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CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF PHILLIPSITE FROM THE PACIFIC AND INDIAN OCEANS[1]

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ABSTRACT

Twelve new chemical analyses of deep-sea phillipsite show that this zeolite is alkalic and has a Si/Al ratio of 2.44–2.79. Potassium is generally in excess of sodium. The BaO content is 0.00–0.73 weight percent. The mean index of refraction for the analyzed phillipsites is 1.477–1.486, and an increase in the index can be correlated with an increase in the BaO content and a decrease in the Na_2O content. Cell parameters for the analyzed phillipsites show the following ranges: $a=9.92$–10.06 Å, $b=14.11$–14.20 Å, $c=14.18$–14.32 Å, and $V=1{,}994$–$2{,}027$ Å^3.

INTRODUCTION

Phillipsite was first recognized in deposits on the Pacific Ocean floor by Murray and Renard in 1891. Since then, this zeolite has become a commonly reported constituent of deep-sea sediments. Large areas of the Pacific Ocean floor are covered with sediments that contain concentrations of phillipsite that are locally in excess of 50 percent (Bonatti, 1963; Goldberg, 1963). Three chemical analyses given by Murray and Renard (1891) showed that deep-sea phillipsites are alkalic and relatively siliceous as compared with phillipsites from mafic igenous rocks. These chemical characteristics were supported by two more recent analyses (Goldberg, 1961; Rex, 1967).

In the present study we give 12 new chemical analyses of deep-sea phillipsites. The chemical compositions of these marine phillipsites are compared with the compositions of phillipsites from other geologic environments. We also attempted to correlate variations in the indices of refraction and cell dimensions of the deep-sea phillipsites with variations in their chemical compositions.

The phillipsites were separated from cored and dredge-haul samples taken by Scripps Institution of Oceanography from widely scattered localities in the Pacific and Indian Oceans (Table 1). The original core samples contained 25 percent or less phillipsite, whereas the dredge-haul samples contained about 50 percent phillipsite. In addition to phillipsite, the original samples consisted of clay minerals (chiefly montmorillonite), hydrous iron-manganese oxides, quartz, plagioclase,

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clinopyroxene, anatase, rutile, zircon, and siliceous and phosphatic debris of organic origin. Relatively pure concentrates of the phillipsites were made utilizing a heavy liquid mixture of tetrabromoethane and n,n-dimethylformamide.

CHEMICAL COMPOSITION

The phillipsite concentrates weighed only 0.5 gram or less, so the classical analytical techniques for silicate minerals could not be used. The H_2O content was determined by weight loss after heating at 1,000°C for 30 minutes. Inasmuch as the samples did not contain a carbonate mineral, the weight loss represents the H_2O content of the zeolites. Contents of the other constituents were then determined on the anhydrous residues. SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, and BaO were determined by X-ray fluorescence. The Na_2O and MgO contents were determined by atomic absorption because these constituents could not be determined accurately with the X-ray fluorescence equipment at hand. In order to recast the analyses (Table 2) to a hydrous base and correct for Fe_2O_3 impurities, the following calculations were necessary: (1) the determined H_2O content of each analysis was assumed to be correct, and the other constituents were prorated to 100 percent minus the H_2O content; (2) all Fe_2O_3 was assumed to be an impurity and was subtracted; (3) the analyses were then recalculated to 100 percent and are given in Table 3. The molecular ratio $Al_2O_3/(Ca, Mg, Ba, Na_2, K_2)O$ for zeolites should be unity. This ratio is 0.96–1.10 for the corrected analyses of deep-sea phillipsites. Most of the phillipsites that have a ratio greater

TABLE 1. LOCATION AND LITHOLOGY OF SAMPLES FROM WHICH ANALYZED PHILLIPSITES WERE SEPARATED[a]

Sample No.	Core or dredge haul No.	Location	Water depth (in meters)	Sample position within core (in centimeters from top)	Lithology
1	JYN V-8G	13°26′ N., 152°17′ W.	5746	15–25	Light-brown clay
2	JYN V-8G	13°26′ N., 152°17′ W.	5746	15–25	Light-brown clay
5	Proa 171G	16°43′ N., 165°10′ W.	5556	10–15	Light-brown clay
9	Ris 80G	14°02′ S., 134°55′ W.	4250	70–80	Dark-brown clay
10	Ris 80G	14°02′ S., 134°55′ W.	4250	70–80	Dark-brown clay
11	Ris 79G	14°03′ S., 131°44′ W.	4110	40–45	Dark-brown clay
14	Dodo 113D	23°16′ S., 74°59′ E.	4520	—	Manganese-coated boulder
15	Proa 11	6°08′ N., 136°11′ E.	4600	Unknown	Light-brown silty clay
17	Dodo 232D	5°23′ S., 97°29′ E.	4119	—	Manganese-coated boulder
18	Amph 48PG	13°58′ S., 161°03′ W.	4510	20–25	Light-brown and red clay
21	JYN V-49PG	17°10′ N., 132°50′ W.	5188	30–45	Dark-brown clay
22	Dodo 113D	23°16′ S., 74°59′ E.	4520	—	Manganese-coated boulder

[a] Sample Nos. 14, 17, and 22 are from dredge hauls; all others are from cores.

