

# Water-Rock Interaction

*Edited by*

**YOUSIF K. KHARAKA**

*U.S. Geological Survey, Menlo Park, California, USA*

**OLEG V. CHUDAEV**

*Far East Geological Institute, Vladivostok, Russia*

*Associate editors:*

**JAMES J. THORSEN, HALDOR ARMANNSSON, GEORGE N. BREIT,**

**WILLIAM C. EVANS & TERRY E. C. KEITH**



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# Geochemical evidences of the accelerated growth of ferromanganese nodules due to hydrothermal supply

Y.G. Volokhin & N.N. Barinov

*Far East Geological Institute, Vladivostok, Russia*

Wayne C. Isphording

*University of the South Alabama, Mobil, Ala., USA*

**ABSTRACT:** A comparison of geochemistry of 97 ferromanganese nodules and crusts of the north equatorial Pacific had shown an anomalous composition of nodules from the northeastern ending of the Siqueiros Fracture Zone that is explained by their accelerated growth due to hydrothermal supply of Mn and some other elements. High contents of Mn (up to 44.1%), Ba, Zn, Li, and low values for of Pb, Co, Zr, Ce, Y, Nb are characteristic for Siqueiros nodules. The ratio of Mn/Fe (5-80) and (Fe+Mn)/Ti (110-660) indicates a mostly hydrothermal source of matter as well as a high accretionary rate of the Siqueiros nodules. Low mass equivalent ratio O/Mn (1.784 to 1.860) suggests suboxidized environment of the Siqueiros nodules, diagenesis.

## 1 INTRODUCTION

Rifts of the East Pacific Rise (EPR) are the main sources of hydrothermal Mn and some heavy metals in the Pacific during the latest geological periods. Mixed with the matter of other origin (river influx and others) hydrothermal material has taken a part in ferromanganese nodules and crusts formation. A comparative geochemistry is one of the useful tools to differentiate ferromanganese deposits of hydrothermal origin from hydrogenetic (that is deposits that have settled from sea water and have been lost all specific features that can be attributed to specific sources). It is also useful to estimate the contribution of initially hydrothermal matter to hydrogenetic nodules and crusts. The aim of this paper is to present results of the study of ferromanganese nodules and crusts from the North Equatorial Pacific dredged during 7th, 13th cruises of R/V "Academic A. Vinogradov", and 13th cruise of R/V "Academic A. Nesmeyanov" which were undertaken by the Pacific Institute of Oceanology (Vladivostok) during 1986-1989. Localities of the study include Ogasawara Plateau, Mikhelson and Magellan seamounts South Emperor (Jenkins, Kammu, O'Brian), Eastern Clarion FZ, and Siqueiros FZ at its joint with Tekuantepec FZ. The effects of hydrothermal activity on ferromanganese nodules and crusts occurred in many sites, but we focused our study at the Siqueiros nodules which were the best example of hydrothermally influenced nodules.

## 2 METHODS

Nodule and crust mineralogy was determined by X-ray diffraction of air-dried and heated powder samples (DRON-3, Cu-K $\alpha$  radiation with a graphitic monochromator), as well as TEM microdiffraction study using "TESLA" BS-540 (U accel.=120 kv). Wet chemical technique (for major oxides), atomic absorption spectrophotometry by "HITACHI" 180-50 spectrophotometer (for Mn, Fe, Ni, Cu, Zn, Pb, Mo, Sr, Ba, Ti, V, Co, Rb, Li, Al, Mg, Ca, Na), and neutron activation analysis (for Nb, Y, Ce, La, Nd, Zr) were used for geochemical study.

## 3 LOCATION OF SEQUEIROS NODULES

The Siqueiros manganese nodules were dredged at stations V13-8 (9°46'N, 99°57'W, water depth is 4120-4070m) and V13-70 (9°45'N, 100°01'W, water depth is 3770-3660m). These sites are located at the north-eastern ending of the Siqueiros FZ close to its junction with the Tekuantepec FZ. The place is on a flank of EPR eastwards about 500 km from its crest. Submarine topography represents an alternation of small ridges and valleys of the north-eastern extension with water depths changing over from 3300m to 4200m. Nodules were gained (3 kg at st. V13-68, and 50 kg at st. V13-70) from a slope of the same ridge together with a piece of basalt and pumice one.

