

Authigenic Phillipsite in Deep-sea Manganese Nodules from the Clarion-Clipperton Fracture Zones, NE Equatorial Pacific

Chan Hee Lee* and Sung-Rock Lee**

ABSTRACT : The occurrence, optical property, chemical composition, crystal structure and formation environments of the phillipsite within deep-sea manganese nodules were systematically investigated in this study. Phillipsite in manganese nodules occurs in nucleus of nodules along with consolidated bottom sediments, weathered volcanic debris, and interstitial grains in the each layer of manganese encrusts. Phillipsite is predominantly pseudomorphs of volcanic shards, and occurs as white to pale yellow in color lath-shaped and equant crystals. These show aggregations of prismatic, blocky, and bladed of 2 to 20 μm long, and 2 to 5 μm thick. The simplified average chemical formula of phillipsite is $(\text{Ca}_{0.1}\text{Mg}_{0.3}\text{Na}_{1.1}\text{K}_{1.5})_3(\text{Fe}_{0.3}\text{Al}_{4.2}\text{Si}_{11.8})\text{O}_{32} \cdot 10\text{H}_2\text{O}$ with a very siliceous and alkalic. The $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio is 2.37 to 2.78 and alkalis greatly exceed the divalent exchangeable cations, and Na/K ratio is 0.59 to 0.81. The phillipsite is monoclinic ($P2_1/m$) with the unit-cell parameters, $a=10.005\text{\AA}$, $b=14.129\text{\AA}$, $c=8.686\text{\AA}$, $\beta=124.35^\circ$, and $V=1013.6\text{\AA}^3$. Phillipsites in manganese nodules formed apparently authigenically at a temperature less than 10°C , and they crystallized at a pressure of less than 0.7 kb, and pH of about 8 in deep-sea environments.

INTRODUCTION

Phillipsite is one of zeolite group minerals now recognized as occurring in marine sediments, and also occurs in some saline lakes of terrestrial deposits. Zeolites, hydrated aluminosilicates containing alkali and alkaline elements, are common authigenic silicates reported from sedimentary deposits, especially which originally consist of volcanic glasses. Hay (1964) reported the common occurrences, physical properties, chemistry, crystal structure, and mineral assemblages of phillipsite in the saline, and alkaline lakes deposits, but since more than 100 years phillipsite was first discovered in deep-sea sediments from the Pacific (Murray, Renard, 1891). Phillipsites are important diagenetic minerals in deep-sea bottom which are actively forming in sediments, burial histories, thermal gradients, sediment ages, and pore water chemistries are reasonably well known, much can be learned about zeolitization process by their occurrence in this environment (Glaccum, Bostrom, 1976; Stonecipher, 1976).

The ideal composition of phillipsite is $(\text{Ca}_{0.5}\text{Na}_{1.0}\text{K}_{1.0})_5\text{Al}_5\text{Si}_{11}\text{O}_{32} \cdot 10\text{H}_2\text{O}$, but considerable substitution

of Al for Si may occur, with corresponding increase of Ca, Na, and K. Depending on the environment, the Si/Al ratio can range from 1.3 to 3.4 (Sheppard *et al.*, 1970). Marine phillipsites are generally more siliceous than terrestrial phillipsites associated with mafic volcanic rocks, but less siliceous than those from saline lakes. The basic structure of phillipsite is a framework composed of $(\text{Si},\text{Al})\text{O}_4$ tetrahedra. The net negative charge on the framework is balanced by the presence of cations, in most cases Ca, Na or K, which are situated in cavities within the framework structure.

Phillipsite constitutes about 1.5% of deep-sea sediments (Kastner, 1979), and it has also been observed to occur and to form within manganese nodules (Murray, Renard, 1891; Bonatti, 1963; Burns, Burns, 1978a, b). However, their studies dealt with simple description of mineralogy. The present study was undertaken to characterize the occurrences, optical properties, chemical compositions, crystal structures, and reviews of the phillipsites within manganese nodules from the Clarion-Clipperton Fracture Zones, northeastern equatorial Pacific.

MATERIALS AND METHODS

In Korea from 1992 to 1994, nine cruises using the R/V Onnuri were carried out reconnaissance surveys to evaluate economic grades of manganese nodules in the Clarion-Clipperton fracture zones of the northeast-

*Department of Geology, Chungnam National University, Taejeon 305-764, Korea

**Korea Institute of Geology, Mining and Materials, P.O. Box 111, Taedok Science Town, Taejeon 305-350, Korea

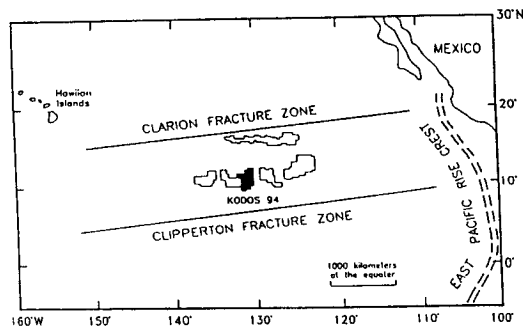


Fig. 1. Location map of the study area. Boxed zones are surveyed area of the KODOS cruises.

tern equatorial Pacific. These surveys revealed occurrence, distribution, classification, texture, geochemistry, and mineralogy of manganese nodules in this zones (Chang *et al.*, 1994; Lee *et al.*, 1994, 1995, 1996), although their growth history and formation environment are not well understood. The phillipsites used in the present study were separated from manganese nodules collected during the cruises as a part of the Korea Deep Ocean Study-'94 (KODOS-'94) area (Fig. 1).

