

THE FATE OF ARSENIC IN SUBMARINE HYDROTHERMAL
ENVIRONMENTS: A SUMMARY OF RECENT DATA

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ABSTRACT

In the past 25 years, active hydrothermal systems, polymetallic mineral deposits, and robust biological communities have been discovered in a variety of submarine settings including sediment-free and sediment-covered ocean ridges, rifted continental margins, volcanic arcs, back-arc basins, and seamounts. Chemical analyses of vent fluids, massive sulfide deposits, Fe-Mn oxyhydroxide precipitates, and suspended plume particles from submarine hydrothermal systems reveal that arsenic and other metals are effectively mobilized from the oceanic crust and overlying sedimentary strata, transported to the sea floor and into the overlying water column, and concentrated in surficial mineral deposits. Although biological data are more limited, elevated arsenic contents have also been analyzed in macroorganisms such as mussels and shrimp that inhabit fluid discharge zones.

Arsenic concentrations in unmixed, end-member hydrothermal fluids venting onto the ocean floor are enriched from 2X to 500X seawater concentrations (~2 ppb in deep ocean waters). For example, arsenic contents range from 5 to 50 ppb in high-temperature (to 400°C) vent fluids at ocean ridges underlain by basalt, 20 to 80 ppb at ocean ridges covered by terrigenous sediment, and 450 to 825 ppb at back-arc basins underlain by andesite and rhyodacite. The highest arsenic values (to 1,050 ppb) in a submarine

hydrothermal fluid were measured in CO₂-rich fluids with temperatures near 100°C that were venting in shallow water on the flanks of a Quaternary arc volcano offshore Papua New Guinea (Tutum Bay site; Pichler et al., 1999).

The amount and speciation of arsenic in hydrothermal deposits are a function of source rock composition, the Eh, pH, and temperature of the ambient fluid, and the relative concentrations of other elements in solution such as iron and sulfur. Arsenic is concentrated in sulfide minerals in mounds and chimneys that form during discharge of high-temperature fluids at the sea floor-seawater interface. Bulk arsenic contents of sulfide deposits range from 50 to 1,000 ppm at sediment-free ocean ridges and from 2,000 to 20,000 ppm at sediment-covered ridges and back-arc basin settings. Although arsenic-bearing minerals such as arsenopyrite, realgar, orpiment, tennantite, enargite, proustite, löllingite, and Pb-As sulfosalts are present in trace quantities in most sea-floor massive sulfides, they are abundant in some sites at sediment-covered ridges (e.g., Escanaba Trough; Koski et al., 1988) and back-arc basins (e.g., Okinawa Trough; Halbach et al., 1993).

The arsenic content of oxyhydroxide deposits precipitated at lower temperatures (<100°C) varies by more than two orders of magnitude with maximum measured values of 180 ppm in Mn-rich oxyhydroxide sediment at the Galapagos Ridge vent field (Corliss et al., 1978), 5,500 ppm in Fe-Mn oxyhydroxide deposits at Franklin Seamount (Binns et al., 1993), and 62,000 ppm in Fe(III) oxyhydroxides at the Tutum Bay site (Pichler and Veizer, 1999). The latter deposit also contains scorodite (FeAsO₄·H₂O) and claudetite (As₂O₃). In addition to arsenic concentration in surficial mineral deposits, colloidal Fe(III) oxyhydroxide particles suspended in plumes of mixed hydrothermal fluid and

seawater above discharge sites rapidly adsorb arsenic from the vent fluid as well as additional arsenic from ambient seawater. The concentration of arsenic by Fe oxyhydroxides at vent fields represents a net sink for this element in the oceans (Feely et al., 1994).