#### 4 LITHOLOGY AND MINERALOGY

The Siqueiros nodules are dominantly botryoidal, mononucleate, and range from 5 to 12.5 cm in diameter. They sometimes have a smooth (eroded by bottom currents) upper surface and rough bottom side impregnated with red clay. The Siqueiros nodules do not have cores of allochthonous material like basalt, phosphorite, volcanic glass, or other debris that is in contrast to nodules from Ogasawara, Magellan, Mikhelson, South Emperor, and Clarion areas. Their nuclei are homogeneous poorly shaped clots of ferromanganese oxihydroxides impregnated with dusty red clay particles. Nuclei are coated with alternating friable and dense manganese layers (1-3 mm). Poorly ordered tunnel-structured todorokite dominates in mineral composition of Siqueiros nodules. Buserite-1, buserite-2, birnessite and some mixed-layered asbolan-buserite were also recognized. Other minerals include ferrismectite, illite-smectite, and some impurities of plagioclase and quartz. In other areas of the North Equatorial Pacific todorokite occurs rarely in the inner parts of nodule coatings. They consist of vernadite, buserite, some asbolane with impurities of hydrogoethite, amorphous ferroxihydroxide, feldspar, quartz, smectite, phillipsite, illite, and francolite.

#### 5 CHEMICAL COMPOSITION OF SIQUEIROS NODULES

The Siqueiros nodules are geochemically distinct compared with ferromanganese crusts and nodules from other areas. They have high contents of Mn (27.8-44.1%) and low Fe (0.66-5.8%). Ratio Mn/Fe varies from 5 to 80, and (Fe+Mn)/Ti is from 110 to 660, while in other places these ratios are 0.5-5, and 25-85 respectively (Table 1, Fig. 1). Average contents of Zn, Ba, and Li in Siqueiros nodules are significantly higher, and Pb, Co, Sr, Zr, Nb, Ce, Nd are sometimes lower than in ferromanganese deposits of the other areas of the Pacific (Table 1). Equivalent ratios O/Mn of Siqueiros nodules are from 1.784 to 1.860, evidencing suboxidized environment of diagenesis. In comparison with the O/Mn ratio of Clarion FZ nodules ranges from 1.946-1.988 that is characteristic to oxidized environment of diagenesis.

Cores and bottom parts of manganese coatings are enriched in Pb, Cu, Zr, Fe, Al, and Li, while Mn enriched upper and middle parts of coatings comparatively are enriched in Ti, Nd, Co, Mo, and V. Mn/Fe ratio ranges across a single nodule from 13 to 73, and (Fe+Mn)/Ti ranges from 375 to 550, respectively in clayey bottom and core, and manganic upper part and middle layers of the coating.

Table 1. The average chemical composition of ferromanganese deposits from Mikhelson ridge (MR), Magellan seamounts (MS), Ogasawara Plateau (OP), South Emperor Ridge (SER), Clarion (CFZ) and Siqueiros (SFZ) Fracture Zones.

	Crusts				Nodules	
	OP (9)	MR (30)	MS (28)	SER (22)	CFZ (11)	SFZ (24)
Mn, %	21.54	19.70	17.87	19.50	20.90	38.44
Fe	10.41	10.92	14.00	14.49	12.99	1.94
Ti	0.69	0.63	0.92	0.79	0.80	0.13
Al	0.82	1.39	1.80	1.23	1.85	1.69
Mg	1.17	1.05	1.00	0.94	1.23	1.98
Ca	6.77	6.10	3.92	1.43	1.67	1.10
Na	1.63	1.63	1.54	1.61	1.75	2.28
K	0.54	0.73	0.82	0.61	0.74	0.97
Ni, ppm	4210	6373	3408	3145	3980	4290
Cu	678	697	1204	945	3300	2280
Zn	625	650	516	468	707	1240
Pb	1550	1724	1201	1315	688	99
Co	4380	5870	4924	3960	2970	211
Sr	1576	1742	1631	1508	1170	626
Rb	60	30	33	47	63	58
Li	10	18	10	15	30	109
V	606	577	601	710	1251	682
Mo	742	474	274	465	366	471
Ba	732	634	621	1274	705	1721
Zr	454	356	484	539	736	100
Nb	84	66	78	47	56	<10
Y	177	120	117	125	257	98
Ce	803	680	606	1658	1234	423
La	254	220	234	901	608	574
Nd	203	176	183	497	384	90
Ce/La	3.2	3.1	2.6	1.8	2.0	0.7
Mn/Fe	2.07	1.80	1.28	1.35	1.61	19.8
Fe+Mn	46.2	48.6	34.6	43.0	42.4	323.0
Ti						

Values in parentheses indicate a number of analyses from each site.

