Characteristics of rare-earth elements, Ba, Sr and Rb abundances in natural zeolites

YASUTAKA TERAOKA and WAITSU NAKAJIMA

Division of Earth and Environmental Sciences, Faculty of Human Development, Kobe University,
Tsurukabuto 3-11, Kobe 657, Japan

(Received June 2, 1994; Accepted July 7, 1995)

Abundances of rare earth elements (REE), Ba, Sr and Rb were determined for several kinds of zeolites occurred in cavities of volcanic rocks from Japan with relevance to peculiar crystal chemical properties of zeolites. Because of the scarcity of REE data of zeolites, the following points would be noteworthy: (1) REE abundances for those zeolites are extremely low, ranging from about 0.01 to 0.1 in chondrite normalized unit; (2) Mutual fractionation among REE is rather small aside from small Eu and Ce anomalies; (3) Three different zeolite species from Maze area, Niigata Prefecture, show considerable resemblance with respect to REE, Ba and Sr concentrations. It is suggested that the REE incorporation in zeolites seems to be affected by their genetic process or formation environment rather than by difference in zeolite species. Moreover, relatively low REE abundances in zeolites may reflect extremely low REE abundances in the solutions from which those zeolites were precipitated. The Ce anomalies for the Maze samples show that those zeolites have not been deposited from magmatic solutions but from meteoric water.

INTRODUCTION

Zeolites (hydrated aluminosilicates of alkali and alkali earth cations) are a family of minerals which are produced by processes related to hydrothermal activity or diagenesis, and occur widely in sedimentary rocks and in cavities of igneous rocks. They are structurally tectosilicates consisting of three-dimensional frameworks of SiO_4^{4-} tetrahedra. Some of the quadrivalent silicon is replaced by trivalent aluminum, and the charge is balanced by the presence of mono and divalent cations (Na^+ , K^+ , Ca^{2+}) elsewhere in the structure. The empirical formula can be expressed as follows:

where M is any alkali or alkali earth cation, n is the valence of that cation, x is a number from 2 to 10, and y is a number from 2 to 7 (e.g., Mumpton, 1977). Thus, the zeolite has similar

chemical and structural characteristics to those of feldspar and feldspathoid aside from H_2O -bearing property of the zeolite (Flanigen, 1977).

It is important that zeolites are characterized by remarkable void cavities and channels in the framework. Such void spaces are related to the interconnected secondary building units which consist of both single and double rings of several tetrahedra and of larger polyhedra (e.g., Gottardi and Galli, 1985). Zeolites are further characterized by an ability to lose and gain water which is present as an occluded phase, and to exchange constituent cations without major changes of structure. Such ion exchange (or adsorption) property has been used in industries for purification of effluents especially of radioactive wastes. Moreover, the porous property has also been utilized for molecular sieves of synthetic zeolites in industries.

It is interesting to analyze rare-earth element (REE) abundances in zeolites, since REE is an important tool for examining genetic processes of

various geological materials. Moreover, zeolites have interesting properties as mentioned above and REE show wide and regular variations in ionic radius (101~86.1 pm; Shannon and Prewitt, 1969), which must be an important factor in trace element behaviors in nature. However, REE abundance data for natural zeolites are limited to deep-sea phillipsite (Piper, 1974; Bernat and Church, 1978). There are many kinds of zeolites and their occurrence is rather wide. Therefore, more data are necessary for better understanding the REE characteristics of zeolites and their related alteration processes. In this study, we present REE, Rb, Sr and Ba abundance data of several zeolites and related host rocks from Japan.