The biogeochemical fate of arsenic at submarine hydrothermal sites is less well known. The average arsenic contents in soft tissues of mussels (40 ppm) from the Mid-Atlantic Ridge (Larsen et al., 1997) are higher than arsenic contents of mussels (2 to 20 ppm) from coastal environments (Francesconi and Edmonds, 1993). In contrast, shrimp recovered from the Mid-Atlantic Ridge have lower arsenic contents (average 13 ppm) and mussels from the Galapagos Ridge have similar arsenic contents (average 15 ppm) compared to shrimp and mussels from surface waters and coastal zones (Larsen et al., 1997; Smith and Flegal, 1989). The high levels of arsenic (to 70 ppm) in gill tissues and digestive tracts of these organisms, mostly in the form of arsenobetaine and arsenosugars, suggest that arsenic is assimilated through the activity of symbiotic bacteria and by filtration of Fe oxyhydroxide particles. The presence of arsenic-bearing sulfosalt minerals proustite (Ag_3AsS_3) and pearceite ($\text{Ag}_{16}\text{As}_2\text{S}_{11}$) in filamentous bacteria from a vent site on the northern Gorda Ridge (Zierenberg and Schiffman, 1990) is a further indication that microorganisms play a key role in the chemistry of arsenic in submarine hydrothermal environments.

REFERENCES

Binns, R.A., Scott, S.D., Bogdonav, Y.A., Lisitzin, A.P., Gordeev, V.V., Gurvich, E.G., Finlayson, E.J., Boyd, T., Dotter, L.E., Wheller, G.E., and Muravyev, K.G., 1993, Hydrothermal oxide and gold-rich sulfate deposits of Franklin Seamount, Western Woodlark Basin, Papua New Guinea: *Economic Geology*, v. 88, p. 2122-2153.

Corliss, J.B., Lyle, Mitchell, Dymond, Jack, and Crane, Kathy, 1978, The chemistry of hydrothermal mounds near the Galapagos Rift: *Earth and Planetary Science Letters*, v. 40, p. 12-24.

Feely, R.A., Massoth, G.J., Trefry, J.H., Baker, E.T., Paulson, A.J., and Lebon, G.T., 1994, Composition and sedimentation of hydrothermal plume particles from North Cleft segment, Juan de Fuca Ridge: *Journal of Geophysical Research*, v. 99, p. 4985-5006.

Francesconi, K.A., and Edmonds, J.S., 1993, Arsenic in the sea: *Oceanography and Marine Biology, Annual Review*, v. 31, p. 111-151.

Halbach, P., Pracejus, B., and Marten, A., 1993, Geology and mineralogy of massive sulfide ores from the central Okinawa Trough, Japan: *Economic Geology*, v. 88, p. 2210-2225.

Koski, R.A., Shanks, W.C., III, Bohrsen, W.A., and Oscarson, R.L., 1988, The composition of massive sulfide deposits from the sediment-covered floor of Escanaba Trough, Gorda Ridge: Implications for depositional processes: *Canadian Mineralogist*, v. 26, p. 655-673.

Larsen, E.K., Quetel, C.R., Munoz, Riansares, Fiala-Medioni, Aline, and Donard, O.F.X., 1997, Arsenic speciation in shrimp and mussel from the Mid-Atlantic hydrothermal vents: *Marine chemistry*, v. 57, p. 341-346.

Pichler, Thomas, and Veizer, Jan, 1999, Precipitation of Fe(III) oxyhydroxide deposits from shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea: *Chemical Geology*, v. 162, p. 15-31.

Pichler, Thomas, Veizer, Jan, Hall, G.E.M., 1999, The chemical composition of shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea and their effect on ambient seawater: *Marine Chemistry*, v. 64, p. 229-252.

Smith, D.R., and Flegal, A.R., 1989, Elemental concentrations of hydrothermal vent organisms from the Galapagos Rift: *Marine Biology*, v. 102, p. 127-133.

Zierenberg, R.A., and Schiffman, Peter, 1990, Microbial control of silver mineralization at a sea-floor hydrothermal site on the northern Gorda Ridge: *Nature*, v. 348, p. 155-157.