TABLE 2. CHEMICAL ANALYSES OF DEEP-SEA PHILLIPSITES[a]

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	BaO	Na_2O	K_2O	Total (anhydrous)	H_2O
1	60.4	19.2	1.90	0.70	0.56	0.09	4.71	7.68	95.24	14.4
2	60.2	18.7	2.26	.86	.60	.08	4.50	7.42	94.62	13.9
5	63.0	19.2	1.80	.75	1.65	.13	3.35	7.61	97.49	15.3
9	58.9	19.1	2.42	.33	1.31	.12	4.20	8.22	94.60	15.5
10	56.6	19.2	3.58	.34	1.28	.11	4.08	7.98	93.17	14.9
11	59.4	19.3	3.60	.22	2.47	.24	3.02	7.55	95.80	15.1
14	62.1	21.6	.48	.09	.12	.00	6.58	8.71	99.68	16.8
15	63.2	20.7	.04	.02	.02	.00	6.55	8.57	99.10	15.3
17	59.7	20.3	2.04	.63	.90	.08	6.05	7.33	97.03	16.1
18	58.9	20.2	2.95	.36	6.10	.78	1.26	5.41	95.96	17.1
21	60.8	18.9	4.73	1.40	1.08	.80	2.30	6.75	96.76	15.0
22	59.4	20.4	1.90	.76	1.11	.31	4.82	7.41	96.11	14.3

[a] H_2O determined by J. S. Wahlberg by weight loss at 1,000°C. SiO_2, Al_2O_3, Fe_2O_3, CaO, BaO, and K_2O determined by J. S. Wahlberg by X-ray fluorescence on anhydrous residues. Na_2O and MgO determined by Wayne Mountjoy by atomic absorption on anhydrous residues.

than unity have a ratio of 1.03 or less. Inasmuch as only two phillipsites have a ratio less than unity, substitution of ferric iron for aluminum seems unlikely in these zeolites. The assumption that the analyzed Fe_2O_3 is an impurity is justified.

Unit cell contents (Table 4) were calculated from the corrected analyses in Table 3 on the basis of 32 oxygen atoms. The Si/Al ratio

TABLE 3. CORRECTED CHEMICAL COMPOSITIONS OF DEEP-SEA PHILLIPSITES[a]

Sample	SiO_2	Al_2O_3	MgO	CaO	BaO	Na_2O	K_2O	H_2O	Total
1	55.23	17.57	0.64	0.51	0.08	4.30	7.02	14.65	100.00
2	55.92	17.38	.80	.56	.07	4.19	6.89	14.19	100.00
5	55.60	16.95	.67	1.46	.11	2.96	6.71	15.54	100.00
9	53.78	17.44	.31	1.20	.10	3.83	7.50	15.84	100.00
10	53.46	18.13	.32	1.21	.10	3.84	7.54	15.40	100.00
11	54.38	17.66	.21	2.26	.22	2.76	6.91	15.60	100.00
14	52.05	18.09	.08	.10	.00	5.51	7.30	16.87	100.00
15	54.03	17.70	.02	.02	.00	5.60	7.33	15.30	100.00
17	52.54	17.87	.56	.79	.07	5.33	6.45	16.39	100.00
18	52.22	17.90	.32	5.41	.70	1.11	4.79	17.55	100.00
21	55.72	17.33	1.28	.99	.73	2.11	6.19	15.65	100.00
22	53.89	18.50	.69	1.01	.27	4.37	6.72	14.55	100.00

[a] Analyses from Table 2 were recast to a hydrous base, Fe_2O_3 was subtracted, and then the analyses were recalculated to 100 percent.