SAMPLES AND ANALYTICAL METHOD

We have analyzed five zeolites and two host rock samples of Tertiary age from three localities (i.e., Maze, Izu and Ishizuchi). Maze, Niigata Prefecture, is a well known locality at which various kinds of zeolites were found in altered basalt (Shimazu and Kawakami, 1967; Harada *et al.*, 1967). The texture of Maze samples is illustrated schematically in Fig. 1. Three different kinds of zeolites growing in a cavity were separated (MZ-1, MZ-2, and MZ-3). MZ-1 occurs as well-shaped subhedral and transparent crystals, and MZ-2 and -3 as a radial aggregate of fibrous materials. MZ-3 covers MZ-2. The X-ray powder diffraction method was applied for mineral identification, and these minerals were found to be analcime, gonardite and scolecite, respectively. Moreover, textural relationships between them indicate that these minerals were formed in this sequence. The host rock is altered significantly and contains many vecicules which are sometimes filled with secondary minerals including zeolites.

Another zeolites samples (ZO-1) and its host rock are from Shimokawatsu, Shizuoka Prefecture (Izu-peninsular). This zeolite sample occurs as subhedral cubic crystals growing in a cavity but the same kind zeolite crystals form many thin veins in its host rock. ZO-1 was identified as chabasite including a small amount of quartz by

Fig. 1. Schematic illustration showing Maze zeolite samples. MZ-1 occurs as well-shaped subhedral crystals, growing on the wall of the cavity. MZ-2 and MZ-3 consist of fibrous crystals, forming spherules. The latter covers the former. Vesicles are common in the host basalt, sometimes filled by zeolites and other alteration minerals.

the X-ray diffraction method. The other zeolite sample, ZO-2, which fills the cavity in an andesitic rock, was collected from Ishizuchi-san, Ehime Prefecture. The X-ray examination indicates that this sample is a mixture of heulandite and stilbite.

Trace element concentrations were measured by the mass-spectrometric isotope dilution method. About 110 mg of sample was decomposed by HF-HClO₄-HNO₃ mixtures in a teflon beaker. Conventional ion exchange method was applied for the separation of trace elements. Purifications of HCl, HClO₄, HNO₃, HF, and H₂O were performed by distillation more than twice by using a quartz glass still and a teflon one for HF under sub-boiling temperatures. The total analytical blanks for the entire chemical procedures for the samples were tested (see Table 1 and Fig. 2). The blank values for Rb, Sr, and Ba were negligible in all cases, but corrections were necessary for REE. Uncertainties estimated for trace element concentrations are believed to be less than three percent, but sometimes relatively large errors up to about 10 per cent occur owing to a somewhat large contribution of blank corrections and to relatively low precision due to weak ion beam intensities in the mass-spectrometry. However, major features of the REE patterns shown in the figures are considered to be well established.

Table 1. Analytical data on zeolites and host rocks together with blank data

Mineral or rock type	Maze ^(a)				Izu ^(b)			Ishizuchi ^(c)		Blank
	MZ-1	MZ-2	MZ-3	MZ-host	ZO-1	ZO-1-host	ZO-2		(×10 ⁻⁹ g)	
La	0.0412	n.d.	0.0187	11.2	0.0193	6.89	n.d.	n.d.	0.318	
Ce	0.118	0.0627	0.0676	43.3	0.0778	19.4	0.0335	0.0335	0.488	
Nd	0.0253	0.0241	0.0273	15.2	0.0456	14.0	0.0102	0.0102	0.135	
Sm	0.00865	0.00590	0.00609	3.80	0.0799	3.97	0.00197	0.00197	0.0276	
Eu	0.00148	0.00105	0.00193	1.28	0.0144	1.29	0.00145	0.00145	0.00866	
Gd	0.00573	0.00651	0.00692	4.44	n.d.	4.81	n.d.	n.d.	0.0389	
Dy	0.00840	0.00616	0.00971	4.71	n.d.	5.50	0.00277	0.00277	0.0491	
Er	0.00543	0.00792	0.00785	3.00	0.00837	3.57	0.00191	0.00191	0.0326	
Yb	0.00766	0.0102	0.0107	n.d.	0.00911	3.68	0.00278	0.00278	0.0391	
Lu	0.00161	0.00182	0.00187	0.489	0.00417	0.574	n.d.	n.d.	0.0132	
Rb	44.4	1.31	14.6	21.4	25.6	9.74	62.7	6.8		
Sr	31.1	110	63.4	503	3477	197	1333	1.4		
Ba	2.78	2.34	4.79	380	42.4	132	164	6.50		
Na ₂ O	13.2	8.98	4.41	n.d.	0.220	n.d.	1.85			
K ₂ O	b.d.	b.d.	b.d.	n.d.	0.994	n.d.	0.120			
CaO	b.d.	6.09	11.6	n.d.	8.16	n.d.	6.39			
H ₂ O ⁻	0.59	2.1	1.0	n.d.	6.5	n.d.	4.2			
H ₂ O ⁺	9.0	13	14	n.d.	17	n.d.	17			
Mineral or rock type	Analcime	Gonnardite	Scolecite	Altered-basalt	Chabazite (Quartz)	Altered-andesite	Heulandite Stilbite			

