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MASSIVE SULFIDES WITH FLUID-INCLUSION-BEARING QUARTZ FROM A YOUNG SEAMOUNT ON THE EAST PACIFIC RISE

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ABSTRACT

One dredge haul from a young East Pacific Rise seamount, located approximately 15 km off-axis, recovered exclusively hydrothermal material that included massive sulfide, crusts consisting of euhedral drusy atacamite, and reddish brown iron oxide crusts and mud. The massive sulfide is primarily quartz, pyrite, and sphalerite, with accessory chalcopyrite, covellite, digenite, and galena; the sulfide fraction contains up to 2 ppm Au and 150 ppm Ag. Conditions of formation were estimated from fluid inclusions in quartz. Inclusion trapping temperatures were 240 ± 35°C at the ambient seafloor pressure of 26 MPa, and the fluid had 4.0 wt.% equivalent NaCl. The massive sulfide is atypical because it contains silica as quartz rather than an amorphous variety, suggesting that the usual kinetic barrier to quartz precipitation was overcome. Some of the quartz apparently replaced earlier amorphous silica, but much of it precipitated as primary quartz, entrapping fluid inclusions. Active hot springs on the seafloor that precipitate quartz have not been directly observed; however, these massive sulfides and other quartz-bearing samples from seafloor deposits suggest that subsurface diffuse flow and conductive heat-loss may overcome the unfavorable kinetics of quartz precipitation.

Keywords: sulfide, massive sulfide, fluid inclusions, East Pacific Rise, seamount, hydrothermal, atacamite, gold, silver, seafloor hot springs.

SOMMAIRE

Une suite d'échantillons prélevés des flancs d'un jeune guyot situé environ 15 km de l'axe de la crête Est-Pacifique consiste exclusivement des produits hydrothermaux suivants: sulfures massifs, croûtes d'atacamite idiomorphe, croûtes riches en oxyde de fer brun rougeâtre, et boues. Les échantillons de sulfures massifs contiennent surtout quartz, pyrite et sphalérite, avec chalcopyrite, covellite, digénite et galène accessoires. La fraction sulfurée contient environ 2 ppm d'or et 150 ppm d'argent. Nous avons évalué les conditions de formation à partir des inclusions fluides dans le quartz. Les températures de piégeage sont de 240 ± 35°C à la pression ambiante à cette profondeur, 26 MPa; la phase fluide contient 4.0% (poids) de NaCl (équivalent). La présence de quartz plutôt que d'une forme amorphe de silice dans les échantillons de sulfures massifs les rend atypiques, et montre que les facteurs qui entravent normalement la précipitation du quartz ont été contrés. Une partie du quartz remplace la silice amorphe précoce, mais une plus grande partie semble primaire, tout comme les inclusions fluides. Les évents hydrothermaux sous-marins qui produisent du quartz n'ont pas encore été observés directement. Ces sulfures massifs et les autres échantillons quartzifères de gîtes sous-marins font penser que le flux diffus d'une phase fluide hydrothermale sous la surface et une perte de chaleur par conduction pourraient expliquer la nucléation réussie du quartz à cet endroit.

(Traduit par la Rédaction)

Mots-clés: sulfure, sulfures massifs, inclusions fluides, crête Est-Pacifique, guyot, hydrothermal, atacamite, or, argent, évents hydrothermaux sous-marins.

INTRODUCTION

Seafloor sulfide deposits have been discovered at many sites along the world's mid-ocean ridge system, as well as atop several deep-sea volcanoes (Rona 1988). Known sulfide deposits from seamounts are less abundant than from ridge crests, probably as a consequence of sparse sampling. Those from young seamounts near the East Pacific Rise (EPR) have been described and analyzed by Alt and co-workers (Alt *et al.* 1987, Alt 1988a,b) and Hekinian & Fouquet (1985). A silica–sulfide–sulfate deposit from Axial Seamount on the Juan de Fuca Ridge has been studied extensively by Hannington & Scott (1988). Other examples are from a submarine volcanic arc seamount (Urabe *et al.* 1987) and from a Mediterranean seamount (Minniti & Bonavia 1984). Hydrothermal deposits devoid of sulfides occur at Loihi seamount (Malahoff *et al.* 1982), Red seamount on the EPR at 21°N (Alt 1988a), and other seamounts in the Pacific and Mediterranean (*e.g.*, Exon & Cronan 1983, Vanko *et al.* 1984, Varnavas *et al.* 1988, Uchupi & Ballard 1989). The relative importance of submarine hydrothermal activity associated with seamounts is unknown. However, in terms of net crustal cooling, net amount of seawater reacted with crustal rocks, and potential for creating seafloor sulfide deposits, seamounts could play an important role in global budgets (Lonsdale *et al.* 1982, Batiza 1982).