Mode of occurrences and optical properties of the phillipsites were observed under the optical microscopy. Scanning electron microscope (SEM) of Philips 505 attached with energy dispersive X-ray spectrometer (PV 9100/60) was used to study freshly broken fragments of phillipsite-rich parts, which had been coated with a film of gold. The chemical analysis was performed by using CAMECA SX-55 electron microprobe (EPMA). In quantitative microprobe analyses, accelerating voltage of 15 kV, specimen current of 20 nA, and spot size of 1 to 2 μm were employed. X-ray powder diffraction (XRD) was carried out using Philips PW-1730 with $\text{CuK}\alpha$ radiation with step scans of 3° to 90° using size of 0.02° . Unit-cell parameters were calculated with the least-square refinement program of Appleman, Evans (1973).

RESULTS AND DISCUSSIONS

Occurrence and optical properties

In manganese nodules, phillipsites are common constituent occurring in the nucleus, which is indurated residual sediments, altered volcanic debris and weathered rock fragments. Phillipsite occurs as milky white to pale yellow in color, white streak, and vitreous luster, although the some grains have a

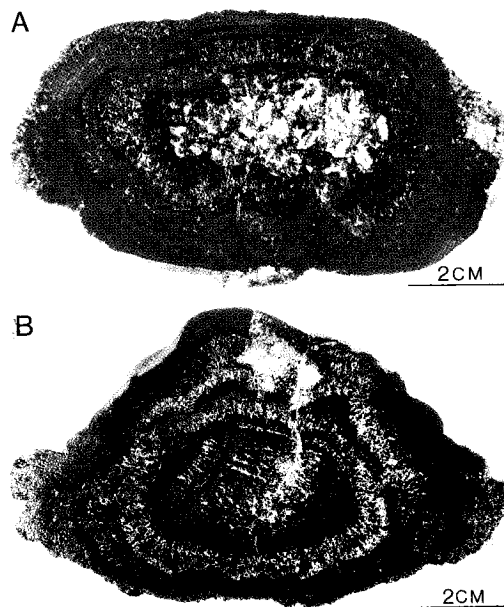


Fig. 2. Representative photographs showing phillipsites within manganese nodules. A; Phillipsites (white) composed of highly altered basaltic rock fragment in nuclei within manganese nodule (black). B; Phillipsite (white) within layer by layer in manganese encrust (black).

yellowish brown, possibly caused by oxidation. In Fig. 2, phillipsites composed of nuclei with highly altered basaltic rock fragment (A), and interstitial grains within layer to layer of manganese encrust (B). These commonly coexist with quartz, plagioclase, barite, and clay minerals of smectite and illite based on XRD patterns. Phillipsite commonly occurs as discrete, cement, cavity, and fracture fillings in manganese nodules.

SEM examination of the phillipsite-rich samples separated from manganese nodules shows that are aggregates of semi-prismatic crystals (Fig. 3, A). Some prismatic phillipsite occurs of euhedral crystals in cavities with ferromanganese oxides (Fig. 3, B, C) with 2 to 20 μm long and 2 to 5 μm thick. The clusters of phillipsites are 25 to 200 μm in diameter, and generally show well-developed crystal habits. In most cases, phillipsites occur as blades and laths of pseudomorphs texture of volcanic glass shards in nuclei of manganese nodule are very common (Fig. 3, D). Under the microscopy, phillipsite occurs both lath-shaped and as equant crystal, which are associated with detrital quartz, plagioclase, microfossils, and other authigenic clay minerals. Most phillipsites appear isotropic and colorless, but a few

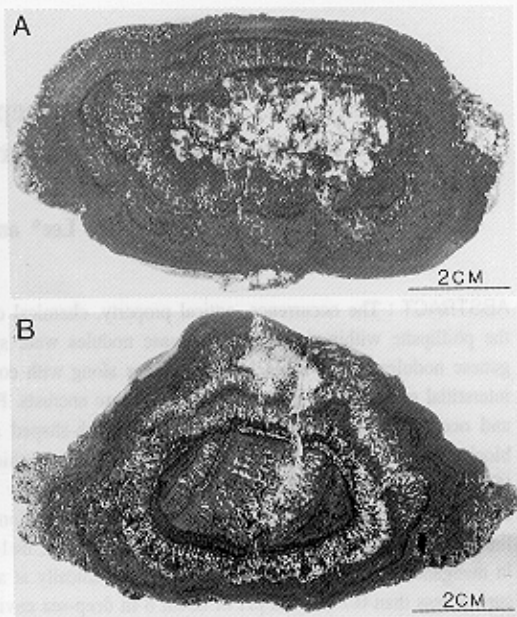


Fig. 2. Representative photographs showing phillipsites within manganese nodules. A; Phillipsites (white) composed of highly altered basaltic rock fragment in nuclei within manganese nodule (black). B; Phillipsite (white) within layer by layer in manganese encrust (black).

