HIGH ARSENIC CONCENTRATIONS IN GLOBALLY DISTRIBUTED SEAFLOOR IRON-MANGANESE OXYHYDROXIDE DEPOSITS

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Very high mean concentrations of arsenic (165 to 1050 ppm) characterize extensive deposits of hydrogenetic iron-manganese crusts (Fe-Mn crusts) that occur throughout the ocean basins (Fig. 1). Fe-Mn crusts occur on seamounts, ridges, and plateaus where currents have kept the rocks swept clean of sediments for millions of years. Fe-Mn crusts precipitate out of cold ambient seawater onto hard-rock substrates forming pavements up to 250 mm thick. The crusts grow at the incredibly slow rates of 1-6 mm/Ma and occur at water depths of 400-4000 m (Hein et al., 2000). Fe-Mn crusts are composed of δ-MnO_2 (vernadite), X-ray amorphous iron oxyhydroxide, minor detrital quartz and aluminosilicates, and minor to moderate amounts of carbonate fluorapatite in the older parts of thick crusts. The crusts have an extreme amount of specific-surface area (mean 325 m^2/g) and high porosity (mean 60%) that along with slow growth rates promote the acquisition of elements from seawater by co-precipitation along with the major iron and manganese oxyhydroxides, adsorption, and redox reactions (Hein et al., 2000). These crusts comprise the substrate on which many sessile marine organism live.

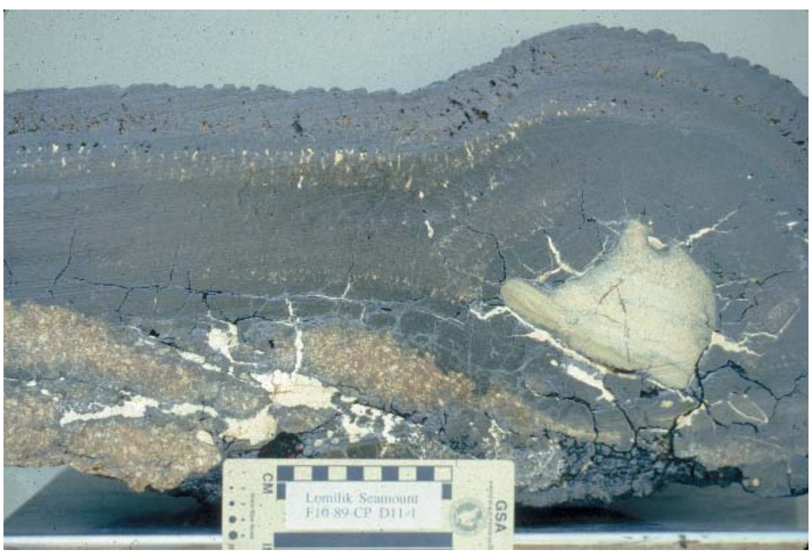

Figure 1. Cross-section of cobalt-rich Fe-Mn crust and altered hyaloclastite substrate rock. The Fe-Mn crust is about 18 cm thick and shows distinct growth layers. The crust began to grow on the substrate rock about 60 Ma ago. A mudstone cobble occurs within the crust on the right side.

Arsenic concentrations were determined on one set of samples using neutron activation and on another set using graphite furnace atomic absorption. The global mean concentration of arsenic in Fe-Mn crusts is 273 ppm based on analyses of 637 bulk crusts (standard deviation is 362 ppm; minimum 64 ppm; maximum 1920 ppm). The mean arsenic content is highest (1050 ppm) in Fe-Mn crusts collected from the region surrounding the Hawaiian Islands and lowest in northwest Pacific (165 ppm) and Indian Ocean (181 ppm) crusts. Fe-Mn crusts from various other regions of the Pacific average 212 to 544 ppm arsenic and Atlantic Fe-Mn crusts average 289 ppm (Table 1).

Table 1. Mean composition of Fe-Mn crusts from the global Ocean compared with C-C zone Fe-Mn nodules; USGS data (columns 1-5, 8-9, 10, 13-14) normalized to 0% H_2O^-; Fe-Al wt.%; As-Zn ppm; Hg ppb.