REE, Rb, Sr, Ba in ppm, others in wt. %.

(a)-(c) Sampling locality name ((a) = Niigata Prefecture, Japan; (b) = Kanagawa Prefecture, Japan; (c) = Ehime Prefecture, Japan).

b.d. = below the detection limit.

n.d. = not determined.

Fig. 2. Chondrite normalized trace element abundances for the Maze zeolites and their host basalt. Blank data obtained from the total chemical procedures are represented by the values for the typical sample amount used in this study.

Na, K and Ca contents were determined by the atomic absorption method. Weight loss during heating at 110°C is expressed by H_2O^- and ignition loss by H_2O^+ .

RESULTS

The analytical data are summarized in Table 1. In Figs. 2 and 3, chondrite normalized abundances of trace elements are illustrated together with the blank values for the typical sample amounts used in the analyses. Normalization values for REE and Ba are taken from Masuda *et al.* (1973), and Nakamura (1974), respectively, and

Fig. 3. Chondrite normalized trace element abundances for the Izu and Ishizuchi samples.

for Rb and Sr, 2.2 and 11 ppm are adopted, respectively (cf., Minster *et al.*, 1982).

Maze zeolites and their host basalt

As for the Maze samples, Na and Ca contents vary regularly in the order of formation: i.e., MZ-1 to MZ-3. MZ-1 (analcime) has the highest Na and lowest Ca contents, whereas the MZ-3 (scolecite) has the lowest Na and the highest Ca ones. Both values are intermediate in MZ-2 (gonnardite). The Rb concentration varies largely, whereas variations in Sr, Ba and REE are rather small. It is remarkable that the REE concentrations of these zeolites are extremely low in comparison with those of its host rock or of usual crustal materials. Their patterns are in weakly convex-upward shape but mutual fractionations among REE are relatively small. The REE pattern for the host ba-

salt shows a slightly light REE enriched one with somewhat positive Ce anomaly.

Izu and Ishizuchi data

Figure 3 shows the trace element data for the zeolites from the Izu and Ishizuchi areas. Although the localities of these samples are quite diverse, they have the following common features: (1) relatively high Sr and K concentrations; (2) extremely low REE concentrations; and (3) positive Eu anomalies. Note that K concentrations for the Maze samples are below the detection limit of the atomic absorption spectroscopy. The high K contents of the Izu and Ishizuchi zeolites seem to be in harmony with their relatively high Rb concentrations in comparison with those of the Maze zeolites. The host rock of the Izu sample shows a flat REE pattern which is similar to those previously reported for andesitic rocks from the Izu area.