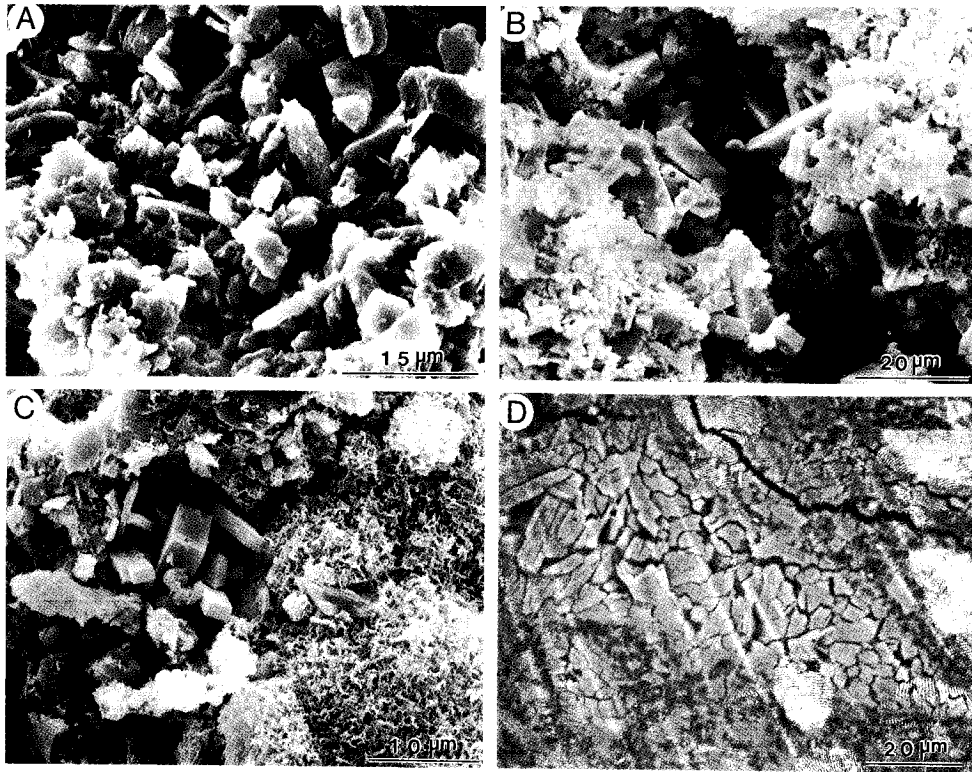


Fig. 3. Micrographs of phillipsites within manganese nodules. A; SEM of phillipsites showing cluster of semi-prismatic crystals, B; SEM of phillipsites showing aggregates of prismatic crystal, C; SEM of coexisting with blocky crystals of phillipsite and honey-comb textured todorokite, D; Back scattered electron micrograph of phillipsites aggregate with blades and laths in volcanic glass shard.

are weakly birefringent and cleavage perfect, and are parallel or nearly parallel extinction.

A variety of biogenic debris and detritus are seen in manganese nodules (Fig. 4). The biogenic debris in the nodules is composed of fragments of siliceous tests of radiolaria, diatoms, sponge spicules, and the others, but is calcareous tests, because the seafloor between the Clarion and Clipperton Fracture Zones is generally deeper than calcium carbonate compensation depth (CCD). Lining the walls of the cavities and voids in leached areas are euhedral crystals of phillipsite (Fig. 3, B, C). The crystals to leached biogenic debris indicate that phillipsite grew *in situ* at the expense of the siliceous debris after the nodule was formed (Burns, 1978a; 1978b).

Chemical compositions

The simplified chemical formula of marine phillipsite is $(K_xNa_{1-x})_5Al_5Si_{11}O_{32} \cdot 10H_2O$, but sub-

stitution of Al for Si may occur (Cronan, 1980). The Si/Al ratio ranges between 2.3 and 2.8, and the mineral is rich in alkalis with K in excess of Na (Sheppard *et al.*, 1970). The elements Si, Al and K show little overall variation between different phillipsites (Stonecipher, 1976). The loss of alkali cations in zeolitic and micaceous minerals by electron-beam irradiation is widely recognized during electronprobe microanalyzer and analytical electron microscope (Ahn *et al.*, 1986; Van der Fluijm *et al.*, 1988). Especially, K contents tend to be highly underestimated with extended electron-beam exposure as a result of the diffusion of K from the analyzed area. Decrease of accelerating voltage and beam current and increase of electron-beam size in general decrease the rate of K diffusion (Ahn, 1995).

The chemical compositions and unit-cell contents of phillipsites in the nodules of present study are given in Table 1, where they have been recalculated on the basis of 32 oxygens, the anhydrous cell constants, and the Si/Al ratio for these analyses are fairly constant.

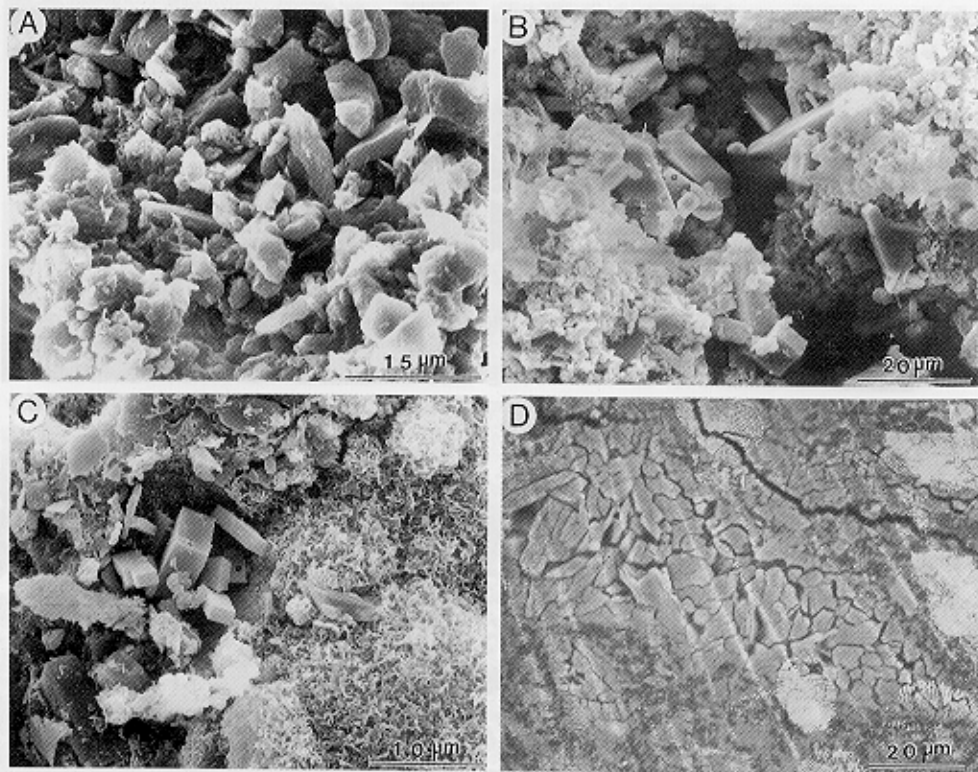


Fig. 3. Micrographs of phillipsites within manganese nodules. A; SEM of phillipsites showing cluster of semi-prismatic crystals, B; SEM of phillipsites showing aggregates of prismatic crystal, C; SEM of coexisting with blocky crystals of phillipsite and honey-comb textured todorokite, D; Back scattered electron micrograph of phillipsites aggregate with blades and laths in volcanic glass shard.

