Abundance of Cadmium in Paleozoic Limestones in Japan

Shoichi Aizawa* and Hideo Akaiwa
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376
(Received April 28, 1992)

Cadmium is significantly enriched in Paleozoic (Permian and Carboniferous) limestones in Japan. The geometric mean of Cd in these limestone samples (n=111) is 0.57 ppm, which is an order of magnitude higher than that of Quaternary ones. Most of divalent heavy metals in these limestones exist in accessory minerals such as silicates, whereas Cd is contained in calcite. Submarine volcanoes which were active during Paleozoic period might be responsible for the high Cd content of Japanese limestones of this age.

The fixation of Cd^{2+} in calcite is probably an important mechanism in regulating the concentration of this ion in seawater, since the ionic radius (1.09 Å[1] in 6-hold coordination) of Cd^{2+} is almost identical with that (1.14 Å[1]) of Ca^{2+}. In fact, remarkable incorporation of Cd^{2+} into calcite was observed in laboratory experiments.[2—5] Limestone of marine origin may therefore serve as a potential reservoir for Cd. However, the abundance of Cd in limestone is not well established due to lack of data, although much information on this metal in other geological materials is available in connection with environmental pollution.

Mason and Moore[6] proposed 0.09 ppm as the abundance of Cd in carbonate rocks in 1982. Recently, we reported similar Cd contents (geometric mean: 0.07_1 ppm, n=94) for Quaternary limestones in southwest Japan.[7] These values are quite similar to the abundance of this element in the continental crust (0.098 ppm)[8] or igneous rocks (0.08 ppm).[6]

On the other hand, markedly high Cd contents (av. ca. 0.5 ppm; max. 2.4 ppm) have been found in Permian and Carboniferous limestones from several localities in Japan.[9—12] Large scale deposits of Japanese limestones often occur during the Carboniferous to the Permian stage.[13] We therefore aimed to confirm the difference in Cd content between Japanese Paleozoic and Quaternary limestones by using new data and to discuss the mechanism of incorporation of this element into these ancient limestones.

Experimental

Twelve sampling localities are shown in Fig. 1, together with those of other samples previously analyzed by the authors.[7,10—12,14] Yoron-jima samples were collected from the