DISCUSSION

Crystal structure versus formation environment

It is interesting that the REE concentrations in deep-sea phillipsite (Piper, 1974; Bernat and Church, 1978) are not so low in comparison with extremely low REE abundances in the zeolites

studied in the present study. (Note that the available REE data for zeolites in literature are restricted to deep-sea phillipsite.) The REE distribution in those phillipsites is similar in absolute abundance and pattern to those contained in the sediments aside from strong negative Ce anomalies. It would be interesting to examine the difference in crystal structure between phillipsite and other zeolites used in this study. According to Breck's classification, for example, phillipsite and analcime are classified as group 1, whereas chabasite, gonnardite, scolecite, heulandite and stilbite belong to group 4, 5, 5, 7 and 7, respectively (Breck, 1974; see Table 2). Breck's division is based on a combination of framework topology as well as secondary building units. Although the differences among these groups are rather complex, larger-numbered groups tend to have wider space in the channel and have more complex configuration of tetrahedron in the secondary building unit. Judging from such classification as well as other parameters in Table 2, it is difficult to conclude that phillipsite has a special crystal structure among other zeolites. Moreover, REE-zeolite can be easily synthesized by ion exchange of synthetic NaY-zeolite (zeolite Y) with a REE chloride solution (e.g., Ward, 1968; Roelofsens *et al.*, 1986). Zeolite Y has the same framework to-

Table 2. Crystal chemical properties of zeolites

Name	Group ^(a)	Typical unit cell contents	Void fraction ^(b)	Free aperture ^(c)
Analcime	1	Na ₁₆ (Al ₁₆ Si ₃₂ O ₉₆)·16H ₂ O	0.18	2.6
Gonnardite	5	Na ₄ Ca ₂ (Al ₈ Si ₁₂ O ₄₀)·14H ₂ O	0.31	2.6 × 3.9
Scolecite	5	Ca ₈ (Al ₁₆ Si ₂₄ O ₈₀)·24H ₂ O	0.31	2.6 × 3.9
Chabasite	4	Ca ₂ (Al ₄ Si ₁₆ O ₂₄)·13H ₂ O	0.47	3.7 × 4.2
Heulandite	7	Ca ₄ (Al ₈ Si ₂₈ O ₇₂)·24H ₂ O	0.39	4.0 × 5.5
				4.0 × 7.2
Stilbite	7	Ca ₄ (Al ₈ Si ₂₈ O ₇₂)·28H ₂ O	0.39	4.1 × 6.2
				2.7 × 5.7
Phillipsite	1	(K,Na) ₁₀ (Al ₁₀ Si ₂₂ O ₆₄)·20H ₂ O	0.31	4.2 × 4.4
				2.8 × 4.8

^(a)Breck's classification (Breck, 1974).

^(b)The void fraction taken mainly from Breck (1974) is determined from the water content of the hydrated zeolite (cf., Flanigen, 1977).

^(c)Free aperture of main channels based on the structure of the hydrated zeolite (*A*) (Breck, 1974; cf., Flanigen, 1977).

pology as faujasite and belongs to group 4. As mentioned above, group 4 includes chabasite, a sample of which we have analyzed in this study. These facts suggest that REE can be accommodated in zeolite crystal structures in cases of appropriate conditions. Moreover, although it is difficult to draw a definite conclusion at present, the difference between relatively moderate REE concentrations in those phillipsites and extremely low REE concentrations in our zeolites may not be ascribed to the difference in crystal structure but to the difference in their formation processes or conditions.

The deep-sea phillipsites are found mostly as authigenic microcrystalline deposits in sediments. The amount of phillipsite in such deposits usually ranges from 3 to 12% and the zeolite is associated with montmorillonite and commonly with other minerals altered from volcanic rocks and debris (Bernat and Church, 1978). The REE uptake might be performed directly from interstitial sea water or by incorporation of particle inclusion. The former mechanism is supported by the fact that Ce displays the same strong negative anomaly as sea water, but the level of absolute REE abundances in sea water, as a whole, is less than 10^{-5} of that for the phillipsites (e.g., De Baar *et al.*, 1985; Piepgras and Jacobsen, 1992). Since deep-sea phillipsites crystallize in small interstitial spaces within sediments, it is likely that chemical elements are redistributed in such a small space where REE are easily supplied by decomposition of surrounding materials, such as marine organisms, fine-grained detrital or altered volcanic debris (paragonite). The participation of particle will be discussed later with respect to Eu anomaly.