The present paper gives results of petrographic and geochemical studies on hydrothermal rocks dredged from a young volcanic seamount near the East Pacific Rise at 14°09'N. Rock types recovered in a dredge haul of the seamount summit included abundant earthy, low-density reddish orange crusts and poorly consolidated sediments, several denser and harder pieces of massive sulfide, and rare crusts coated by euhedral crystals of atacamite. These samples are described, and results of partial chemical, X-ray diffraction, and fluid inclusion analyses are presented.

METHODS

Samples were obtained by dredging after the volcano was mapped using the Sea Beam multinarrow-beam echo-sounding system aboard the R/V *Thomas Washington*. Navigation was carried out by conventional transit satellites, which limit locational uncertainties to roughly 1 km. Dredge positioning was aided by using real-time Sea Beam data in conjunction with the previously produced Sea Beam map of the seamount.

The mineralogy of the samples was determined by transmitted- and reflected-light microscopy and powder X-ray diffraction. Fluid inclusions were analyzed by conventional heating–freezing techniques on a modified USGS-type gas-flow microscope stage. The accuracy of routine determinations of temperature is estimated to be ± 0.1°C during the freezing runs and ± 1.0°C during the heating runs.

Several bulk samples were analyzed for Au, Ag, Cu, Pb, Zn, and Fe by Bondar–Clegg, Vancouver, B.C.

GEOLOGICAL SETTING

The seamount at 14°09'N, 104°22'W is located on crust about 150,000 years old 15 km west of the EPR (Fig. 1). Lavas and hydrothermal deposits seem to be fresh and to have formed recently. The volcano is roughly 4 km wide and 7 km long at its base, and is 800 m high above the surrounding 3000-m-deep sea floor. It has a broad flat cross-section, similar to that of many previously described young East Pacific volcanoes (Batiza & Vanko 1983). It has no caldera at present, similar to roughly 20–60% of those young deep-sea