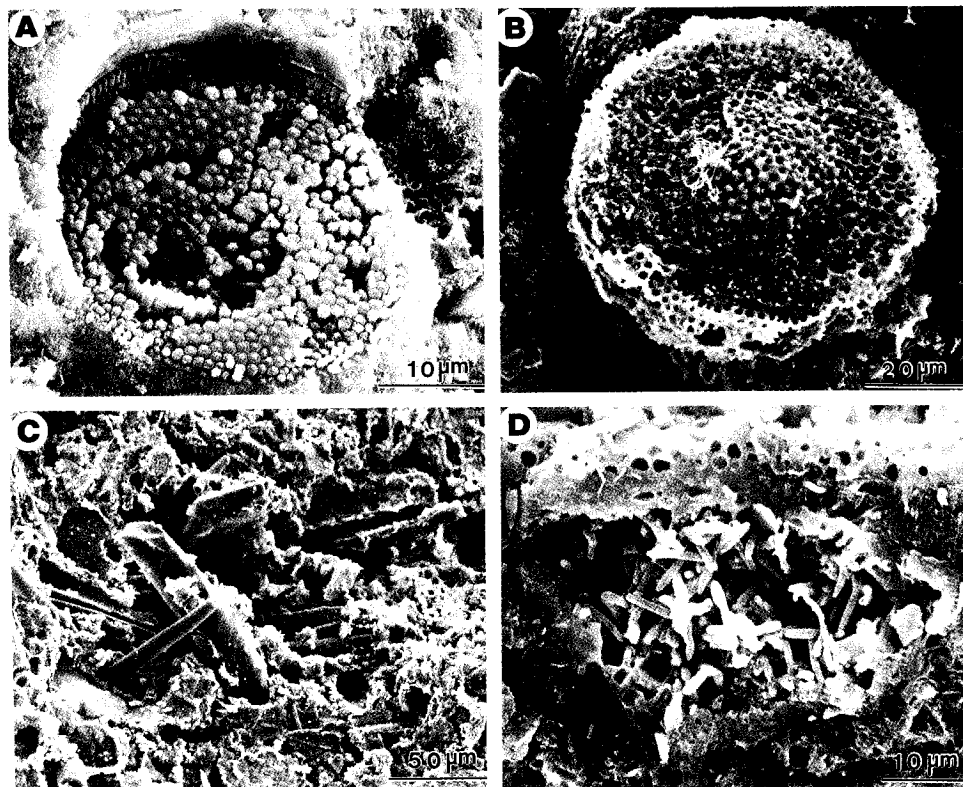


Fig. 4. SEM micrographs of siliceous biogenic debris composed of diatom, radiolaria, sponge spicules within manganese nodules showing dissolution features.

The phillipsite is very siliceous and alkalic with the simplified chemical formula of $(Ca_{0.1}Mg_{0.3}Na_{1.1}K_{1.5})_3(Fe_{0.3}Al_{4.2}Si_{11.8})O_{32} \cdot 10H_2O$, but the ratio of Si/Al ranges between 2.80 and 2.84. Ferric iron may substitute for Al^{+3} in these phillipsite, judging from the fact that the molecular sum of Al_2O_3 slightly exceeds the mole fraction of MgO, CaO, Na_2O , and K_2O in all samples, but almost equals the sum of Al_2O_3 and Fe_2O_3 . Especially, CaO, MgO, SiO_2 , and Al_2O_3 seem to be richer than the stoichiometric phillipsite, and alkalis are poorer than the stoichiometric phillipsite from the saline lakes (Fig. 5). Saline phillipsites are siliceous and alkalic, and this is characteristics that set them apart from phillipsites that occur in rocks of other compositions and depositional environments (Sheppard, Fitzpatrick, 1989).

For any phillipsite, the sum of Si+Al in the unit-cell (based on 32 oxygens) should be 16. In Table 1, however, (Si+Al) is close to 16, but is improved to 16 or more than 16 if the Fe^{+3} is added. The analyses suggest that Fe^{3+} is part of the tetrahedral framework of phillipsite rather than being present in

an impurity. The Si/(Al+ Fe^{+3}) ratio is 2.37 to 2.78, and framework of tetrahedral Si contain 57.8 to 61.4%. Monovalent exchangeable cations greatly exceed divalent cations, and K exceeds Na, resulting in Na/K ratios of 0.59 to 0.81. These phillipsites have distinctive composition of high Si/Al, (Na+K)/(Na+K+Ca+Mg) and Na/K ratios (Fig. 6). Undoubtedly, the principal factors responsible for these particular compositions are the palagonitic mud parent, siliceous biogenic debris, and saline in depositional deep-sea environment.