#### 6 DISCUSSION

The majority of ferromanganese crusts and nodules of North Equatorial Pacific plotted to ternary Bonatti et al. (1972) and Dymond et al. (1984) diagrams are inside the field of hydrogenetic deposits. Nodules of Siqueiros FZ are close to hydrothermal and suboxidized diagenetic fields.

The asymmetry existing in the distribution of ferromanganese deposits is demonstrated on maps (Ferromanganese..., 1976), that show that Mn-rich (Mn/Fe > 5) nodules and crusts tend to be located close to EPR region. Another part of the Pacific is the



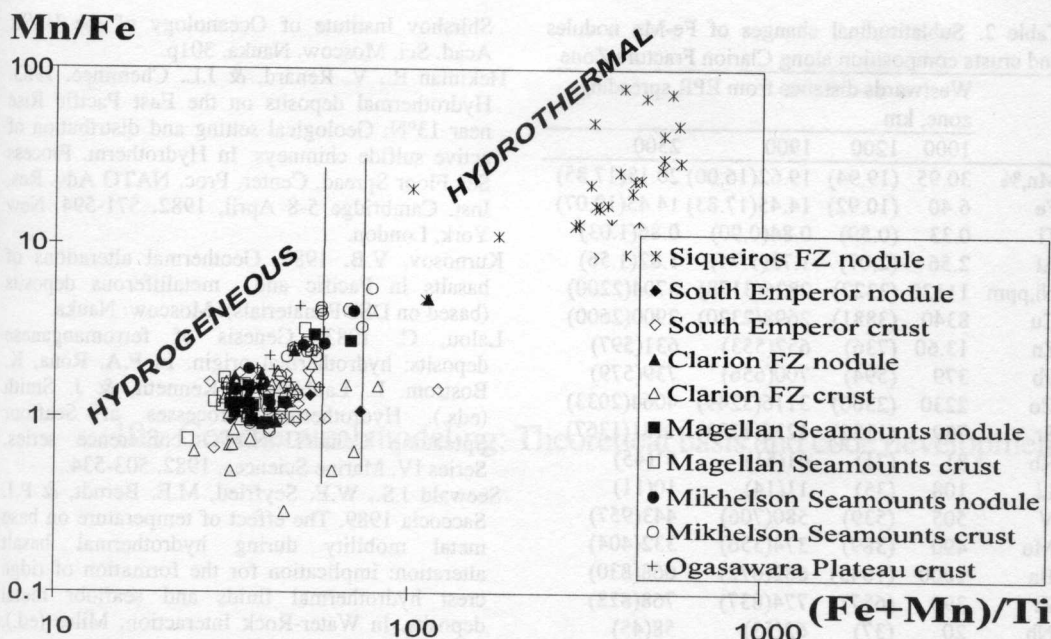


Fig. 1. Mn/Fe versus (Fe+Mn)/Ti in ferromanganese deposits from North Equatorial Pacific.

realm of ferromanganese deposits which have characteristic hydrogenous crusts ratio Mn/Fe from 0.5 to 5, in average: 1.2-2.0 (Table 1).

Endogenous influx of Mn (mostly by hydrothermal vents of EPR) into the Pacific likely dominates over rivers' supply from 3 times (Wolery & Sleep 1976) up to 10-12 times (Kurnosov 1986). The concentration of Mn in active vents of EPR rift is a million times more than in ambient sea water. The concentration of barium, zinc, and lithium are a thousand times more in hydrothermal vents at 21°N of EPR than in seawater (Von Damm et al. 1987). The differentiation of elements during the migration of solutions produces sediments rich in Cu and Fe near the vents, while the Zn and Mn tends to accumulate on some distance from them (Seewald et al. 1989). Active hydrothermal vents are known at 21°N and 13°N of EPR, and recent hydrothermal Mn encrustations are at the intersection of EPR rift and Siqueiros FZ (Hekinian et al. 1983, Lalou 1983).