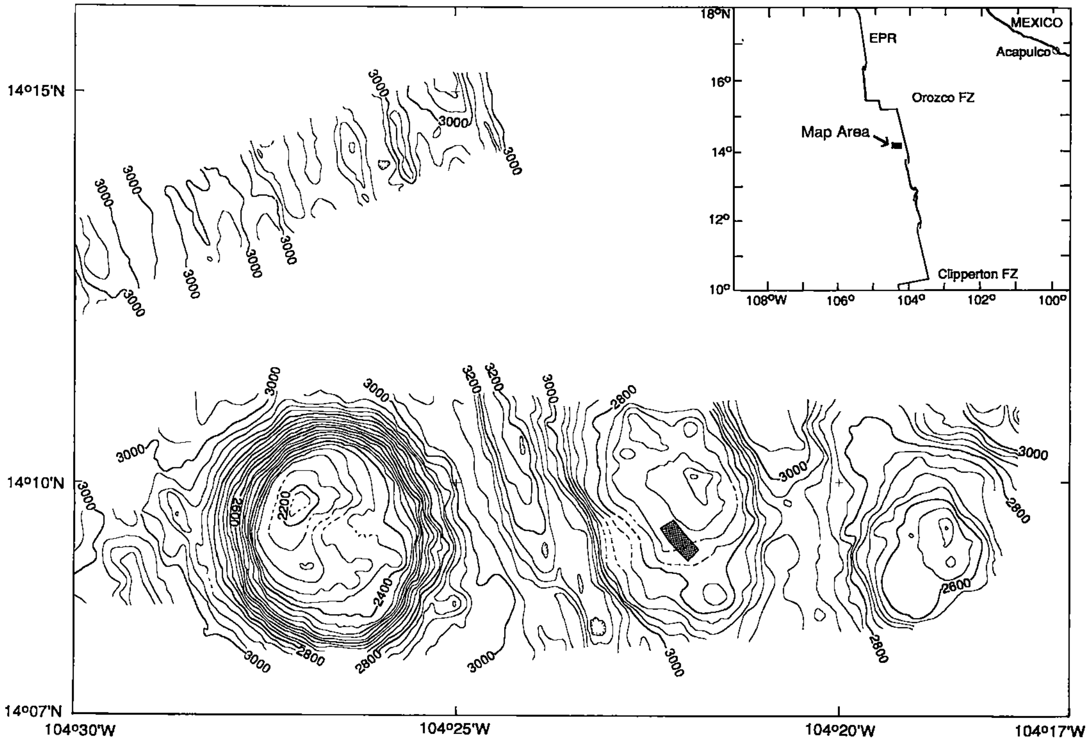

FIG. 1. Sea Beam map of three volcanoes located on the west flank of the East Pacific Rise (labeled EPR on the inset, after Macdonald *et al.* 1984). The rise axis at this latitude is at 104° 15'W, about 15 km east of the seamount dredge haul (shown as a stippled rectangle).

volcanoes examined during Sea Beam or side-scan sonar surveys (Batiza & Vanko 1983, Searle 1983, Fornari *et al.* 1987). Instead, the summit contains several high points separated by broad saddles. Three dredges of the summit recovered basaltic lava in all but one: the shallowest dredge recovered several tens of kilograms of hydrothermal material, but no basalt. The hydrothermal material consists of massive sulfide, atacamite crusts, and reddish orange crusts.

NATURE OF THE MASSIVE SULFIDES

The massive sulfide is gray, fine grained, and porous. The porosity, varying from about 5 to 20%, is due to small millimeter-scale vugs and irregular tubes that are about 1 mm across and several millimeters long. Some of these tubes are lined by drusy (subhedral crystalline) quartz, and others are filled completely with quartz. The exterior surfaces of these samples are weathered to a rust-red color, probably owing to an assemblage of iron oxides and hydroxides, and several samples have accessory atacamite in the weathered crust.

TABLE 1. MODAL COMPOSITIONS OF MASSIVE SULFIDES

Sample #	102-3	102-4	102-5	102-7	102-8	102-9
# of points counted	1000	500	500	500	1000	1000
Mineral	Area percentages					
quartz	61	58	65	52	65	57
pyrite	21	20	15	16	18	26
chalcopyrite	<1	2	<1	3	<1	1
other opaques	2	<1	2	<1	<1	<1
sphalerite	9	3	<1	25	9	4
voids	7	16	17	5	8	13

Note: "Other opaques" includes covellite, digenite, and iron oxy-hydroxide.

X-ray diffraction of the massive sulfides indicates quartz and pyrite as ubiquitous and dominant constituents, but optical petrography indicates the presence of sphalerite in variable proportions up to 25%, and chalcopyrite present in accessory amounts (< 3%; Table 1). Traces of covellite, digenite, and galena also occur.

The massive sulfide rocks appear to be a mosaic of fine-grained (of the order of 0.1 mm and less) anhedral quartz containing abundant embedded