Crystallography

The structure of natural phillipsite has been reported as monoclinic $P2_1/m$ or $P2_1$ with $Z=1$ by Sadanaga *et al.* (1961), and also as orthorhombic $B2mb$ with $Z=4$ by Steinfink (1962). After all unambiguously indexed reflections were located, those having multiple indexing were resolved whenever possible using intensities calculated from the monoclinic system ($P2_1/m$ or $P2_1$) with no evidence of order to disorder in the Al/Si

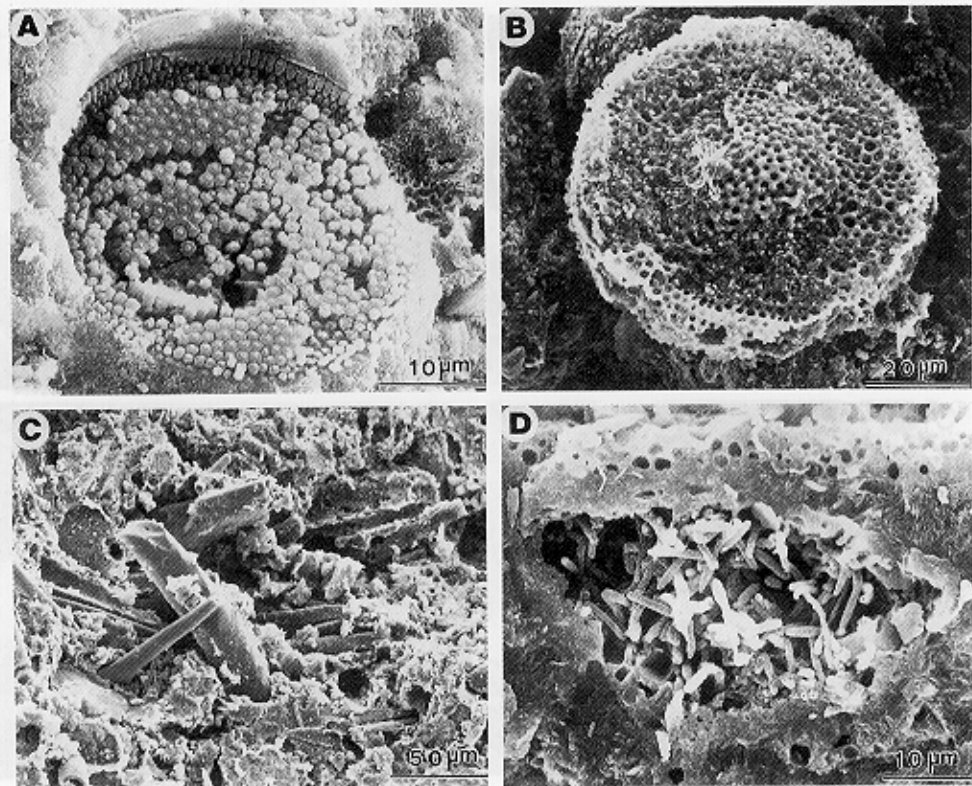


Fig. 4. SEM micrographs of siliceous biogenic debris composed of diatom, radiolaria, sponge spicules within manganese nodules showing dissolution features.

Table 1. Representative chemical compositions and unit-cell constants of phillipsite within manganese nodules.

	(1) n=6	(2) n=5	(3) n=6	(4) n=5
SiO ₂	61.38	61.49	57.75	57.98
TiO ₂	0.06	0.01	0.04	0.27
Al ₂ O ₃	18.56	18.34	17.28	17.57
Fe ₂ O ₃	1.15	0.53	0.71	4.94
MnO	0.04	0.07	0.09	0.00
MgO	0.44	0.20	0.32	2.44
CaO	0.09	0.19	0.27	0.48
BaO	0.02	0.01	0.06	0.04
Na ₂ O	3.28	2.19	3.15	2.45
K ₂ O	6.46	5.64	6.02	5.26
Total	91.48	88.76	85.69	91.43
Unit-cell contents based on 32 oxygens				
Si	11.90	12.11	11.95	11.36
Al	4.24	4.28	4.21	4.06
Fe ⁺³	0.17	0.08	0.11	0.73
Mn	0.01	0.01	0.02	0.00
Mg	0.13	0.06	0.10	0.72
Ca	0.02	0.04	0.06	0.10
Na	1.23	0.84	1.26	1.08
K	1.60	1.42	1.59	1.32
*	16.31	16.47	16.27	16.15
**	2.70	2.78	2.76	2.37
***	0.73	0.74	0.73	0.70

n=number of analytical points, *, Si+Al+Fe⁺³, **, Si/(Al+Fe⁺³), ***, Si/(Si+Al+Fe⁺³)

(1) Phillipsite from altered rock fragments of nucleus in nodules, (2) Phillipsite from consolidated clay of nucleus in nodules, (3) Interlayered phillipsite from manganese encrust, (4) Phillipsite from pumice for nucleus in nodule.

distribution (Rinaldi *et al.*, 1974). More recently, Sheppard and Fitzpatrick (1989) was reported as a=9.985Å, b=14.155Å, c=8.684Å, β=124.96°, and V=1006.0Å³ of monoclinic unit-cell parameters.

In X-ray powder diffraction, an indexed powder pattern for phillipsites from manganese nodules are given in Table 2. There is an excellent agreement, and is similar to that published by Hay (1964), Galli, Loschi Ghittoni (1972), Gottardi, Galli (1985), and Passaglia, Vezzalini (1985). The unit-cell parameters, determined least-squares refinement program for phillipsites in Table 3 show the following ranges: a=9.976 to 10.024Å, b=14.097 to 14.143Å, c=8.672 to 8.703Å, β=124.09 to 124.59°, and V=1006.7 to 1019.2Å³ of monoclinic with P2₁/m of space group. Except for a significantly smaller b, these parameters are within the ranges reported for phillipsite from a variety of rocks and geologic environments. Galli, Loschi Ghittoni (1972) found a strong correlation between the Si/(Si+

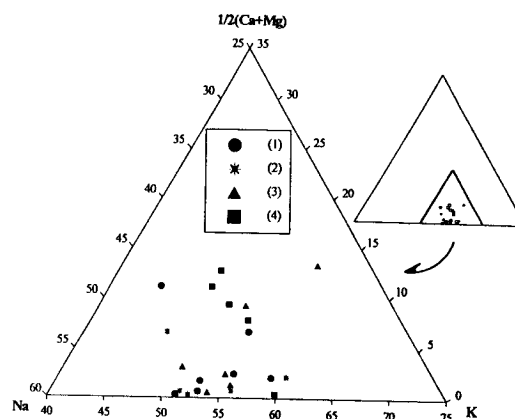


Fig. 5. Plotted ternary diagram of 1/2(Ca+Mg)-Na-K for phillipsites within manganese nodules. Full circle; stoichiometric phillipsite, Sample numbers are the same as in Table 1.

