32. METALLIC TRACE ELEMENTS IN SOME CHERT NODULES OF PACIFIC SEAMOUNTS: A COMPARATIVE STUDY[1]

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ABSTRACT

The concentrations of trace metals in some chert nodules, radiolarian mudstones and cherts, abyssal red clays, and chalks were investigated by atomic-absorption spectroscopy. The metallic elements, such as Cu, Ni, Mn, Fe, and Mg, are mainly concentrated in clastic and biogenic sediments. A possible association of radiolarians and Ni is suggested by the fact that the radiolarian mudstones and cherts contain more than 0.1% Ni.

INTRODUCTION

Chert is a sedimentary rock whose microscopic texture is characterized by microcryptocrystalline quartz or opal-CT. The silica is known to be biogenic (Hurd and Theyer, 1975; Kastner et al., 1977; Keene, 1978). The cherts recovered from deep-sea floors can be placed in several categories. Von Rad et al. (1977) placed silicified sediments in three categories, according to the degree of silicification: (1) "immature," weakly silicified sediments, (2) porcellanites, and (3) "mature" quartz cherts. They recognized that silicified sediments usually occur as beds in clayey facies and as nodules in calcareous facies, within each category. Yamamoto (1977) recognized two types of deep-sea cherts: (1) stratigraphic chert (S-chert), which usually occurs as lenticules in chalky ooze; and (2) tectonic chert (T-chert), which is occasionally interbedded with brown clays. According to Yamamoto (1977), S-chert is distributed locally, such as on the crests of seamounts, whereas T-chert may have wider distribution in the abyssal basins of the deep-sea floor.

Multicolored, nodular cherts associated with chalky ooze were recovered from the Mid-Pacific Mountains and Hess Rise during DSDP Leg 62 (Fig. 1). At three sites on Hess Rise and one site on the Mid-Pacific Mountains, numerous chert nodules in chalky ooze were recovered. These chert nodules are compared with nodular S-type cherts on other Pacific seamounts and with T-type cherts recovered from the deep-sea floor as well as on land.

SITE LOCATIONS AND PETROLOGY

Chert specimens recovered from DSDP Site 463 (Mid-Pacific Mountains) and Sites 464 through 466 (Hess Rise) were investigated petrographically, and they are compared with chert specimens recovered from the Shatsky Rise (Sites 47–50) and the abyssal sea floor (Sites 45, 46, and 52). Numerous chert nodules are commonly found in chalky ooze on the crests of seamounts, whereas bedded cherts are found in brown clays at Sites 45 and 46 (mid-Pacific abyssal floor) and Site 52 (abyssal floor near the Izu–Bonin Trench). The chalky ooze in which nodular cherts occur is Cretaceous. At Site 465, a continuous Upper Cretaceous and Paleocene succession consists of chalky ooze and chert nodules.

The color of the chert nodules is variously light-gray, gray, yellowish-brown, brown, or reddish-brown. Nodules contain envelopes of unsilicified carbonates about 1-mm thick. Generally, gray chert nodules in chalky ooze occur at Site 463 (Mid-Pacific Mountains), and the chalky ooze at this site is silicified to become consolidated limestone. Replacement of foraminifer walls and filling of chambers with SiO_2 are common in the nodular cherts recovered from these sites. Occasionally, unsilicified micritic calcite is present in a weakly crystallized silica matrix.

Mesozoic to Paleozoic chert beds in the Hidaka Mountains and Aomori Prefecture in Japan and a flint nodule from the Maastrichtian chalk of Stevns Klint in Denmark were investigated as reference specimens in this study.

ANALYTICAL PROCEDURES

Hand specimens were crushed into small rock chips, and selected chips were powdered with a W-C SPEX mixer mill (Fig. 2); 200 mg of powdered sample were weighed and digested by concentrated HF and HCl for about 2 hours at temperatures of 50 to 80°C. The evaporated pelletal residue was dissolved in 10 ml of concentrated HCl. If the residue did not dissolve well in HCl, another digestion by HF–HCl was done. The final dissolved solution was brought to 50 ml with distilled water.