One the other hand, the zeolites used in our study might have crystallized from aqueous solutions which infiltrated into the cavities or cracks of volcanic rocks. These solutions might have been transported in a distance from the position where original materials were dissolved. If REE have been absorbed into secondary minerals during such transportation, REE in the transferring solutions would be scavenged, which results in the formation of REE poor zeolites. In the reverse cases, i.e.,

REE concentrations in the solution have been increased during such transportation, REE concentrations in the zeolite must show rather high values similar to those of the phillipsite, because REE can be accommodated in zeolite structures as mentioned in the preceding paragraph. Therefore, low REE concentrations in the zeolites could be attributed to extremely low REE concentrations in the solution.

Moreover, such immobility of REE during the zeolite-related transportation is supported by the comparison between the host rock REE abundances of those zeolites and the available data of the fresh rock in each area. The REE data reported by Fujimaki (1981, 1982) for andesitic rocks from Izu area indicate quite similar REE features to that of the host andesite of ZO-1. Furthermore, the REE pattern for the Maze host rock seems to fall within the range of possible fresh rocks inferred from the REE data of the Tertiary volcanic rocks from Northeast Japan (Ebihara *et al.*, 1984). Thus, such overall similarities suggest that REE have been immobile during the alteration processes of slightly alkaline conditions. (Note that neutral to slightly alkaline conditions are required for zeolite crystallization.)

Inference on Ce anomaly

The zeolites and their host rock from the Maze area appear to have small Ce anomalies. The zeolite REE abundances normalized to the host rock values are plotted against atomic number in Fig. 4. It is interesting that their Ce seem to fall almost on a smooth light REE trend. Such smoothness indicates that Ce anomalies in these zeolites are inherited from that of their host basalt. If this is the case, these zeolites were formed after the formation of the Ce anomaly in the host rock. It has been accepted that Ce anomaly is not produced during magmatic processes but created by secondary processes such as alteration or weathering (e.g., Schreiber *et al.*, 1980). Therefore, it is conceivable that the solution from which these zeolites were deposited is not magmatic but meteoric water. This point would be important for the genesis of zeolites, because magmatic solutions

Fig. 4. REE distribution patterns for the Maze zeolites normalized to the host basalt. Note that the patterns for the light REE span do not show Ce anomalies.

have been considered as a candidate of the solution from which the zeolites in amygdals or cavities of igneous rocks were deposited (Coobms *et al.*, 1959). The zeolitization might have taken place at relatively later stages when alteration of the host rock was considerably proceeded.

Effect of ion exchange property

Since ion exchange property is an important characteristic of zeolites, the REE concentrations in zeolites are affected by the latest solution to which they were exposed. This effect must be examined carefully for the Maze case, because the resemblance of REE patterns for three Maze zeolites is obvious. Such resemblance may be explained by considering that the initial REE concentrations in the Maze zeolites (especially for MZ-1 and MZ-2) have changed during later stages and the observed REE concentrations reflect those in the final solution to which they were exposed. However, in the light of ion exchange properties of zeolites, it is unlikely that the differences among REE, Ba and Sr do not come out clearly, because thermodynamic constants for REE, Ba and Sr are considered to be different in each zeolite. For example, thermodynamic equilibrium constant for $\text{La}^{3+} \leftrightarrow 3\text{Na}^{+}$ ion exchange reaction on clinoptilolite is $4.3 \cdot 10^{-5}$, whereas those for $\text{Na}^{+} \leftrightarrow \text{Sr}^{2+}$ and $\text{Na}^{+} \leftrightarrow \text{Ba}^{2+}$ are 0.77 and 1.4, respectively (cf., Tsitsishvili *et al.*, 1992). Note

that not only REE but also Ba and Sr abundances for the Maze zeolites are quite similar. Moreover, clinoptilolite is a typical ion exchangeable zeolite (Nishimura, 1975), and ion exchange ability for REE must be different in species of zeolites. Furthermore, it is known that trivalent cations are generally not found in the exchange sites of most zeolite minerals (Mumpton, 1977). Therefore, REE might have been preserved in the zeolites during the exposure to later stage solutions, and the effect of ion exchange seems to be negligible at least in our samples.

