Iron-Manganese Nodules from Nares Abyssal Plain: Geochemistry and Mineralogy

Abstract. *Three nodules from a core taken north of Puerto Rico are composed chiefly of an x-ray amorphous, hydrated, iron-manganese oxide, with secondary goethite, and minor detrital silicates incorporated during growth of the nodules. No primary manganese mineral is apparent. The nodules are enriched in iron and depleted in manganese relative to Atlantic Ocean averages. The formation of these nodules appears to have been contemporary with sedimentation and related to volcanic activity.*

Three iron-manganese nodules were recovered from a 95-cm core taken on Nares Abyssal Plain (25°N, 65°W), a deep southeastern extension of Hatteras Abyssal Plain (*1*), from a depth of 5729 m. Two of the nodules came from the top 5 cm of the core; the third, from a depth of 73 cm. They provided a rare opportunity for study of geochemical variations of nodules with depth in a sediment column; they were spherical, 3 cm in diameter, and friable, showing uniform distribution of black submetallic grains in an ocherous matrix; a unique feature was their identical size, shape, texture, mineralogy, and concentration of minor elements although the 73-cm nodule predates the other two by at least 30,000 years on the basis of estimates of the rate of accumulation of clay in the North Atlantic (*2*). The core sediment was typically abyssal (*3*), had uniform texture, contained sparse micronodules, and was oxidized throughout; there was no physical evidence of disturbance of sediment within the core, and the extremely friable nature of the nodules precludes any postformational transport.

The nodules were crushed, and washed repeatedly by centrifugation and decantation for removal of soluble salts and adherent clay. Subsamples were taken for x-ray diffraction, differential-thermal, thermogravimetric, and atomic-absorption analyses. The fractions for x-ray diffraction analysis were examined under a microscope, and apparent mineral phases were segregated. Bulk samples were used for all other analyses.

Table 1. Chemical compositions (percentages by weight) and characteristics of iron-manganese nodules compared with some Atlantic averages. Results: 1 and 2, for the two surface nodules; 3, for the 73-cm nodule; 4, average of 16 other analyses (*8*).

Result	Element						Ignition loss	Insoluble residue*	Mn:Fe ratio
	Fe	Mn	Co	Cr	Cu	Zn			
1	28.42	19.35	0.41	0.01	0.14	0.07	41.22	27.10	0.681
2	31.61	17.52	.39	.02	.16	.05	34.39	19.59	.554
3	34.96	13.21	.37	.02	.14	.05	37.72	25.40	.378
4	25.85	21.20	.58	.003	.22	.10			.820

* After ignition loss.

Table 2. X-ray powder data for nodule phases in the range 500° to 1000°C, hematite, and jacobsite; for the last two, lines of intensity less than 20 are not included. For the nodule phases, line intensities were determined visually; Fe radiation, $\lambda = 1.9373$ Å; camera diameter, 114.6 mm. Lines for detrital-silicate phases are not included. Abbreviations: *I*, intensity; v, very (V refers to breadth only); w, weak; B, broad; m, medium; s, strong.

Hematite, ASTM 13-534 (*d* Å, *I*)	Nodule phases (*d* Å, *I*)				Jacobsite, ASTM 10-319 (*d* Å, *I*)
	500°C	650°C	870°C	1000°C	
3.66,25	3.66,vwB	3.66,mwB	3.68,mw	3.679,vw	
		2.97,wB	2.98,m	2.981,m	3.005,35
2.69,100	2.70,mwB	2.69,s	2.70,m	2.699,w	
			2.54,vs	2.544,vvs	2.563,100
2.51,50	2.51,mwB	2.52,vsVB	2.52,m		
2.201,30	2.20,wB	2.20,mw	2.21,w	2.206,vvw	
		2.101,wB	2.107,mw	2.107,m	2.124,25
1.838,40	1.837,vwB	1.833,mwB	1.839,w	1.8430,vw	
1.690,60	1.692,wB	1.687,ms	1.692,mw	1.6923,vw	
		1.617,wB	1.621,m	1.6227,m	1.6355,35
			1.488,s	1.4904,ms	1.5031,40
1.484,35	1.483,vwB	1.483,ms			
1.452,35	1.450,vwB	1.449,m	1.452,mw	1.4543,vw	

The fractions for x-ray diffraction analysis were ground in ethanol and dried at 70°C. Other bulk samples, for determination of phase relations at elevated temperatures, were heated in a muffle furnace in air for 72 hours at 200°, 500°, 650°, 870°, or 1000°C (each sample at one temperature) before cooling in air. All samples were mounted in silica capillaries and x-rayed in a powder camera with Mn-filtered Fe radiation.

Differential-thermal and thermogravimetric analyses were used to determine thermal stability, recrystallization, and dehydration, and to supplement and confirm x-ray diffraction results in the determination of composition and phase relations in the nodules. Thermograms and dehydration curves were obtained between 25° and 1200°C.

A sample, ranging from 0.5 to 1.0 g, was collected from each nodule and ignited at 1000°C; the ignition loss was measured, and the sample was leached with concentrated hydrochloric acid. The resultant solution was filtered, and the filtrate was diluted to a known volume. The concentrations of the elements investigated were determined by atomic-absorption spectroscopy (Table 1); analytical error is 5 percent of the amount present. The insoluble material was collected on filter paper, ignited, and measured (Table 1). The elemental values are expressed as weight percentages on a detrital-mineral-free basis. Ignition loss and insoluble residue, determined gravimetrically, are expressed as weight percentages of the bulk nodule.