The absorbance of the sample solution was compared with that of a standard elemental solution, using an atomic-absorption spectrophotometer (UNICAM SP 90 and HITACHI 304). Determinations of concentrations were made for Ca, Mg, Zn, Fe, Mn, Cu, Ni, Pb, Sr, and Ti (Yamamoto, 1977). Contaminations by these elements during digestion were checked using pure quartz crystal and silica powder (Table 1).

RESULTS

Analytical results are shown in Table 2. Element concentrations in some nodular cherts are compared with those in radiolarian mudstones from the abyssal sea floor, deep-sea chalk and clay, and chert (flint, jasper, and radiolarite) specimens from land.

The compositions of nodular cherts on the Mid-Pacific Mountains and Hess Rise resemble the composition of a flint nodule from the Cretaceous chalk of

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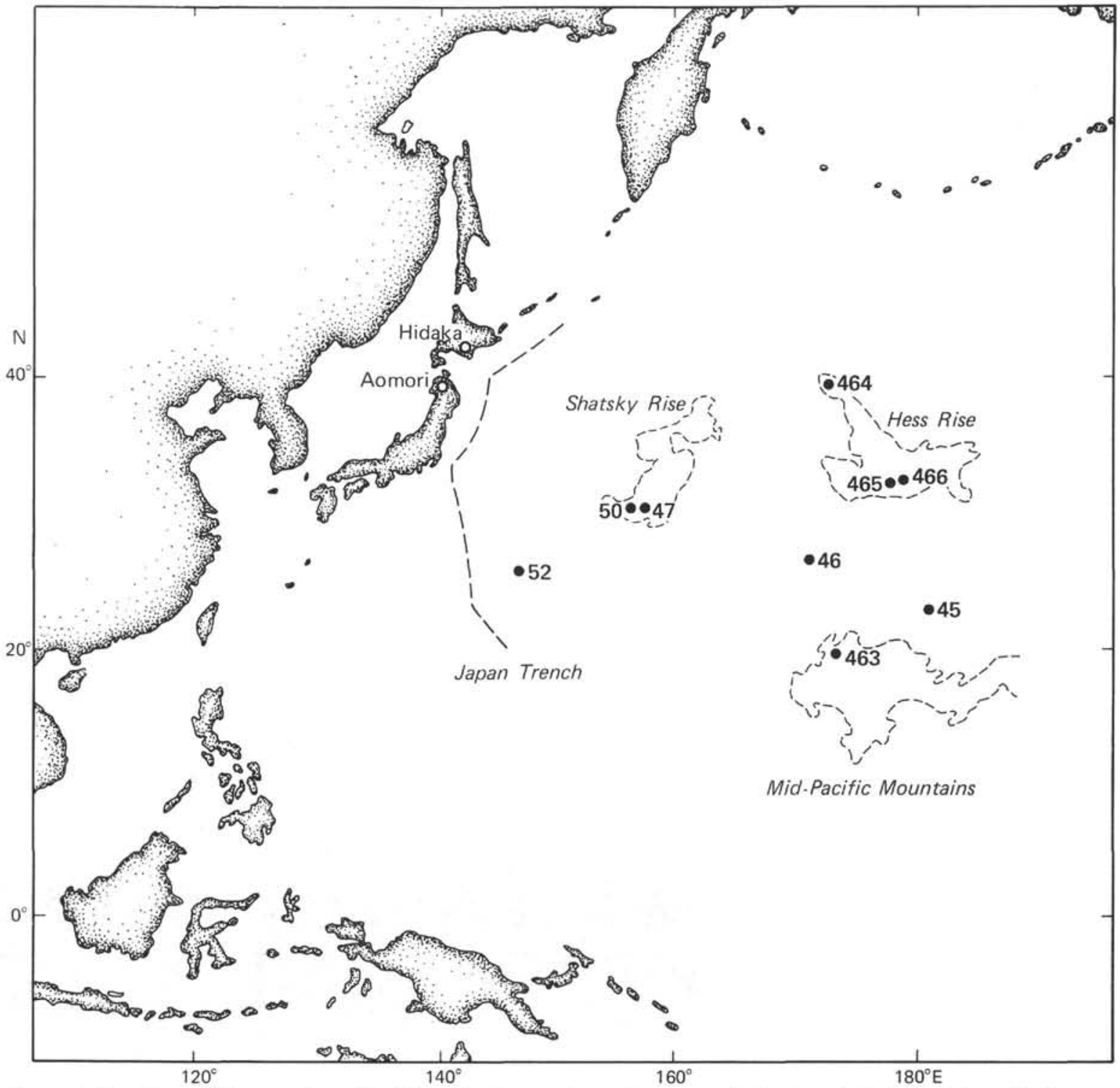

Figure 1. Locations of sites investigated in this study. Sites at the southern part of Shatsky Rise include 47 through 50.