			Fe/Mn	Fe	Mn	Si	Al	As
1	FSM- Palau	n=35	1.00	20.2	20.1	5.50	1.31	271
2	Marshall Is.	n=116	0.67	15.7	23.3	2.80	0.63	212
3	NW of Marshall Is.	n=43	0.76	16.6	21.7	5.38	1.15	234
4	Johnston I.	n=103	0.71	17.4	24.4	4.06	0.81	258
5	California Margin	n=71	1.24	19.5	15.7	10.5	1.95	246
6	NW Pacific	n=1478	0.68	15.1	22.1	3.70	1.00	165
7	Hawaii	n=182	0.85	17.8	21.0	6.26	1.69	1050
8	Far N Pacific	n=6	0.95	20.3	21.4	4.52	1.02	259
9	Shatsky Rise	n=20	0.93	22.5	24.3	9.45	1.97	210
10	EC-SE Pacific Margin	n=6	1.07	25.9	24.1	8.28	2.10	246
11	S Pacific 0-25° Lat	n=228	0.98	21.2	21.6	4.28	1.30	254
12	Far S Pacific >25° Lat	n=51	1.14	19.0	16.7	7.14	3.55	544
13	Atlantic	n=25	1.54	21.6	14.0	5.50	1.54	289
14	Indian	n=14	1.52	23.6	15.6	7.78	1.34	181
15	C-C Zone Nodules	n=x	0.27	6.90	25.4	7.60	2.90	159

		Co	Cu	Ni	Pb	Tl	Zn	Hg
1	FSM- Palau	3991	876	3487	1327	107	658	15
2	Marshall Is.	6410	963	4626	1505	150	719	9
3	NW of Marshall Is.	5019	1310	3927	1713	226	646	11
4	Johnston I.	7441	1059	4398	1723	193	697	10
5	California Margin	2746	679	2926	1207	54	620	39
6	NW Pacific	6372	1075	5403	1777	--	680	--
7	Hawaii	6904	760	3651	1715	--	531	--
8	Far N Pacific	4349	298	3393	1746	128	535	1448
9	Shatsky Rise	2713	1270	3241	1740	80	674	38
10	EC-SE Pacific Margin	1918	558	2654	833	76.6	597	91
11	S Pacific 0-25° Lat	5508	1100	4237	1207	190	688	27
12	Far S Pacific >25° Lat	3878	761	3385	1531	--	822	--
13	Atlantic	3574	774	2685	1108	94.5	598	141
14	Indian	3126	1254	2558	1058	89.4	533	48
15	C-C Zone Nodules	2400	10200	12800	450	169A	1400	0.15