Inference on Eu anomaly

Since REE abundances for the zeolites analyzed in this study are extremely low, it can be considered that the REE in the zeolites were carried mainly by small particles (dusty materials) as impurities. However, such mechanism does not seem to be consistent with the positive Eu anomalies observed in ZO-1 and ZO-2, because most of the crustal materials show almost no or negative Eu anomalies and the materials having positive Eu anomalies are substantially restricted to feldspars. Although the host rocks for these zeolites contain feldspar phenocrysts, it may be unlikely that feldspars rather than matrix materials were selectively broken and contributed much to the dust in the solution.

It is also inferred that the positive Eu anomaly

lies and relatively high Sr concentrations for those zeolites may reflect relatively high Eu and Sr concentrations in the solutions. Such Eu and Sr might have been derived from feldspars because of their high Eu (Sr) features as mentioned above. The similarity between feldspars and zeolites in chemical composition suggests that the solution formed by alteration of feldspar-bearing rocks tends to have more zeolite-like chemical component and to precipitate zeolites more easily. Speculatively, zeolites might have been produced at the stage when feldspar alteration had significantly proceeded.

CONCLUDING REMARKS

Although the number of our analyses is limited, our study presents trace element characteristics for several kinds of zeolites which occur in cavities of volcanic rocks. REE concentrations for them are extremely low in comparison with those for host rocks or usual crustal materials. Such low REE abundances in the zeolites seem to reflect extremely low REE concentrations in solutions from which those zeolites were precipitated. Moreover, such low REE concentrations in solution are consistent with a hypothesis that REE are immobile under alkaline conditions which are required for zeolitization: REE released from the rock might be adsorbed immediately in secondary minerals. Furthermore, difference of zeolite species does not seem to be important for determining REE incorporation. Solution chemistry and formation environment (or mechanism) may affect much on REE uptake in zeolites. Although there remain many unresolved problems, our study suggests that REE data (e.g., absolute level of concentrations, Eu and Ce anomalies) would be useful for better understanding the low temperature and pressure processes such as alteration and weathering. The Ce anomalies in the Maze zeolites indicate that the solution related to the zeolite formation is not magmatic but meteoric water. Furthermore, we like to emphasize that this study would be a first step for REE geochemistry on zeolites.

Acknowledgments—We thank Mayumi Terakado for her assistance in chemical analysis. One of us (Y. T.) is grateful to Professor A. Masuda for his kind donation of a mass-spectrometer. We also thank two anonymous reviewers for their critical comments and suggestions for an early version of the manuscript. This work was partly supported by the grants Nos. 02640597 and 05640550 to Y. T. from the Ministry of Education and Culture, Japan.