Stevns Klint of Denmark. Dissolution in a shallow-water environment of shelf depths along with diagenetic replacement is suggested for the formation of flint nodules in the upper Maastrichtian chalk at Stevns Klint (Håkansson et al., 1974; Yamamoto, 1977). Similar diagenetic replacement along with dissolution might form nodular cherts in chalky ooze from the Pacific seamounts, such as the Mid-Pacific Mountains and Hess Rise.

Radiolarian mudstones from the abyssal sea floor are enriched in Mg, Fe, Mn, and Ni by about an order magnitude compared to the nodular cherts. Samples 45.1-2,CC and 46.0-1-6 (P) contain well-preserved Eocene radiolarians and are from strata interbedded with unfossiliferous clays [for example, 46.0-1-6 (S)]. Sample 52.0-8-3 (M) is from Cretaceous radiolarian mudstone and contains well-preserved radiolarians. The concentrations of Mg and Fe are well correlated for all specimens except a chert from the abyssal floor near the Izu-Bonin Trench [52.0-8-3 (F)], as shown in Figure 3.

Jaspers from the Hidaka Mountains in Hokkaido are believed to be Mesozoic, and radiolarian cherts from Aomori Prefecture are believed to be Paleozoic (Yamamoto, unpublished data). The high correlation coefficient ($r = 0.973$) between Mg and Fe in cherts, clay, and chalk can be explained by concentrations of clay minerals: a certain clay mineral may be contained in all the chert, red-clay, and chalk samples. Magnesium and iron commonly substitute in montmorillonite clays (Krauskopf, 1967, p. 183). The chert nodules contain extremely small amounts of Fe and Mg in comparison with radiolarite and radiolarian mudstone, jasper, and deep-sea chalk and red clay.

As illustrated in Figure 3, the chert nodule from the abyssal floor near the Izu-Bonin Trench [52.0-8-3 (F)] deviates far from other samples; this sample is well lithified and from a band in silicified chalk. Samples 52.0-8-3 (M) and 52.0-8-3 (F) are from in the same section as angular pieces; however, they might be derived from different lithologic horizons. During DSDP Leg

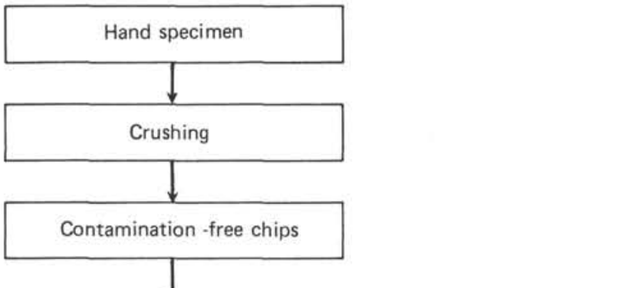

Figure 2. Flow chart of chemical digestion for atomic-absorption spectroscopy.

20, four sites were drilled at the abyssal floor near the Izu–Bonin Trench (Heezen, MacGregor, et al., 1973). At Site 196, Core 3 (cored interval 197–203 m) contained red, brown, and black cherts interbedded with brown and yellow laminated mudstone, chalk, and siliceous porcellaneous limestone (in descending order). The deviation of sample specimen 52.0-8-3 (F) might be due to enrichment of Fe in the chert nodule, rather to depletion of Mg from the radiolarian mudstone, because the chert nodule may be associated with chalk or silicified limestone at this site. Although the stratigraphy of the banded chert (probably equivalent to chert nodules in silicified chalk) in silicified chalk is indicative of turbidity deposits on the abyssal basin, the petrography of this chert indicates fragmented radiolarians, which are often recognized in the chert nodules of Shatsky Rise (Yamamoto, 1977).