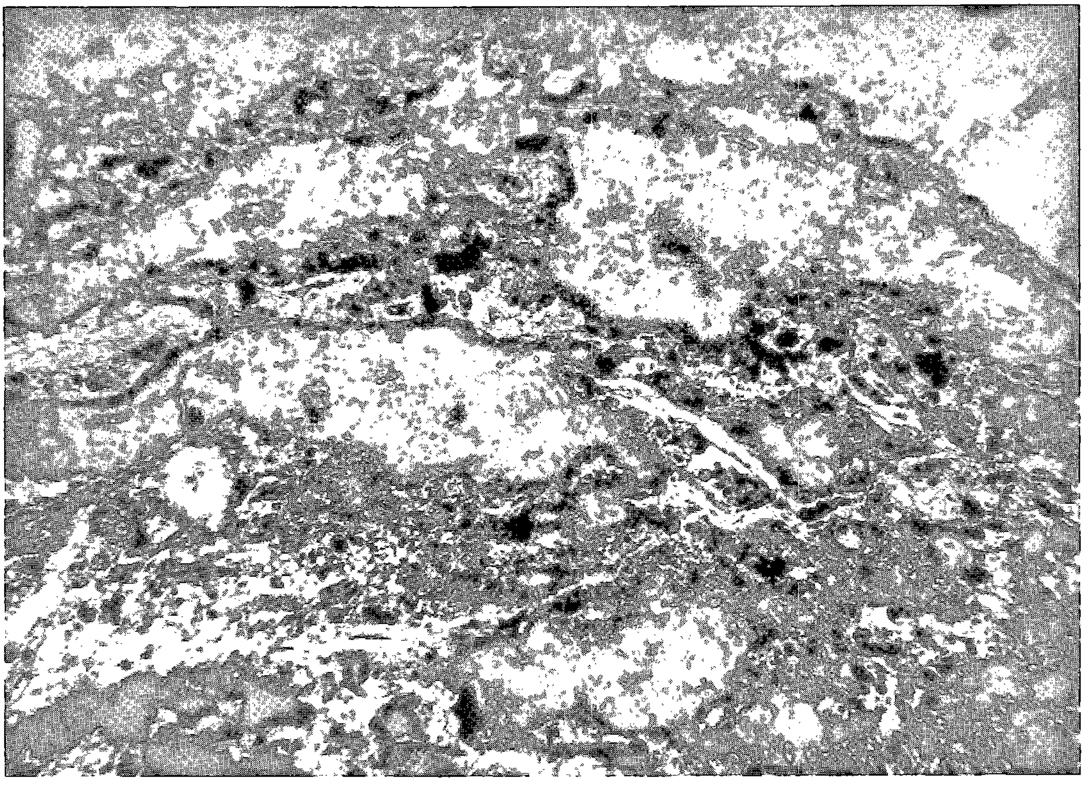

FIG. 2. Photomicrograph of domal lamination in massive sulfide, consisting of granular and colloform sulfide (mainly pyrite) and mosaic quartz. Field of view is 5 mm wide. Plane-parallel light.

blebs and stringers of colloform pyrite, which commonly align into curved stringers or domal features up to several cm long (Fig. 2). Quartz is coarser and clearer in pockets and small veinlets that measure up to about 2 mm in maximum dimension. These correspond to the quartz-filled vugs seen in hand specimens. Pyrite occurs with this coarser quartz as cubes measuring about 0.5 mm. Transparent isotropic sphalerite occurs as interstitial grains up to 0.25 mm across, in stringers and thin colloform layers, and rarely in euhedral grains 2 mm in diameter. Chalcopyrite forms small interstitial patches and irregular replacements within sphalerite; it is rimmed and in places completely replaced by covellite and digenite. Galena(?) forms tiny inclusions in sphalerite.

Practically all of the quartz grains exhibit undulose extinction. Furthermore, in some filled vugs, concentric layering and the development of plumose growth-habits are common, indicating that the quartz here may be primary. Some mosaic quartz encloses faint spherulitic outlines, a texture interpreted by Alt *et al.* (1987, their Fig. 4B) to represent quartz replacement of primary opaline silica. Therefore, as for other examples from East Pacific seamounts (Alt *et al.* 1987), some early silica was precipitated as opaline or amorphous silica. Such material later recrystallized, and vugs and veins were subsequently filled by primary quartz.

Quartz grains, particularly the primary vug-filling quartz, contain sparse fluid inclusions that consist of liquid and a vapor bubble. The inclusions are equant but have irregular walls. They are isolated inclusions, and are interpreted to represent primary trapping of fluids from which the quartz was precipitated or which induced recrystallization from pre-existing amorphous silica. Ice melting temperatures of 64 inclusions in six samples (Fig. 3) gave an average of -2.4°C ± 0.5°C (one standard deviation), corresponding to 4.0 ± 0.8 wt.% equivalent NaCl (Roedder 1984, p. 233). This value for the ice melting temperature is slightly lower than that for seawater [-1.9°C, corresponding to 3.2 wt.% NaCl equivalent (Weast 1973)]. Ice melting temperatures obtained from each of the six samples have identical average values.