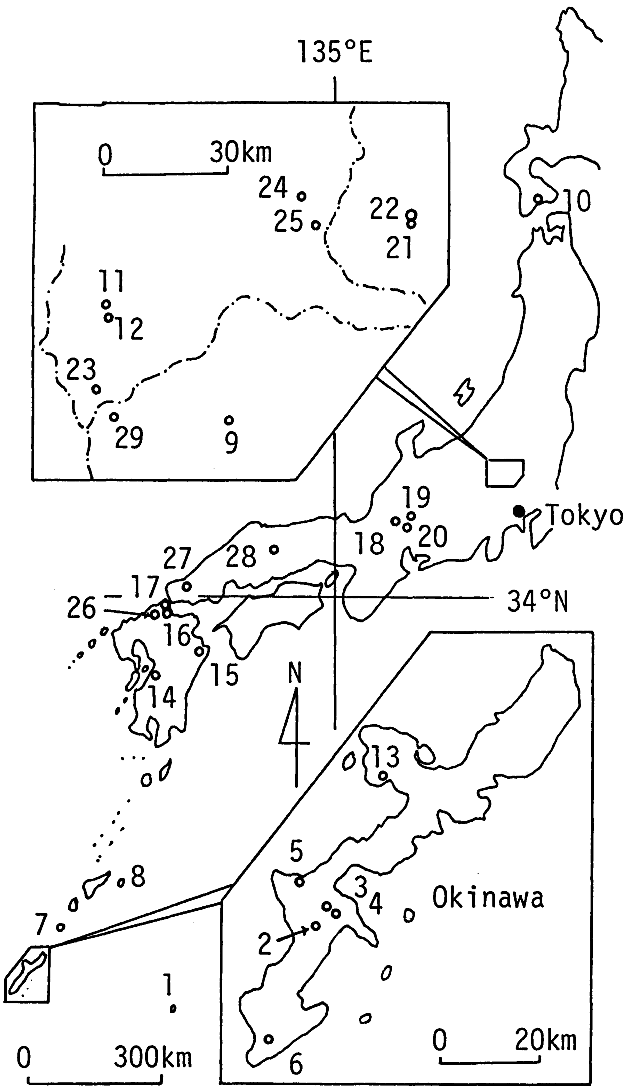

Fig. 1. Sampling localities.

1.	Minamidaito-jima	(Q)	16.	*Tsunemi*	(P)
2.	Itoman	(Q)	17.	*Yotsudaka*	(P)
3.	Akamichi	(Q)	18.	*Ibuki*	(P)
4.	Chibana	(Q)	19.	*Takaradani*	(P)
5.	Okinawa City	(Q)	20.	*Akasaka*	(P)
6.	Yomitan	(Q)	21.	Kuzuu(Upper)	(P)
7.	*Yoron-jima*	(Q*P?)	22.	Kuzuu(Lower)	(P)
8.	Kikai-shima	(Q)	23.	Ueno	(P)
9.	Chichibu	(T)	24.	Kurohone	(P)
10.	*Garo*	(T)	25.	Kiryu	(P)
11.	Aokura	(T-P)	26.	*Kawara*	(P-C)
12.	Shimonita	(T-P)	27.	*Ofuku*	(P-C)
13.	Motobu	(P)	28.	*Niimi*	(P-C)
14.	*Ashikita*	(P)	29.	Oku-Chichibu	(P-C)
15.	*Tsukumi*	(P)			

Italic: Samples analyzed in this work.
Q: Quaternary, Q*P(?): Quaternary and Permian(?), T: Triassic, T-P: Triassic or Permian, P: Permian, P-C: Permian or Carboniferous.

southern shore of this island, and Takaradani samples were from a road cut. The samples of other 10 localities were taken from pits of working or abandoned mines. The geological ages of these samples were identified as the Triassic, Permian, and Permian or Carboniferous.[15-17] The Ritcho Formation from which Yoron-jima samples were taken is nonfossiliferous and estimated to be the Permian.[18] The present Paleozoic limestone deposits are closely associated with basic volcanic rocks.[17,19] In addition, they are massive and not stratified. Neither sandstones nor shales are interbedded in these limestone deposits.[19] From these geological features, Horii[20,21] proposed a mechanism that submarine volcanism may be responsible for the formation of these limestones.

Samples were pulverized to <0.15 mm in an agate mortar. After the decomposition of samples (2.00 g) with a mixture of nitric and perchloric acids, Cd was determined together with Ni, Cu, and Zn(<5 ppm) by flame atomic absorption spectrometry coupled with a solvent extraction technique using APDC (ammonium pyrrolidinedithiocarbamate). The detection limit of this method is 0.005 ppmCd, and three determinations of a limestone sample give 0.14±0.01 ppmCd. Details of the sample preparation and the analytical procedure were reported previously.[14]

Results

The arithmetic means of Cd contents were summarized in Table 1, together with those of some major and trace elements. The prominent feature of the present samples is low SiO_2, Al_2O_3, and Fe contents, indicating that amounts of impurities such as silicates are small. Most of the Ashikita, Tsukumi, and Yotsudaka limestone samples contain a small amount of dolomite. However, X-ray diffractometry for the bulk samples of other localities gave no peak of other mineral than low-Mg calcite. Discussion was carried out by using the present and our previous data (the sampling localities were given in Fig. 1).