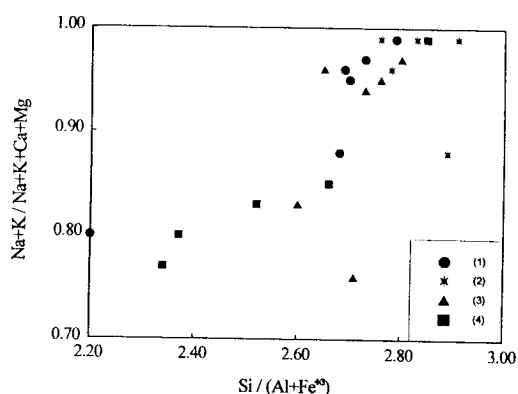


Fig. 6. Plotted diagram of (Na+K)/(Na+K+Ca+Mg) versus Si/(Al+Fe⁺³) showing the compositional range of phillipsites within manganese nodules. Full circle; stoichiometric phillipsite, Sample numbers are the same as in Table 1.

Al+Fe⁺³) ratio and cell parameters for the entire phillipsite group.

A decrease in b was accompanied by an increase in the Si/(Si+Al+Fe⁺³) ratio, and relationship was expressed by the following equation of b=14.879~0.938 (Si/(Si+Al+Fe⁺³)). If this equation is solved for the Si/(Si+Al+Fe⁺³) ratio using the measured b of Table 3, the calculated ratio is 0.78 to 0.83. This range, although slightly higher, matches well with the Si/(Si+Al+Fe⁺³) ratio obtained from the chemical analyses 0.70 to 0.74 (Table 1). Thus these values conform the applicability of the regression equation to the Si-rich members of the phillipsite group (Galli, Loschi Ghittoni, 1972). Although a chemical analysis

Table 2. X-ray powder diffraction data of phillipsite within manganese nodules.

(1)		(2)		(3)		(4)		<i>I/I_o</i>	<i>h k l</i>
<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)		
8.425	8.115	8.192	8.148	8.147	8.139	8.345	8.160	14	101,101-
7.173	7.145	7.149	7.158	7.161	7.181	7.208	7.198	100	001
6.454	6.378	6.417	6.383	6.483	6.403	6.511	6.414	12	011
5.386	5.304	5.373	5.351	5.405	5.382	5.418	5.377	19	120,121-
5.022	5.026	5.028	5.022	5.039	5.038	5.068	5.043	50	021,201
4.287	4.284	4.291	4.289	4.311	4.285	4.319	4.305	10	102-
4.134	4.129	4.108	4.103	4.145	4.163	4.144	4.162	40	111,112
3.934	3.952	4.082	3.946	4.081	3.982	4.044	3.975	14	221-
3.666	3.664	3.688	3.664	3.701	3.664	3.696	3.677	4	121,122-
3.250	3.249	3.205	3.239	3.255	3.252	3.267	3.250	41	140,301-
3.187	3.189	3.180	3.191	3.191	3.201	3.193	3.207	100	041,022
2.956	2.956	2.957	2.948	2.967	2.967	2.940	2.946	19	321-,322
2.747	2.753	2.744	2.745	2.747	2.746	2.755	2.755	20	141,142
2.677	2.676	2.700	2.678	2.699	2.677	2.700	2.710	28	150,223-
2.546	2.546	2.540	2.554	2.540	2.560	2.528	2.567	4	123
2.398	2.394	2.399	2.388	2.422	2.400	2.421	2.400	14	341-
1.835	1.834	1.820	1.830	1.810	1.841	1.854	1.859	7	242,521
1.778	1.779	1.776	1.775	1.798	1.789	1.787	1.787	12	440
1.727	1.727	1.722	1.722	1.727	1.727	1.727	1.727	8	543-,181-
1.667	1.667	1.672	1.663	1.680	1.670	1.680	1.681	14	034,205

Sample numbers are the same as in Table 1.

Table 3. Unit-cell parameters of phillipsite within manganese nodules.

	(1)	(2)	(3)	(4)
<i>a</i> (Å)	10.001	9.976	10.024	10.018
<i>b</i> (Å)	14.143	14.097	14.140	14.135
<i>c</i> (Å)	8.681	8.686	8.672	8.703
β (°)	124.60	124.50	124.10	124.21
<i>V</i> (Å ³)	1010.7	1006.7	1017.9	1019.2

Sample numbers are the same as in Table 1.

was not available for phillipsite from a silicic tuff in a saline, alkaline-lake deposits from Pleistocene Lake Tecopa, California (Sheppard, Fitzpatrick, 1989), the measured *b* (14.155Å) was much larger than any parameters given at Table 3. Applying the regression equation of Galli, Loschi Ghittoni (1972), a Si/(Si+Al+Fe⁺³) ratio was calculated as 0.76, suggesting that this lacustrine phillipsite is the most siliceous phillipsite to be reported.