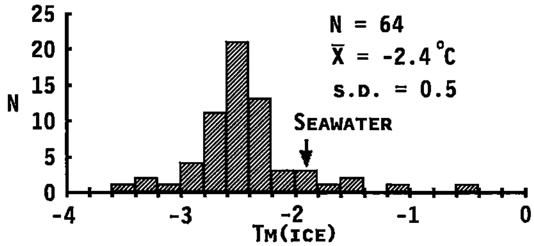

FIG. 3. Frequency histogram of measured temperatures of ice melting from fluid inclusions within quartz. The strong mode at -2.4°C corresponds to 4.0 wt.% NaCl equivalent, *i.e.*, slightly more saline than seawater.

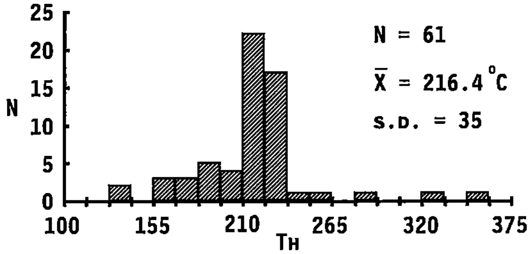

FIG. 4. Frequency histogram of measured temperatures of homogenization of fluid inclusions (all homogenizations to the liquid phase). The presumed trapping temperatures of the fluids are about 25°C higher than the homogenization temperatures because of the ambient 26 MPa pressure at the seafloor.

Temperatures of homogenization of fluid inclusions into the liquid phase [Th L-V (L), hereafter designated Th] vary from about 160 to 350°C, but with a strong mode around 216°C (Fig. 4). Because the massive sulfide was formed at the seafloor (ambient pressure of 26 MPa), a pressure correction of about 25°C ± 5°C should be applied to Th (Roedder 1984, p. 262), which gives a mean trapping temperature of the fluid of about 240°C ± 35°C (one standard deviation). Trapping temperatures of inclusions in anhydrite and calcite in several other studies of seafloor sulfides agree well with the temperatures determined through actual measurements by thermocouple or from coexisting mineral chemistry (Le Bel & Oudin 1982, Kusakabe *et al.* 1982, Koski *et al.* 1985, Peter *et al.* 1986, Brett *et al.* 1987). Thus, the 240°C temperature indicated by the present study is considered to be a good approximation of the temperature of quartz growth.

Five samples of the massive sulfide were analyzed for selected trace and heavy elements (Table 2). If we assume that Au and Ag reside primarily in sulfide phases, the bulk compositions can be recalculated to quartz-free values. Sulfide phases contain from 0.2 to 2.3 ppm Au and from 50 to 150 ppm Ag. Cu and Zn values are elevated because of the presence of chalcopyrite and sphalerite, respectively. The concentration of lead is low (0.02-0.03 wt.%).

THE ATACAMITE CRUSTS

Several small (2-5 cm) pieces of iron oxide crust in the dredge haul contain, on one side only, a coarse drusy layer of atacamite crystals. The

TABLE 2. CHEMICAL DATA ON THE MASSIVE SULFIDES

Sample	Au (ppm)	Ag (ppm)	Cu wt.%	Pb wt.%	Zn wt.%	Fe wt.%
102-3	1.23 2.3	79.8 150	3.4	0.03	4.6	9.0
102-4	0.51 0.9	40.6 72	2.2	0.02	3.2	8.9
102-5	0.14 0.2	34.8 50	1.6	0.02	2.3	10.4
102-7	0.14 0.3	35.5 86	3.8	0.02	7.0	8.1
102-8			3.2	0.03	6.4	8.6