Geochemical comparisons of deep-sea radiolarian mudstones with bedded cherts exposed on land suggest that the deep-sea radiolarian mudstones are characteristically enriched in Ni. As shown in Table 2, the Hidaka jaspers are rich in Fe and Mn, but Ni concentration is less than 100 ppm. The cherts with Ni concentrations greater than 0.1% show high concentrations of well-preserved radiolarians and fragmented radiolarian membranes, which may be derived from the assimilative layer of the radiolarian individual (Shrock and Twenhofel, 1953, p. 64). Christensen and others (1973) reported that pyrite concretions in the Danian fish clay contain about 0.1% Ni, and a limestone concretion with a high content of siliceous sponge spicules contains 0.27% Ni.

It is probable that the characteristic association of Ni and deep-sea radiolarian mudstone and chert is due to extraction of Ni from sea water by radiolarians (Smales and Wiseman, 1955). Horn et al. (1973) noted Ni and Cu concentrations in manganese nodules associated with radiolarian sediments twice as high as those in nodules associated with red clays. Analyses of trace-metal concentrations in some deep-sea sediments are also included in Table 2; concentrations of Zn are lower in chert than in chalk and red clay (recovered from Sites 44 through 52).

CONCLUSIONS

Although volcanic glass and the weathering of silicate minerals can contribute to the production of inorganic silica gel, the silica in nodular cherts is dominantly biogenic and derived from the dissolution of siliceous organic materials such as radiolarians, diatoms, and sponge spicules (Kagami, 1979). Biogenic siliceous particles are abundant in nodular cherts recovered from Shatsky Rise. Radiolarians are highly fragmented in the chert nodules associated with chalky sediments of Shatsky Rise, whereas most of the round spheres in the chert nodules from the Mid-Pacific Mountains or Hess Rise are foraminifer chambers filled with cristobalite and organic matter. Distinction of radiolarian "ghosts" and the foraminifer chambers replaced by silica is difficult if the nodule is well matured.

Nickel and other trace metals are concentrated in clays and other particulate matter. The chert nodules which are considered to be products of diagenesis of

Table 1. Contamination (ppm) from W-C mixer mill and digestion system.

Sample	Ca	Mg	Zn	Fe	Mn	Cu	Ni
Quartz crystal (QC)[a]	46.3 ± 77.1	80.9 ± 105.8	8.7 ± 3.9	92.0 ± 20.8	57.6 ± 59.1	7.9 ± 6.0	2.4 ± 2.5
Reagent SiO_2 powder[b]	118 ± 113	249 ± 278	9.7 ± 3.0	87.7 ± 33.0	4.3 ± 1.0	5.9 ± 2.4	4.1 ± 4.3
QC, blending for 5 min.	<1.0	9.8	57	138	47	17	4.0
QC, blending for 7 min.	7.0	17	112	183	7.0	20	4.0
QC, blending for 10 min.	<1.0	10	29	83	5.0	8.0	10

Note: Pb, Sr, and Ti contamination was in all cases <100 ppm.
[a] Average for 8 samples.
[b] Average for 3 samples.

Table 2. Concentrations of metallic trace elements in the investigated samples.

Ca (%)	Mg (%)	Zn (ppm)	Fe (%)	Mn (%)	Cu (ppm)	Ni (ppm or %)	Sr (ppm)	Ti (ppm)
0.44 ± 0.11	1.21 ± 0.24	43.0 ± 4.0	3.62 ± 0.46	0.155 ± 0.018	53.8 ± 20.0	47.1 ± 4.7	57.6 ± 7.9	0.16 ± 0.02
137 ± 119	0.16 ± 0.12	16.4 ± 4.1	0.43 ± 0.51	208 ± 312	11.2 ± 11.0	8.4 ± 3.2	< 100	133 ± 190
270	520	20	140	<	6.4	6.6	3.8	< 100
0.47	0.60	80	0.87	0.035	< 10	0.18%	—	—
0.13	0.22	50	0.58	< 5	< 10	0.15%	—	—
0 13	0.29	46	0.81	0.220	< 10	0.12%	—	—
0.75	0.04	40	1.66	0.017	< 10	0.24%	—	—
570	67	35	233	16	30	< 100	< 100	—
152	161	20	519	9.0	< 10	< 100	< 100	—
114	40	30	72	< 5	< 10	< 100	< 100	—
0.15	0.80	98	2.28	0.017	< 10	< 100	—	—
1.90	1.13	260	3.76	0.360	< 10	< 100	—	—
36.7 ± 12.5	0.41 ± 0.22	103 ± 71	0.66 ± 0.46	0.040 ± 0.030	< 10	< 100	—	—
14.0	0.49	120	1.04	0.300	< 10	< 100	—	—