REFERENCES

- Bernat, M. and Church, T. M. (1978) Deep-sea phillipsites: trace geochemistry and modes of formation. *Natural Zeolites Occurrence, Properties, Use* (Sand, L. B. and Mumpton, F. A., eds.), 259–267, Pergamon Press.
- Breck, D. W. (1974) *Zeolite Molecular Sieves*. Wiley-Interscience, New York, 771 pp.
- Coombs, D. S., Ellis, A. J., Fyfe, W. S. and Taylor, A. M. (1959) The zeolite facies, with comments on the interpretation of hydrothermal syntheses. *Geochim. Cosmochim. Acta* **17**, 53–107.
- De Baar, H. J. W., Bacon, M. P. and Brewer, P. G. (1985) Rare earth elements in the Pacific and Atlantic Oceans. *Geochim. Cosmochim. Acta* **49**, 1943–1959.
- Ebihara, M., Nakamura, Y., Wakita, H., Kurasawa, H. and Konda, T. (1984) Trace element composition of Tertiary volcanic rocks of northeast Japan. *Geochem. J.* **18**, 287–295.
- Flanigen, E. M. (1977) Crystal structure and chemistry of natural zeolites. *Mineralogy and Geology of Natural Zeolites* (Mumpton, F. A., ed.), 19–52, Mineralogical Society of America, Washington, D.C.
- Fujimaki, H. (1981) Rare earth patterns for theoleitic andesite and its associated calc-alkali andesite. *J. Jpn. Assoc. Min. Petrol. Econ. Geol.* **76**, 93–101.
- Fujimaki, H. (1982) Basalt produced by mechanical mixing of andesite magma and gabbroic fragments: Hakone volcano and adjacent areas, Central Japan. *J. Volcanol. Geotherm. Res.* **12**, 111–132.
- Gottardi, G. and Galli, E. (1985) *Natural Zeolites*. Springer-Verlag, Berlin, 409 pp.
- Harada, K., Iwamoto, S. and Kihara, K. (1967) Erionite, phillipsite and gonnardite in the amygdaloids of altered basalt from Maze, Niigata Prefecture, Japan. *Amer. Mineral.* **52**, 1785–1794.
- Masuda, A., Nakamura, N. and Tanaka, T. (1973) Fine structures of mutually normalized rare-earth patterns of chondrites. *Geochim. Cosmochim. Acta* **37**, 239–248.
- Minster, J. F., Birck, J. L. and Allegre, C. J. (1982) Absolute age of formation of chondrites studied by

- ^{87}Rb - ^{87}Sr method. *Nature* **300**, 414–419.
- Mumpton, F. A. (1977) Natural zeolites. *Mineralogy and Geology of Natural Zeolites* (Mumpton, F. A., ed.), 1–9, Mineralogical Society of America, Washington, D.C.
- Nakamura, N. (1974) Determination of REE, Ba, Fe, Mg, Na and K in carbonaceous and ordinary chondrites. *Geochim. Cosmochim. Acta* **38**, 757–775.
- Nishimura, Y. (1975) Use of natural zeolite. *Zeolites* (Hara, N. and Takahashi, H., eds.), 300–324, Kodansha, Tokyo.
- Piepgas, D. J. and Jacobsen, S. B. (1992) The behavior of rare earth elements in seawater: precise determination of variations in the North Pacific water column. *Geochim. Cosmochim. Acta* **56**, 1851–1862.
- Piper, D. Z. (1974) Rare earth elements in ferromanganese nodules and other marine phases. *Geochim. Cosmochim. Acta* **38**, 1007–1022.
- Roelofsen, J. W., Mathies, H., de Groot, R. L., van Woerkom, P. C. M. and Gaur, H. A. (1986) Effect of rare earth loading in Y-zeolite on its dealumination during thermal treatment. *New Developments in Zeolite Science and Technology* (Murakami, Y., Iijima, A. and Ward, J. W., eds.), 337–344, Elsevier, Amsterdam.
- Schreiber, H. D., Lauer, H. V., Jr. and Thanyashiri, T. (1980) The redox state of cerium in basaltic magmas: an experimental study of iron-cerium interactions in silicate melts. *Geochim. Cosmochim. Acta* **44**, 1599–1612.
- Shannon, R. D. and Prewitt, C. T. (1969) Effective crystal radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925–946.
- Shimazu, M. and Kawakami, T. (1967) Distribution of zeolite and other minerals in the Maze basalts, Niigata Prefecture, Japan. *Rep. Geol. Mineral. Niigata Univ., Ser. E*, **1**, 17–32.
- Tsitsishvili, G. V., Andronikashvili, T. G., Kirov, G. N. and Filizova, L. D. (1992) *Natural Zeolites*. Ellis Horwood, New York, 295 pp.
- Ward, J. W. (1968) A spectroscopic study of the surface of zeolite Y. II. Infrared spectra of structural hydroxyl groups and absorbed water on alkali, alkali earth, and rare earth ion-exchanged zeolites. *J. Phys. Chem.* **72**, 4211–4223.