Analyses for Au and Ag by fire assay. Cu, Pb, and Zn were by atomic absorption, and Fe total was determined titrametrically. All analyses were performed by Bondar-Clegg Ltd.
For Au and Ag, the upper value is the actual analysis, and the value underneath is calculated quartz-free, using the modal data from Table 1. It thus represents the Au and Ag content of the sulfide alone, assuming that the quartz is free of these elements.

crystals measure 1 to 2 mm across, and exhibit the {110}, {011} and {010} forms. X-ray-diffraction patterns show that an indeterminate amount of the hexagonal polymorph paratacamite also is present. In thin section, the crystals are transparent to cloudy, with zones of cloudiness forming a euhedral pattern of concentric growth-zones. No fluid inclusions were observed in the atacamite.

Atacamite also is present, as noted above, as an accessory phase at the margins of some of the massive sulfide samples. There, it is earthy, occurs in veinlets, and resembles atacamite described from many other seafloor hydrothermal settings (*e.g.*, Mossman & Heffernan 1978, Bonatti *et al.* 1976, Alt *et al.* 1987).

THE IRON OXIDES

The majority of the dredged materials are reddish orange rocks and crusts that resemble the iron oxide - hydroxide materials observed and sampled from low-temperature hydrothermal fields on seamounts (*e.g.*, Lonsdale *et al.* 1982, Malahoff *et al.* 1982, Exon & Cronan 1983, Vanko *et al.* 1984, Hekinian & Fouquet 1985, Alt 1988a). Samples are porous, low in density and earthy. Smear slides prepared from the earthy parts contain optically isotropic red translucent grains and abundant red translucent filaments. The filaments are typically 2 to 4 μm wide and may attain lengths of tens of μm: they exhibit curved and convoluted forms, commonly branching, and less commonly intertwined (Fig. 5). In size and shape, they resemble the long branching filaments described, for example, by Alt (1988a) and Juniper & Fouquet (1988). These authors inferred that the filaments probably represent iron-encrusted filamentous bacteria or the molds of such bacteria. Filamentous bacteria isolated from modern living bacterial mats in hydrothermal deposits on the Loihi seamount are generally a few μm across and tens to hundreds of μm long; nonbranching forms are dominant (Karl *et al.* 1988).

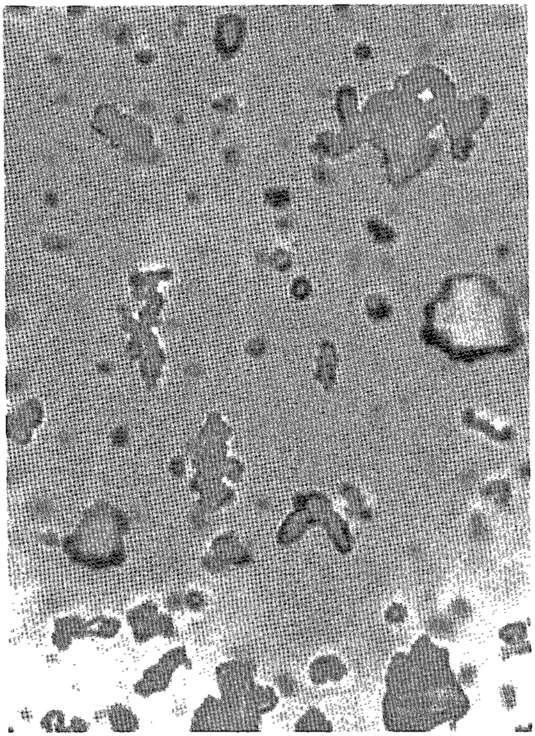

FIG. 5. Photomicrograph of red iron oxide crust material in oil, showing the abundant rod- and filament-shaped sheaths of amorphous iron oxide, interpreted to be molds of filamentous bacteria. Field of view is 75 μm wide, and a typical filament mold is 1 to 2 μm across.