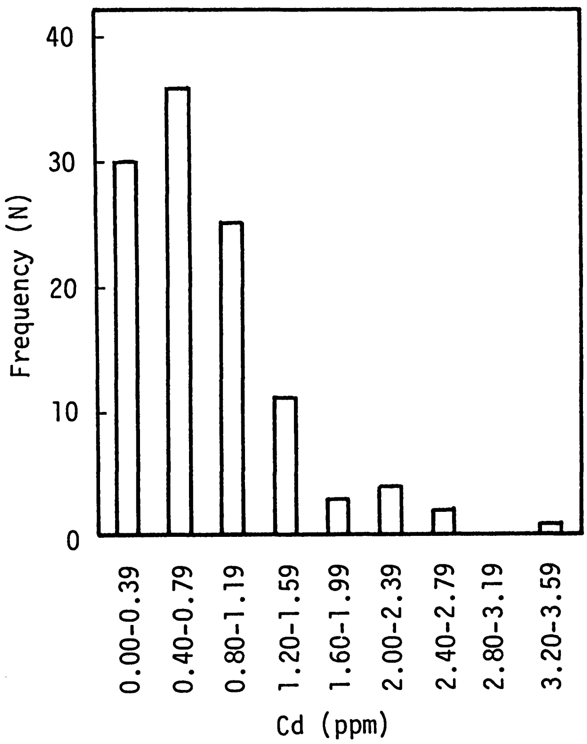

Fig. 2. Frequency distribution of Cd content of Japanese Paleozoic limestone samples.

Table 1. Arithmetic Means of Concentration of Major and Trace Elements in Japanese Limestone Samples (in ppm unless noted as %)

Sampling locality	No. of samples	SiO_2/%	Al_2O_3/%	CaO/%	MgO/%	Sr	Mn	Fe	Ni	Cu	Zn	Cd
Yoron-jima	8	0.06	0.014	55.28	0.34	240	19	160	0.42	0.27	5.1	0.42
		0.07	*0.016*	*0.24*	*0.07*	*100*	*12*	*200*	*0.21*	*0.09*	*1.8*	*0.16*
Garo	10	0.16	0.039	54.42	0.45	500	19	100	0.52	0.14	2.1	0.12
		0.13	*0.001*	*0.79*	*0.24*	*230*	*15*	*59*	*0.22*	*0.08*	*0.9*	*0.04*
Ashikita	9	0.37	0.020	52.03	2.01	540	17	93	0.70	0.22	3.2	0.49
		0.44	*0.028*	*2.50*	*2.21*	*250*	*11*	*51*	*0.23*	*0.14*	*1.4*	*0.26*
Tsukumi	10	0.09	0.020	53.06	1.09	210	19	86	0.31	0.32	4.3	0.91
		0.07	*0.015*	*0.71*	*0.52*	*46*	*13*	*55*	*0.20*	*0.06*	*1.8*	*0.42*
Tsunemi	5	0.27	0.11	52.98	0.93	220	27	300	1.3	0.45	3.8	0.59
		0.25	*0.13*	*0.27*	*0.22*	*29*	*36*	*160*	*1.3*	*0.22*	*1.7*	*0.05*
Yotsudaka	3	0.28	0.11	50.11	3.32	540	350	330	0.55	0.096	1.6	0.34
		0.26	*0.085*	*1.26*	*0.76*	*400*	*460*	*170*	*0.15*	*0.033*	*0.3*	*0.13*
Ibuki	1	<0.02	0.0025	54.51	0.85	85	68	130	2.0	0.93	16.$_1$	1.1
Takaradani	4	0.10	0.0095	53.57	0.75	430	19	77	0.84	0.23	21.$_2$	2.1
		0.09	*0.0065*	*0.42*	*0.13*	*150*	*26*	*91*	*0.45*	*0.17*	*13.$_2$*	*0.77*
Akasaka	10	<0.02	0.0034	54.43	0.48	500	18	37	0.49	1.4	5.7	0.57
		—	*0.0006*	*0.42*	*0.32*	*370*	*20*	*21*	*0.42*	*0.96*	*4.3*	*0.34*
Kawara	4	<0.02	0.0016	54.84	0.40	170	3.6	22	0.36	0.30	14.$_7$	0.66
		—	*0.0003*	*0.26*	*0.16*	*40*	*1.9*	*8*	*0.23*	*0.07*	*9.4*	*0.07*
Ofuku	7	<0.02	0.0020	54.97	0.31	320	6.7	69	0.34	0.41	11.$_8$	0.78
		—	*0.0005*	*0.33*	*0.03*	*400*	*3.3*	*24*	*0.18*	*0.16*	*9.0*	*0.26*
Niimi	5	0.21	0.0023	55.61	0.20	190	8.2	160	0.17	4.8	6.0	0.48
		0.18	*0.0002*	*0.11*	*0.10*	*90*	*2.0*	*40*	*0.16*	*0.93*	*1.4*	*0.25*