Formation environments

Phillipsite can be formed rapidly from volcanic glass in saline and alkaline conditions (Hay, 1964; Sheppard, Fitzpatrick, 1989). The common association of phillipsite with volcanic glass, and its alteration products has led most workers to consider marine phillipsite to be derived from the breakdown

of submarine volcanic materials (Murray, Renard, 1891; Bonatti, Nayudu, 1965; Sheppard *et al.*, 1970). Petzing, Chester (1979) considered the precursor of phillipsite not to be submarine volcanic rocks but glass shards introduced into the ocean largely from terrestrial volcanoes. In some instances, phillipsite has been observed to continue growing within sediments after burial. Furthermore, Czycinski (1973) observed an increase in phillipsite concentration and siliceous organism dissolution with depth in some sediments suggesting that silica from organic remains can increase the depth of promote phillipsite formation.

Experimental studies (Hay, 1966) demonstrated that the formation of phillipsite is assisted by high silica activities, high alkali metal concentrations, and slightly alkaline pH. These factors are fulfilled by the leaching of volcanic glasses. Contact with sea and pore waters in underlying sediments probably is essential for the formation of phillipsite on the seafloor. Glaccum, Bostrom (1976) noted that the relatively high silica content of bottom waters appears to be controlled by dissolution of siliceous tests from plankton, as well as the decomposition of volcanic glass. Burns, Burns (1978b) also suggested that phillipsite is formed by a reaction involving pelagic clays, opaline biogenic silica, and seawater containing dissolved alkalic cations. This diagenetic reaction is consistent with our observations of the growth of authigenic phillipsite in nodules.

Most of the phillipsites have probably formed at temperatures less than 10°C. Fluid pressures in these minerals have commonly formed are less than 0.7 kb, judging from their depth of occurrence below adjacent sediment to water, and assuming maximum water depths of 5,000 m (Boles, 1981). The pH of ocean water is normally 8 (Park, 1966). Phillipsite in marine environments may prove that it can form in normal sea water, which has a pH of about 8. The characteristic association of phillipsite in palagonitic muds of the seafloor suggests, however, that hydrolysis of palagonitized glass to smectite may be essential in creating the marine environment in which phillipsite is formed. Elevation of the pH should be one of the principal effects of this hydrolysis (Hay, 1964).

These informations suggest that reaction kinetics are an important factor in controlling the presence of a given zeolite, and that a phase such as phillipsite forms metastably. Observations such as these are very important; they indicate that authigenic minerals do not just precipitate in the water column or form at the sediment-water interface, but may continue to grow from chemical reactions taking place within the sediments after burial. The phillipsite within manganese nodules probably formed already in this way, and it could be occurred highly crystallized during the nodules growth.

ACKNOWLEDGMENTS

This study was financially supported by KODOS-'94 programme funded of the Ministry of Trade, Industry, and Energy, Korea. We thank the staffs of Deep Seabed Exploration Programme of Korea Ocean Research and Development Institute (KORDI), Korea Mining Promotion Corporation (KMPC), Korea Institute of Geology, Mining and Materials (KIGAM), and captain and crews of R/V Onnuri for the technical assistance and help during cruises. The authors gratefully acknowledge Prof. J.H. Ahn (Chungbuk National University) for the critical review and fruitful comments of this manuscript.

REFERENCES

- Ahn, J.H. (1995) Electron-beam induced K diffusion in stilpnomelane during electronprobe microanalyzer analysis. *Jour. Miner. Soc. Kor.*, v. 8, p. 86-90.
- Ahn, J.H., Peacor, D.R. and Essene, E.J. (1986) Cation-diffusion-induced characteristic beam damage in transmission electron microscope images of micas. *Untramicroscopy*, v. 19, p. 375-382.
- Appleman, D.E. and Evans, H.T.Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. U.S. Dept. Commerce, NTIS Doc., PB-216158, 26p.
- Boles, J.R. (1981) Zeolites in deep-sea sediments. In: Mumpton, F.A. (ed.), *Mineralogy and geology of natural zeolites. Reviews in Mineralogy*, 4, 2nd ed., Mineral. Soc. Amer., p. 137-160.
- Bonatti, E. (1963) Zeolites in Pacific pelagic sediments. *Trans. New York, Acad. Sci.*, v. 25, p. 938-948.
- Bonatti, E. and Nayudu, Y.R. (1965) The origin of manganese nodules on the ocean floor. *Amer. Jour. Sci.*, v. 263, p. 17-39.
- Burns, V.M. and Burns, R.G. (1978a) Post-depositional metal enrichment processes inside manganese nodules from the north equatorial Pacific. *Earth Planet. Sci. Lett.*, v. 39, p. 341-348.
- Burns, V.M. and Burns, R.G. (1978b) Authigenic todorokite and phillipsite inside deep-sea manganese nodules. *Amer. Mineral.*, v. 63, p. 827-831.
- Chang, S.-W., Lee, S.-R. and Lee, C.H. (1994) Internal textures and mineralogy of manganese nodules from '92 and 93-KODOS (Korea Deep Ocean Study) area, Clarion-Clipperton fracture zones, NE equatorial Pacific. In: Lee, S.-R. and Lee, C.H. (eds.), *Proceedings of the '94 Deep-sea mineral resources. Korean working group of IGCP 318 Project: Genesis and Correlation of Marine Polymetallic Oxides*, Nov. 18, 1994, Taejon, Korea, p. 115-140.
- Cronan, D.S. (1980) *Underwater minerals*. Academic Press, London, p. 362.
- Czyscinski, K. (1973) Authigenic phillipsite formation rates in the central Indian ocean and the equatorial Pacific ocean. *Deep-sea Res.*, v. 20, p. 555-559.
- Galli, E. and Loschi Ghittoni, A.G. (1972) The crystal chemistry of phillipsite. *Amer. Mineral.*, v. 57, p. 1125-1145.
- Glaccum, R. and Bostrom, K. (1976) (Na,K)-phillipsite: its stability conditions and geochemical role in the deep sea. *Mar. Geol.*, v. 21, p. 47-58.
- Gottardi, G. and Galli, G. (1985) *Natural zeolites*. Springer-Verlag, New York, p. 409.
- Hay, R.L. (1964) Phillipsite of saline lakes and soils. *Amer. Mineral.*, v. 49, p. 1366-1387.
- Hay, R.L. (1966) Zeolites and zeolitic reaction in sedimentary rocks. *Geol. Soc. Amer. Spec. Pap.*, v. 85, p. 85.
- Kastner, M. (1979) Zeolites. In: Burns, R.G. (Ed.), *Marine minerals. Reviews in Mineralogy*, 6, Mineral. Soc. Amer., p. 111-122.
- Lee, C.H., Chang, S.-W., Lee, S.-R., Chang, J.H., Kang, J.S. and Kong, G.-S. (1994) Geochemical characteristics of manganese nodules from '92 and 93-KODOS (Korea Deep Ocean Study) area, Clarion-Clipperton fracture zones, NE equatorial Pacific. In: Lee, S.-R. and Lee, C.H. (eds.), *Proceedings of the '94 Deep-sea mineral resources. Korean working group of IGCP 318 Project: Genesis and Correlation of Marine Polymetallic Oxides*, Nov. 18, 1994, Taejon, Korea, p. 93-111.
- Lee, C.H., Chang, S.-W., Lee, S.-R., Kong, G.-S., Kang, J.S. and Chang, J.H. (1995) Morphological classification of the manganese nodules from the Clarion-Clipperton fracture zones, Pacific. *Jour. Geol., Soc. Kor.*, v. 31, p. 560-565.
- Lee, C.H., Lee, S.-R., and Chang, S.-W. (1996) Internal texture,