DISCUSSION

The hydrothermal material dredged from the summit of the volcano is part of a seafloor hot-spring deposit. It is unlikely that any of the samples are from a sub-seafloor stockwork (Honnorez *et al.* 1985) because there is no morphological evidence for tectonic exposure such as caldera faulting (Fig. 1). The seamount deposits explored with submersibles near 12°N and 21°N along the East Pacific Rise and described, respectively, by Hekinian & Fouquet (1985) and by Alt *et al.* (1987) are the closest known analogues to the present dredged deposit. The atacamite crusts are analogous to those observed at the TAG Mid-Atlantic site (Thompson *et al.* 1988) and East Pacific Rise seamounts (Alt *et al.* 1987), formed by diagenetic oxidation and remobilization of copper within sulfide mounds.

Elemental analyses of massive sulfide yield values for Au, Ag, Cu, Zn, Pb, and Fe that are typical for samples from many seafloor sulfide deposits (Rona 1988, Hannington & Scott 1989). The gold and silver values match fairly closely those of the primary Fe and Fe–Zn massive sulfide from TAG (Hannington *et al.* 1988), as well as massive sulfide from Axial Seamount and the Southern Explorer Ridge (Hannington & Scott 1989). Gold and silver values exceed those in massive sulfides from 21°N East Pacific Rise (*e.g.*, Zierenberg *et al.* 1984). Levels of copper and zinc are lower than in many seafloor samples (Rona 1988). Despite an association with atacamite, there is no dramatic secondary (supergene) Au enrichment in the sulfides, as has been discovered at TAG (Hannington *et al.* 1988).

An unusual aspect of the seamount massive sulfide samples is the abundance of quartz and the presence of fluid inclusions within primary quartz. Black smoker fluids are generally supersaturated with respect to quartz as well as amorphous silica at seafloor pressures (*e.g.*, Von Damm *et al.* 1985, Bowers *et al.* 1985, Michard *et al.* 1984), but quartz and, to a lesser extent, amorphous silica are rare within many black smoker chimneys. Black smoker fluids apparently rise nearly adiabatically from a deep reaction-zone where the fluids are in equilibrium with quartz at high temperature and pressure. During rapid upwelling, quartz nucleation is suppressed, and dissolved silica ends up being flushed out into the ocean. The presence of amorphous silica or quartz with sulfides in mounds or chimneys attests to a process that allows nucleation of silica to occur; one possibility is that fluid encounters a regime of slower and more diffuse flow, perhaps combined with substantial conductive heat-loss (*cf.* Hannington & Scott 1988; their Fig. 17). Tivey & Delaney (1986) proposed a similar scenario for portions of massive sulfide mounds that were sealed by late-stage precipitation of amorphous silica.

In contrast to black smoker chimneys that are devoid of silica, the other end of what may be a complete natural spectrum is the silica-rich, sulfide-free chimneys from the Galapagos spreading center (Herzig *et al.* 1988). These structures, composed of amorphous silica (opal-A), were precipitated at 32° to 42°C, based on oxygen isotopic values. Herzig *et al.* (1988) suggested that fluids responsible for these inactive chimneys were cooled from high-temperature Si-rich solutions by a combination of conductive cooling and mixing with cold seawater. They hypothesized that associated sulfides may have been deposited in the subsurface.

The massive sulfides described in the present paper fall in the middle of the silica spectrum. They are similar to sulfides from other East Pacific Rise seamounts described by Alt *et al.* (1987) and Hekinian & Fouquet (1985) that contain abundant amorphous silica (opal), as well as quartz that has both replaced opal and has crystallized directly in vugs and fractures. The silica–sulfide–sulfate spires from Axial Seamount (Hannington & Scott 1988) similarly contain abundant amorphous silica. Alt *et al.* (1987) estimated temperatures of quartz precipitation on the basis of oxygen isotopic values; if we assume that the fluid was unshifted from seawater ($\delta^{18}O$ = 0‰), the quartz grew between 230° and 250°C. If the fluid was shifted to a $\delta^{18}O$ of +2.0‰ then the corresponding temperature range was 280° to 320°C. These temperature constraints are in excellent agreement with our range of fluid-inclusion-based temperatures, 240° ± 35°C. We therefore concur with other workers that moderate-temperature hot springs (in the mid-200°C range) may form substantial silica–sulfide deposits either within seafloor mounds or beneath the seafloor.

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