Itatic: Standard deviation.

Table 2. Geometric Means of Concentrations of Major and Trace Elements in Japanese Limestone Samples[a] (in ppm unless noted as %)

Geological age	No. of samples	SiO_2[b]/%	Al_2O_3/%	CaO/%	MgO/%	Sr	Mn	Fe	Ni	Cu	Zn	Cd
Permian-Carboniferous	111[c]	0.14	0.012	53.01	0.62	300	23	160	0.74	0.56	6.2	0.57
Quaternary	94[d]	0.25	0.037	49.36	1.30	470	14	240	0.98	0.83	1.5	0.07_1

a) Including the samples previously analyzed.[7,10–12,14] b) Means were calculated by using 0.02% (detection limit) with respect to the samples having less than 0.02%. c) Collected from 17 localities. d) Collected from 8 localities.

Table 3. Arithmetic Means of Cadmium Contents of Worldwide Limestones

Locality	No. of samples	Geological age	Cd/ppm
Northwest Germany	1[a]	Cretaceous	0.091[22]
Pennsylvania, U.S.A.	8	Carb-Camb[b]	0.028[23]
Germany	1		0.10[24]
Germany and U.S.A.	6		0.094[8]
Germany and France	9		0.16[8]

a) Composite sample of 16 samples (clay fraction: 24%).
b) Carboniferous-Cambrian.

Discussion

Abundance of Cadmium in Japanese Paleozoic Limestones. The frequency distribution of Cd in the Permian and Carboniferous limestone samples is shown in Fig. 2, indicating a logarithmic normal distribution pattern. The geometric mean is therefore appropriate to estimate the abundance of Cd in these rocks (Table 2). The geometric mean (0.57 ppm) of Cd in Permian and Carboniferous limestone samples is an order of magnitude higher than that (0.07_1 ppm) of Quaternary ones, being close to an average Cd content of 0.44 ppm[9] for 82 Akiyoshi limestone samples of Carboniferous-Permian age, southwest Japan. This value is obviously high compared with the corresponding values of limestones of other countries reported so far (Table 3).

Mode of Occurrence of Cd in Japanese Paleozoic Limestones. Japanese limestones usually include impurities such as quartz, feldspars and clay minerals, and sometimes pyrite.[16] In general, Cd tends to concentrate in pyrite together with other chalcophile elements,[11] but pyrite is only found in Kuzuu Lower limestones of all the present Paleozoic samples.

Table 4 clearly shows that Mn, Ni, Cu, and Zn contents are closely related to those of SiO_2, Al_2O_3 or Fe which are major components of silicates. Probably a large portion of these heavy metals may be contained in silicates, not in calcite. On the contrary, no positive correlation can be seen between Cd content and those of major elements. Even pure limestones with extremely small amounts of SiO_2, Al_2O_3, and Fe, such as Akasaka, Kawara, Ofuku samples, contain an appreciable amount of Cd (Table 1). In addition, our previous work[12] revealed that more than 90% of Cd exists in the 1 M (1 M=1 mol dm^{-3}) actetic acid-soluble fraction of impure limestone samples. Considering easy replacement of Ca^{2+} by Cd^{2+} in calcite, we concluded that most of Cd are present in the calcite phase of common Japanese Paleozoic limestones.