- geochemistry and mineralogy of manganese nodules from the Clarion-Clipperton fracture zones, *Pacific. Jour. Geol., Soc. Kor.*, v. 32, p. 187-198.
- Murray, J. and Renard, A.F. (1891) Report on deep-sea deposits. Report on the Scientific Results of the Voyage of H.M.S. Challenger During the Years 1873-1876, Neil and Co., Edinburgh, 520p.
- Park, K. (1966) Deep-sea pH. *Science*, v. 154, p. 1541-1542.
- Passaglia, E. and Vezzalini, G. (1985) Crystal chemistry of diagenetic zeolites in volcanoclastic deposits of Italy. *Contrib. Mineral. Petrol.*, v. 90, p. 190-198.
- Petzing, J. and Chester, R. (1979) Authigenic marine zeolites and their relationship to global volcanism. *Mar. Geol.*, v. 29, p. 253-271.
- Rinaldi, R., Pluth, J.J. and Smith, J.V. (1974) Zeolites of the phillipsite family. Refinement of the crystal structures of phillipsite and harmotome. *Acta Crystall.*, v. 30, p. 2426-2433.
- Sadanaga, R., Marumo, F. and Takeuchi, Y. (1961) The crystal structure of harmotome, $Ba_2Al_4Si_{12}O_{32} \cdot 12H_2O$. *Acta Crystall.*, v. 14, p. 1153.
- Sheppard, R.A. and Fitzpatrick, J.J. (1989) Phillipsite from silicic tuffs in saline, alkaline-lake deposits. *Clays and Clay Minerals*, v. 37, p.243-247.
- Sheppard, R.A., Gude, A.J. 3rd., and Griffin, J.J. (1970) Chemical composition and physical properties of phillipsite from the Pacific and Indian Oceans. *Amer. Mineral.*, v. 55, p. 2053-2062.
- Steinfink, H. (1962) The crystal structure of the zeolite, phillipsite. *Acta Crystall.*, v. 15, p. 644-651.
- Stonecipher, S.A. (1976) Origin, distribution and diagenesis of phillipsite and clinoptilolite in deep-sea sediment. *Chem. Geol.*, v. 17, p. 307-318.
- Van der Fluijm, B., Lee, J.H. and Peacor, D.R. (1988) Analytical electron microscopy and the problem of potassium diffusion. *Clays and Clay Miner.*, v. 36, p. 2199-2202.

Manuscript received 17 May 1996

적도 북동 태평양, 클라리온-클리퍼튼 균열대에서 산출되는 망간단괴내의 자생 필립사이트

이찬희 · 이성록

요 약: 망간단괴내에 자생하는 필립사이트는 단괴의 핵을 이루는 풍화된 화산암편과 고화된 해저퇴적물 또는 단괴를 이루는 망간광물들의 층간에서 산출된다. 이 광물은 주로 화산성 유리질 석기들의 가상조직을 보이고 있으며, 연한 노란색을 갖는 등립질의 판상으로 산출된다. 필립사이트 입자들은 자형의 삼각형, 사각기둥 또는 도변상을 가지며 크기는 길이 2~20 μm , 두께 2~5 μm 정도이다. 이 광물의 화학조성은 $(Ca_{0.1}Mg_{0.3}Na_{1.1}K_{1.5})_3(Fe_{0.3}Al_{4.2}Si_{11.8})O_{32} \cdot 10H_2O$ 이며, $Si/(Al+Fe^{+3})=2.37-2.78$, $Na/K=0.59-0.81$ 로서 Si와 알카리의 함량이 아주 높다. 결정구조는 단사정계($P2_1/m$) 속하며 $a=10.005\text{\AA}$, $b=14.129\text{\AA}$, $c=8.686\text{\AA}$, $\beta=124.35^\circ$ 이고 $V=1013.6\text{\AA}^3$ 이다. 심해저 환경으로 보아 망간단괴에서 산출되는 필립사이트는 보통 10°C 이하의 온도, 0.7 kb 정도의 압력, pH 8 정도의 조건에서 자생하는 것으로 추정된다.