Siqueiros nodules have been sampled about 500 km eastwards from the axial part of the EPR spreading zone. Nodules enriched in Mn were elevated also at the eastern part of the Clarion FZ about 1000 km westwards from the EPR spreading zone (Table 2). The closest to EPR nodules are rich in Mn, Ni, Cu, Li, Ba, Zn, but have the lowest content of Fe, Ti, Pb, Co, Sr, Zr, Nb, Y, Ce to compare with other Clarion nodules and crusts

(Table 2). Ratios Mn/Fe and (Fe+Mn)/Ti are diminished from 5 to 1.5, and from 113 to 38 respectively, also marking a decrease of hydrothermal influence on ferromanganese deposit chemistry.

N.M. Strakhov (1976) has analysed a ratio (Fe+Mn)/Ti as an indicator of hydrothermal material in marine sediments and rocks. The value more than 25 indicates the presence of hydrothermal Fe or Mn in terrigenous, planktonic, and pyroclastic rocks and sediments. During the diagenesis Fe and Mn migrate towards sediment seawater interface. It increases to some extent the (Fe+Mn)/Ti value. The investigation of individual nodules have shown the slight tendency of Ti to accompany Mn during diagenesis and to increase Ti/Al, and Ti/Fe in the richest in Mn layers of nodule coatings. The variation of (Fe+Mn)/Ti values across individual nodules are less than Mn/Fe ones. The majority of ferromanganese deposits from the Western Pacific seamounts, South Emperor ridge, and Clarion FZ are hydrogenetic ones having the (Fe+Mn)/Ti value less than 60, and Mn/Fe less than 5 (Fig. 1). Nodules of Siqueiros FZ are enriched in the elements Mn, Ba, Zn, Li, which are specifically abundant in hydrothermal vents of EPR. They have (Fe+Mn)/Ti more than 100, and Mn/Fe more than 5. Value of ratio (Fe+Mn)/Ti equal to 75-80 could be conventionally accepted as the limit between hydrogenetic and hydrothermal

Table 2. Sublatitudinal changes of Fe-Mn nodules and crusts composition along Clarion Fracture Zone

	Westwards distance from EPR spreading zone, km			
	1000	1200	1900	2500
Mn, %	30.95	(19.94)	19.62(16.00)	20.18(17.85)
Fe	6.40	(10.92)	14.45(17.83)	14.45(19.07)
Ti	0.33	(0.59)	0.84(0.90)	0.86(1.03)
Al	2.56	(2.07)	1.73(1.74)	1.82(1.56)
Ni, ppm	11120	(3327)	2826(3178)	3704(2200)
Cu	8340	(3881)	2698(2320)	2900(2600)
Zn	13.60	(736)	652(553)	631(597)
Pb	379	(594)	700(656)	739(579)
Co	2230	(2360)	3116(3249)	4064(2033)
Sr	789	(1122)	1235(1233)	1181(1367)
Rb	81	(71)	61(51)	61(45)
Li	108	(35)	11(14)	10(11)
V	505	(539)	580(706)	443(957)
Mo	490	(389)	374(356)	332(404)
Ba	1000	(1043)	682(672)	668(830)
Zr	390	(657)	774(837)	768(828)
Nb	20	(37)	62(53)	58(45)
Y	200	(284)	256(288)	270(285)
Ce	690	(1123)	1340(1243)	1236(1071)
La	530	(746)	632(588)	600(667)
Mn/Fe	4.8	(1.8)	1.4(0.9)	1.6(0.9)
Fe+Mn Ti	113	(52)	41(38)	38(36)

Values in parentheses represent average compositions in ferromanganese crusts, others are average values in nodules.

ferromanganese deposits. We estimate the contribution of hydrothermal matter (mostly Fe and Mn) in hydrogenous ferromanganese deposits as ranging at least 30% at Magellan seamounts up to 56% at Clarion FZ.

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