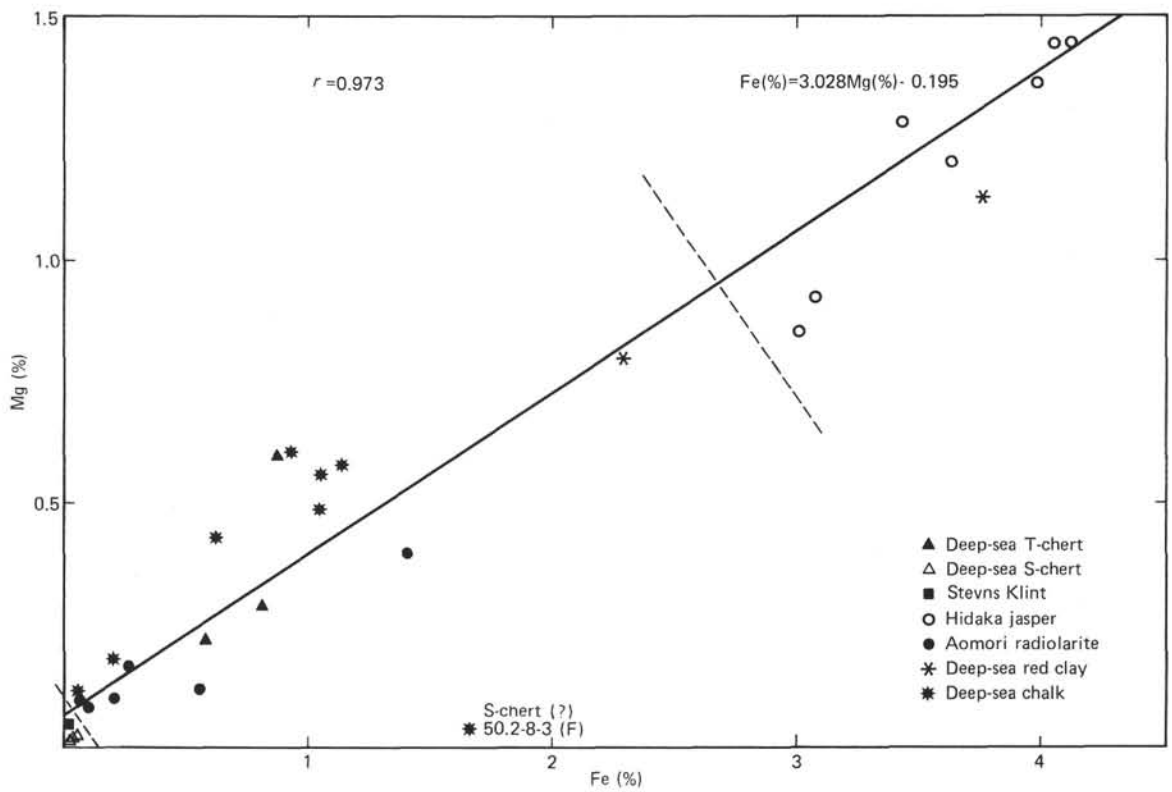

Figure 3. Relationship between Fe and Mg in all samples. The regression line and correlation coefficient are for all samples except "S-chert (?)."

biogenic silica other than radiolarian sediments accumulate extremely small amounts of metallic elements, whereas red clays and radiolarian mudstones contain considerable amounts of metallic elements such as Fe, Mn, Cu, and Ni. An association of radiolarian sediments and Ni is suggested by the fact that radiolarian mudstones and cherts from the abyssal sea floor contain more than 10 times as much Ni as the diagenetic flint nodules.

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