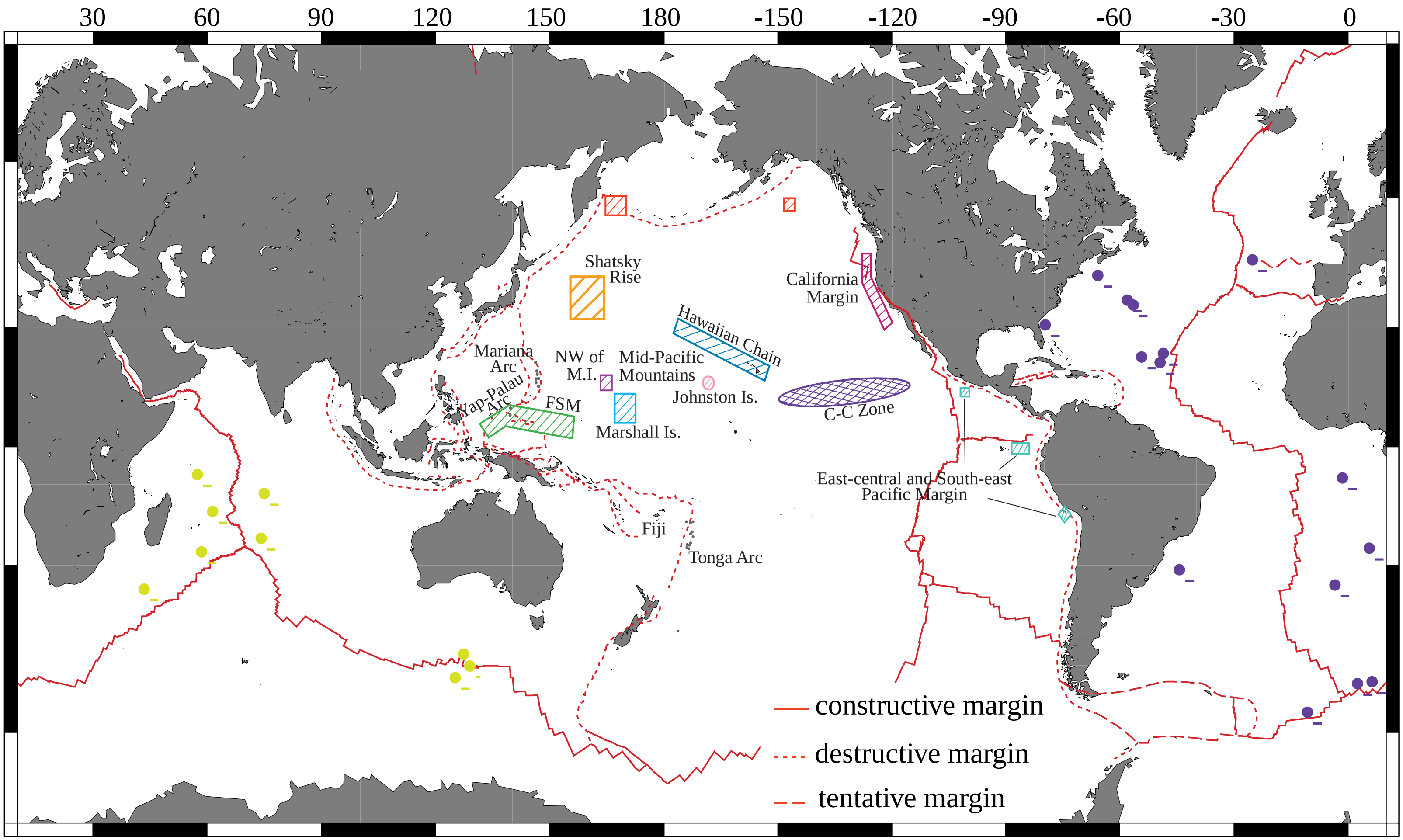

Figure 1. Lined boxes in the Pacific are regions with mean Fe-Mn crust compositional data listed in Table 1; far north Pacific data are from the two northernmost regions; the California margin includes the Oregon margin; the far south Pacific data cover areas mostly offshore New Zealand and southern Australia; the south Pacific data span most of the area between South America and the west Pacific arcs and between the equator and 25° south latitude; the cross-hatched oval region is the Clarion-Clipperton prime Fe-Mn nodule zone for comparison; data for all the stations in the Atlantic and Indian Oceans were averaged for Table 1.

Arsenic occurs in seawater as an oxyanion and is redox sensitive, occurring in its more oxidized arsenate state ($HAsO_4^{2-}$) in normal seawater and in its reduced arsenite state in low-oxygen seawater, such as in regions of the oxygen-minimum zone that is produced by oceanic upwelling. The dissolved arsenate is adsorbed from seawater onto colloidal Fe oxyhydroxide in seawater as well as onto the crust surface once the colloids are precipitated. This mechanism is capable of significantly concentrating arsenic. For example, enrichments of arsenic in Fe-Mn crusts range from 1.7×10^4 to 5.2×10^5 times the mean seawater concentration (0.0037 ppm). Relative to the Earth's crustal mean (2 ppm), arsenic is enriched in Fe-Mn crusts 32 to 960 times. The ultimate sources of arsenic in seawater are hydrothermal fluids (5-50 ppb) from globe-encircling oceanic spreading ridges and input from rivers. Other sources include hydrothermal fluids from volcanic arcs, hot-spot volcanoes, back-arc basin spreading centers, and shallow-water hydrothermal systems.

Correlation coefficients indicate that the arsenic is associated with the iron oxyhydroxide, which is supported by sequential leaching studies. Sequential leaching indicates the following associations for arsenic: About 2% is associated with the acidic acid-leachable phase; 6% with the Mn oxyhydroxide phase; 90% with the Fe oxyhydroxide phase; and 2% with the residual (mostly quartz and aluminosilicate) phase.

The degree to which arsenic is bioavailable and bioconcentrated is not known, but it is essential that we learn what are the biological consequences of these extensive, high-arsenic seafloor deposits, and how the organisms that live on this substrate have adapted to the high concentrations of arsenic and other toxic elements.

Reference Cited

Hein, J.R., Koschinsky, A., Bau, M., Manheim, F.T., Kang, J.-K., and Roberts, L., 2000. Cobalt-rich ferromanganese crusts in the Pacific. In Cronan, D.S. (ed.), Handbook of Marine Mineral Deposits. CRC Press, Boca Raton, Florida, p. 239-279.