Origin of Cd in Japanese Paleozoic Limestones. The distribution of Cd contents plotted against geological age shows that significant high concentrations of this element are found in only Paleozoic limestones (Fig. 3). Thus these limestones might have already enriched in Cd upon formation from Paleozoic seawater. However, the high Cd content of Paleozoic limestones might be a local phenomenon occurring in ancient Japan rather than a world-wide one, because there are some unfavorable points to the universal enrichment of Cd in Paleozoic limestones. First, low Cd contents (av. 0.028 ppm, n=8) were reported for Cambrian-Carboniferous limestones in North America (Table 3). Second, the concentrations of heavy metals in seawater probably remained unchanged during past one billion years.[25]

Table 4. Correlation Matrix for Concentration of Chemical Species in Japanese Limestone Samples

	SiO_2	Al_2O_3	Fe	Mn	Ni	Cu	Zn	Cd
			[Paleozoic (n=111)]					
SiO_2	—	0.57	0.73	0.68	0.72	0.53	0.51	0.10
Al_2O_3	0.79	—	0.91	0.068	0.75	0.27	0.70	−0.016
Fe	0.83	0.93	—	0.29	0.88	0.38	0.76	0.068
Mn	0.58	0.77	0.78	—	0.39	0.44	0.19	0.27
Ni	0.82	0.89	0.96	0.73	—	0.48	0.68	0.20
Cu	0.68	0.89	0.88	0.72	0.84	—	0.29	0.21
Zn	0.76	0.96	0.95	0.78	0.92	0.90	—	0.39
Cd	−0.10	0.042	0.018	−0.037	0.058	0.18	0.10	—
			[Quaternary (n=94)]					

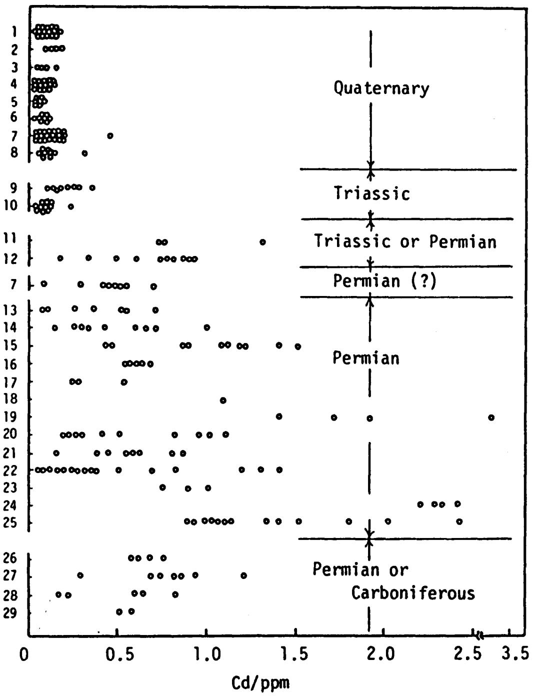

Fig. 3. Cadmium contents of limestone samples from Japan. Numbers on the ordinate correspond to the numbers in Fig. 1.