No primary manganese mineral was detected in the nodules, although spectroscopic analysis demonstrated the presence of 13 to 19 percent (by weight) manganese (Table 1). Other studies of iron-manganese nodules have reported the presence of some form of manganese mineral on the basis of x-ray diffraction analyses which, alone, are inadequate for accurate characterization of the mineralogy of nodules. X-ray diffraction analyses of the black submetallic grains indicated that the material is amorphous, but the ocherous matrix consists of cryptocrystalline goethite.

Our studies indicate that the manganese is diadochic in an x-ray-amorphous, hydrous, iron oxide phase; this conclusion is based partly on x-ray diffraction analyses of bulk samples heated to between 200° and 1000°C. At no stage was a discrete manganese oxide phase observed although, from studies of amorphous manganese oxide gels (*4*), crystallization of some form of an oxide below 500°C is expected. Below 200°C, dehydration occurs and the nodules lose as much as 20 percent water by weight. Between 200° and 400°C the predominant iron-manganese oxide phase crystallizes as Mn-hematite with an empirical formula α-$Fe_{2-x}Mn_xO_3$; simultaneously goethite from the ocherous matrix undergoes dehydroxylation to α-Fe_2O_3 (hematite). Above 650°C the Mn-hematite and hematite spinel (jacobsite); the transition is nearly begin to recrystallize, forming Fe-Mn complete at 870°C (Table 2).

Other workers (*5*) have shown that the lower limit for the formation of Fe-Mn spinel from stoichiometric mixtures of the oxides is approximately 1000°C. If manganese is diadochic in an iron mineral such as the Fe-Mn oxide phase observed in these nodules, jacobsite could be formed appreciably below 1000°C.

Differential-thermal analyses provide further evidence of the existence of a hydrous iron-manganese oxide phase. Thermograms of the nodules compare favorably with those reported by other workers (*6, 7*) for hydrated iron oxide gels. No observed reaction could be attributed to the crystallization of manganese oxide from a gel, although differential-thermal studies of prepared mixtures (*7*) clearly show a resolved exothermal doublet in the range 200° to 400°C, corresponding to the crystallization of iron and manganese oxides from their respective gels.

The ocherous matrix of the nodules consisted chiefly of cryptocrystalline goethite; their sediments and insoluble residues contained abundant illite, minor chlorite and kaolinite, and traces of montmorillonite, quartz, amphibole, plagioclase, and potassium feldspar. The nodules appeared to have no nuclei, although rare shards, and porcelaneous grains apparently pseudomorphic aftershards, were observed under the microscope. The porcelaneous grains were chiefly montmorillonite with minor phillipsite. No carbonate mineral was observed in nodules or sediment.

We suggest that formation of these nodules was contemporary with sedimentation and apparently related to volcanic activity; the basis for our argument is the occurrence within the nodules of large percentages of detrital silicates (from sedimentation) (see Table 1), and of rare shards and shard pseudomorphs from volcanic activity.

The nodules were enriched in iron and depleted in manganese relative to average values for the Atlantic Ocean (Table 1); nevertheless our values fall within the reported ranges for these elements (*8*). The Mn:Fe ratios of the nodules, differing appreciably, are considerably lower than most reported values for Atlantic nodules (*8, 9*).

Although the manganese content of the surface nodules is significantly greater than that of the 73-cm nodule (Table 1), no evidence suggests that manganese has migrated. Migration of manganese requires an environment that reduces manganese IV to manganese II (*10*), and there is no evidence in this core of such a reducing environment. The most probable oxidation state is manganese IV which has t_{2g}^3 electron distribution. The ligand-field stabilization energy associated with this electron distribution is $6/5\ \Delta_0$ (*11*), which is maximum. Manganese II has a $t_{2g}^3e_g^2$ electron configuration and no ligand-field stabilization energy; therefore the energy difference between the two states may be sufficient to deter the migration of manganese IV.

The contents of minor elements (Cr, Co, Cu, and Zn) were similar for the three nodules (Table 1), but our values for them are considerably less than average values for the Atlantic Ocean, with the exception of Cr which is greater by an order of magnitude than reported values (*8*). Our overall analyses suggest a similar history of formation of all three nodules.

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Gulf of California: A Result of Ocean-Floor Spreading and Transform Faulting

Abstract. *Ocean-floor spreading tore southern Baja California from mainland Mexico 4 million years ago and has subsequently rafted it 260 kilometers to the northwest along the Tamayo Fracture Zone. Magnetic-anomaly profiles indicate spreading at the mouth of the gulf at 3.0 centimeters per year and a rise-crest offset of 75 kilometers inside the gulf across the Tamayo Fracture Zone.*

The East Pacific Rise extends northward from the equatorial Pacific and disappears as a distinct bathymetric feature somewhere near the mouth of the Gulf of California (*1*). From the north, the San Andreas fault and a related system of parallel faults trend down through California and disappear under the Salton Sea Trough (*2*). The Gulf of California is generally assumed to have originated from motion on one or both of these structural features. Wilson (*3*) envisions the San Andreas fault as a dextral, ridge-ridge transform fault. As such, it forms a connecting link between the East Pacific Rise at the mouth of the Gulf of California and the reappearance of the rise in the form of the Gorda Rise and the Juan de Fuca Ridge in the North Pacific. Motion on the San Andreas fault is due to ocean-floor spreading from the rise crests. The Gulf of California is then a result of strike and cross-strike separation in relation to the San Andreas fault. The hypothesis has subsequently