7100) and mineralization (0.7096-0.7100 [epithermal goldsilver]; 0.7092-0.7098 [manganese-barium]) close to the ratio for late Pliocene seawater (0.7090-70906) indicates a seawater source somewhat modified by reacting with various rocks. In addition, 87Sr/86Sr ratios for the modern and ancient systems are significantly different from most of the unaltered igneous rocks (0.7050-0.7080) and preclude a magmatic fluid source. Most of the 87Sr/86Sr ratios



Figure 3. Sr isotope data for mineralization on Milos obtained on barite and compared with local igneous rocks (fresh and altered), marine platform sedimentary rocks, basement metamorphic rocks, and geothermal waters (data are from this study; Table DR2 includes individual analyses and standard data [see footnote 1]; Briqueu et al., 1986; Farrell et al., 1995; Hein et al., 2000; Pflumio et al., 1991).

(0.7082–0.7098) for hydrothermally altered igneous rocks cluster within or close to the range recorded by the modern geothermal fluids and seawater.

More than 70% of the fluid inclusions have salinities >4 wt% NaCl equivalent (Table 1; Table DR1 [see footnote 1]), and, in terms of a Broadlands-style model, these cannot be rationalized by the presence of dissolved gas (see Hedenquist and Henley [1985] for an elaboration of this point). Nonetheless, they need to be explained. It could be argued that the origin of salinity is through meteoric water interacting with evaporites (e.g., Salton Sea; McKibben and Hardie, 1997) or that the geothermal system has tapped a magmatic brine reservoir (e.g., Fresnillo; Simmons, 1991). An evaporitic origin is considered unlikely, as there is no record, either from surface geology or geothermal exploration drilling (2 km), of halite-bearing saliferous rocks within the Milos sedimentary rocks. At Fresnillo, though mineralization is associated with high-salinity fluids, the distribution of these fluids is limited and the overall setting of the deposits is akin to a Broadlands-style low-salinity geothermal system with localized input of magmatic brine. This setting is not analogous to that of the Milos epithermal systems, where highsalinity fluids (>4 wt% NaCl equivalent) are the norm, and therefore the Fresnillo model cannot be applied. We recognize that neither of these possibilities can be totally discounted and that elevated salinity alone is not indicative of seawater. However, taken together, the evidence strongly suggests a significant seawater component to the Profitis Ilias-Chondro Vouno epithermal fluids.

## Hybrid Epithermal Systems and Modern Analogs

In terms of modern analogs, we suggest that the best candidates that recognize the key parameters-consistently high fluid-inclusion salinities,  $\delta D$  vs.  $\delta^{18}O$  systematics indicating seawater, and a seawater Sr isotope signature-are geothermal systems with entrained seawater. Typical examples are the active systems on Milos and Nisyros (Fig. 2). These analogs are hybrids, containing elements of both submarine and terrestrial geothermal systems. The occurrence of hybrid mineralizing systems has been predicted (Huston, 2000), though no ancient or modern equivalents have been clearly identified. This hypothesis envisages that in the emergent environment, circulating seawater and meteoric water are the main fluid components. The fluids boil and result in auriferous quartz veins with epithermal textures and proximal quartz + adularia, intermediate-distance quartz + sericite + pyrite, and distal propylitic or quartz + albite alteration halos, features that are comparable to the Milos epithermal mineralization. Thus, we suggest that epithermal mineralization where the involvement of seawater can be clearly demonstrated (e.g., Milos) is a good candidate for a fossil hybrid epithermal system, and active geothermal systems with entrained seawater, such as the Aegean arc type, are their modern counterparts.

Features of hybrid epithermal systems can be reconstructed by putting geothermal systems associated with emergent volcanoes into a conceptual framework. Figure 4 illustrates the model: gold-bearing epithermal veins are located between (1) a shallow, lowtemperature (100-175 °C), steam-heated zone recharged by meteoric water and seawater intrusion and (2) a deep, seawater-recharged, higher-temperature (250-350 °C), base-metal– bearing reservoir.

## CONCLUDING REMARKS

On Milos, the epithermal mineralization is analogous to seawater-entrained geothermal systems associated with emergent volcanoes (e.g., Nisyros, Milos), and data (geologic, isotope, and fluid inclusion) are in accord with this model. We therefore suggest that our Aegean arc model should be considered as an additional analog in the scheme of intrusioncentered metallogenesis. Moreover, in a convergent plate-margin setting, our model provides a link between submarine and terrestrial epithermal mineralization processes. Appropriate indicators for its use are fluid-inclusion data showing consistently elevated salinities (>4 wt% NaCl equivalent) and mineralization hosted in submarine or transitional to subaerial volcanic rocks in an island-arc tectonic setting. However, these criteria by themselves are not definitive, and other corroborating data



Figure 4. Conceptual model of hybrid Aegean arc-type epithermal systems developed by superimposing structure of Milos epithermal systems (this study and Kilias et al., 2001) on hydrological models for active systems on Milos and Nisyros (Kavouridis et al., 1999; Liakopoulos, 1987). Here shallow geothermal reservoir corresponds to steam-heated zone in epithermal systems, and deep metalliferous geothermal reservoir corresponds to deep, base-metal-rich zone seen in epithermal systems. Network of epithermal style veins containing majority of precious metal mineralization links two reservoirs.

must be sought; in the Milos case, these include Sr isotope,  $\delta D$ , and  $\delta^{18}O$  analyses.

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