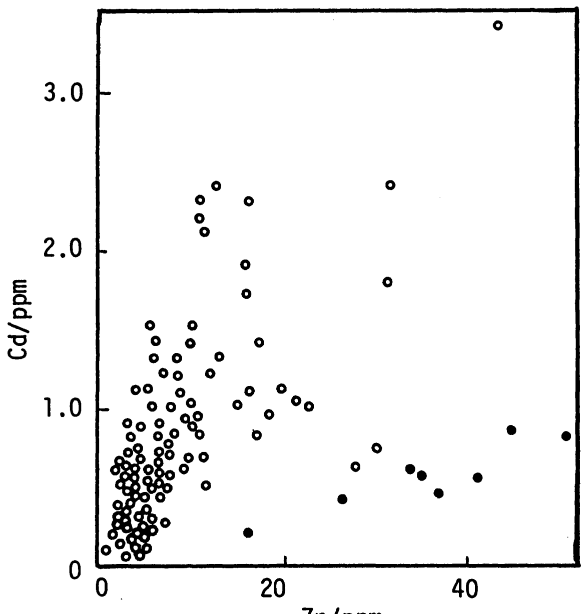

Fig. 4. Relationship between Cd and Zn Contents of Japanese Paleozoic limestone samples.
(●) Kuzuu Lower limestone samples
Except for Kuzuu Lower limestone samples in which an appreciable amount of pyrite is present, correlation coefficient is 0.64 (n=103).

It should be noted that the mode of occurrence of Japanese Paleozoic limestones is quite different from those of other regions such as North America, Europe, and China where stratified limestones are prevailing. Most of Japanese Paleozoic limestones are massive and associated with basic volcanic rocks. This fact suggests that these basic rocks were originated from submarine volcanoes which were highly active during Paleozoic period.[19] Thus, the significant contribution of volcanic activities to high Cd content of these limestones is easily acceptable, because Cd is one of the most enriched elements in volcanic gases or aerosols due to its high volatility[26–34] (0.01—ca. 1 ppm in gas condensates).

A positive relationship between Zn and Cd contents of Paleozoic limestones (Fig. 4) also suggests the volcanic origin of Cd. Zinc in these limestones is in part present in silicates, at the same time it also occurs in calcite by replacing Ca^{2+}.[12,35–37] Zinc contents of volcanic gases and aerosols are one or two orders of magnitude higher than those of Cd,[26–34] and Cd usually behaves geochemically together with Zn. Therefore the high Zn content of Paleozoic limestones relative to that of Quaternary ones (Table 2) and the above positive relationship could be the evidence for the volcanic origin of Cd. On the other hand, the low Ni and Cu contents of Paleozoic limestones comparable to those of Quaternary ones (Table 2) may be due to the difficulty in substituting Ca^{2+} by these ions in calcite,[36,37] although an appreciable amount of Cu^{2+} is contained in volcanic gases and aerosols.[26,27,29,33,34]

We are indebted to Dr. T. Fujinuki of the Japan Society for Analytical Chemistry for collection of limestone samples.

References

1) R. D. Shannon, *Acta Crystallogr., Sect. A,* **32**, 751 (1976).

2) O. Fujino, T. Kumagai, T. Shigematsu, and M. Matsui, *Bull. Inst. Chem. Res., Kyoto Univ.,* Vol. 54, No. 5, 312 (1976).

3) Y. Kitano, N. Kanamori, and R. Fujiyoshi, *Geochem. J.,* **12**, 137 (1978).

4) R. B. Lorens, *Geochim. Cosmochim. Acta,* **45**, 553 (1981).

5) J. A. Davis, C. C. Fuller, and A. D. Cook, *Geochim. Cosmochim. Acta,* **51**, 1477 (1987).

6) B. Mason and C. B. Moore, "Principles of Geochemistry," 4th ed, John Wely & Sons, Inc., New York (1982), p. 176.

7) S. Aizawa and H. Akaiwa, *Chikyukagaku (Geochemistry),* in press.

8) H. Heinrichs, B. Schulz-Dobrick, and K. H. Wedepohl, *Geochim. Cosmochim. Acta,* **44**, 1519 (1980).

9) T. Sakae, K. Yoshimura, and T. Tarutani, *Bull. Akiyoshi-dai Mus. Natl. History,* No. 16, 1 (1981).

10) S. Aizawa and H. Akaiwa, *Chikyukagaku (Geochemistry),* **21**, 21 (1987).

11) S. Aizawa and H. Akaiwa, *Chikyukagaku (Geochemistry),* **21**, 31 (1987).

12) S. Aizawa and H. Akaiwa, *Chem. Geol.,* **98**, 103 (1992).

13) T. Hashimoto, "Limestones in Japan," ed by S. Kawada, Sekkaiseki Kogyo Kyokai, Tokyo (1983), p. 95.

14) S. Aizawa and H. Akaiwa, *Chem. Geol.,* **67**, 275 (1988).

15) S. Sakagami, S. Minamikawa, and M. Kawashima, *Chigaku Zasshi,* **78**, 37 (1969).
16) T. Fujinuki, "Limestones in Japan," ed by S. Kawada, Sekkaiseki Kogyo Kyokai, Tokyo (1983), p. 43.
17) "Limestones in Japan," ed by S. Kawada, Sekkaiseki Kogyo Kyokai, Tokyo (1983), Part 4, pp. 257—485.
18) H. Nakagawa, Tohoku Univ., Inst. Geol. Pal., Contr. No. 63, 1 (1967).
19) K. Kanmera, "Sedimentary Rocks in Japan," ed by S. Mizutani, Y. Saito, and K. Kanmera, Iwanami Shoten, Tokyo (1987), Chap. 3, pp. 123—133.
20) M. Horii, *Sekkaiseki,* **78**, 675 (1962).
21) M. Horii, "Limestones in Japan," ed by S. Kawada, Sekkaiseki Kogyo Kyokai, Tokyo (1983), p. 25.
22) G. Marowsky and K. H. Wedepohl, *Geochim. Cosmochim. Acta,* **35**, 1255 (1971).
23) H. Gong, A. W. Rose, and N. H. Suhr, *Geochim. Cosmochim. Acta,* **41**, 1687 (1977).
24) H. Heinrichs, *Fresenius Z. Anal. Chem.,* **294**, 345 (1979).
25) Y. Kajiwara, *Geochem. J.,* **10**, 43 (1976).
26) E. A. Lepel, K. M. Stefansson, and W. H. Zoller, *J. Geophys. Res.,* **83**, 6213 (1978).
27) P. Baut-Menard and M. Arnold, *Geophys. Res. Lett.,* **5**, 245 (1978).
28) J. M. Phelan, D. L. Finnegan, D. S. Ballantine, and W. H. Zoller, *Geophys. Res. Lett.,* **9**, 1093 (1982).
29) I. A. Menyailov, L. P. Nikitina, V. N. Shapar, and A. Z. Miklishansky, *J. Geophys. Res.,* **87**, 11113 (1982).
30) J. B. Gemmell, *J. Volcanol. Geotherm. Res.,* **33**, 161 (1987).
31) B. M. Crowe, D. L. Finnegan, W. H. Zoller, and W. V. Boynton, *J. Geophys. Res.,* **92**, 13708 (1987).
32) R. B. Symonds, W. I. Rose, M. H. Reed, F. E. Lichte, and D. L. Finnegan, *Geochim. Cosmochim. Acta,* **51**, 2083 (1987).
33) M. Pennishi, M. F. Le Cloarec, G. Lambert, and J. C. Le Roulley, *Earth Planet. Sci. Lett.,* **88**, 284 (1988).
34) J. P. Quisefit, J. P. Toutain, G. Bergametti, M. Javoy, B. Cheynet, and A. Person, *Geochim. Cosmochim. Acta,* **53**, 2591 (1989).
35) A. Tsusue and H. D. Holland, *Geochim. Cosmochim. Acta,* **30**, 439 (1966).
36) Y. Kitano, A. Tokuyama, and N. Kanamori, *J. Earth Sci., Nagoya Univ.,* **16**, 1 (1968).
37) H. Akaiwa, H. Kawamoto, S. Aizawa, and M. Kaneko, Annual Meeting of the Geochemical Society of Japan, Hakodate, October 1978, Abstr., No. 5C10.