TABLE 4. UNIT CELL CONTENTS FOR DEEP-SEA PHILLIPSITES[a]

Sample	Si	Al	Mg	Ca	Ba	Na	K	H_2O	Si/Al	Si+Al
1	11.65	4.37	0.20	0.12	0.01	1.76	1.89	10.31	2.67	16.02
2	11.71	4.29	.25	.12	.01	1.70	1.84	9.91	2.73	16.00
5	11.79	4.23	.21	.33	.01	1.22	1.81	10.99	2.79	16.02
9	11.58	4.42	.10	.28	.01	1.60	2.06	11.37	2.62	16.00
10	11.46	4.58	.10	.28	.01	1.60	2.06	11.01	2.50	16.04
11	11.61	4.44	.07	.52	.02	1.14	1.88	11.11	2.61	16.05
14	11.38	4.66	.03	.02	.00	2.34	2.04	12.31	2.44	16.04
15	11.56	4.46	.01	.01	.00	2.32	2.00	10.92	2.59	16.02
17	11.39	4.56	.18	.18	.01	2.24	1.78	11.85	2.50	15.95
18	11.38	4.60	.10	1.26	.06	.47	1.33	12.76	2.47	15.98
21	11.78	4.32	.40	.22	.06	.86	1.67	11.04	2.73	16.10
22	11.40	4.61	.22	.23	.02	1.79	1.81	10.27	2.47	16.01

[a] Calculated in atoms per unit cell on the basis of O=32.

ranges from 2.44 to 2.79. Monovalent cations are in excess of divalent ones; the sum of the divalent cations is generally less than 0.5 atom per unit cell. Potassium is generally in excess of sodium.

The compositions of deep-sea phillipsites and phillipsites from other geologic environments are represented in Figure 1. Although there is slight overlap, the phillipsites can be classed into three groups on the basis of Si/Al ratios. The least siliceous group is from mafic igneous rocks and is characterized by a Si/Al ratio of about 1.3–2.4. Phillipsites of this group commonly have a higher percentage of alkaline earths than those of the other two groups; some specimens have alkaline earths in excess of alkalis. The most siliceous group has a Si/Al ratio of about 2.6–3.4, although most have a Si/Al ratio greater than 3.0. These siliceous phillipsites are from silicic tuffs in saline lacustrine deposits and are characteristically very high in alkalis. The deep-sea phillipsites comprise an intermediate group and have a Si/Al ratio of about 2.3–2.8. Like the lacustrine phillipsites, these deep-sea phillipsites are rich in alkalis; however, the two groups differ in the predominant alkali. All reported lacustrine phillipsites show sodium in excess of potassium (Hay, 1964; Sheppard and Gude, 1968), but deep-sea phillipsites commonly have potassium in excess of sodium.

Although barium-rich phillipsite or harmotome (a barium zeolite) has been reported as being widespread in the sea-floor deposits (Arrhenius, 1963, p. 698–701), the analyzed samples of this study are not particularly rich in barium. The BaO Content of the 12 analyzed samples (Table 3) ranges from 0.00 to 0.73 weight percent; however, most of the analyzed phillipsites have a BaO content of less than 0.3 percent

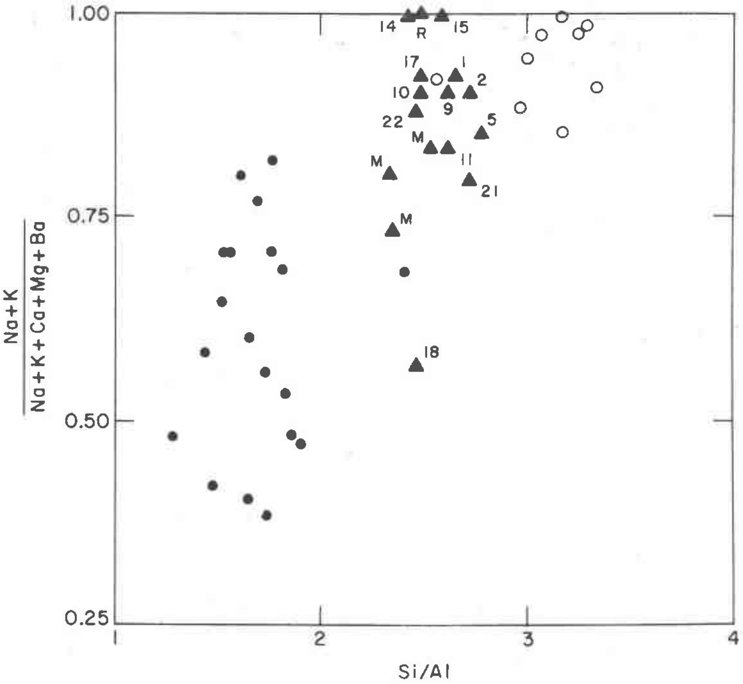

FIG. 1. Plot showing the compositional variation of phillipsite. Open circle, phillipsite from saline lacustrine deposits; solid triangle, phillipsite from deep-sea deposits; solid dot, phillipsite from mafic igneous rocks. Numbered triangles are the analyses listed in Tables 3 and 4. Sources for analyses represented by lettered triangles are: M. Murray and Renard (1891) and R, Rex (1967).

PHYSICAL PROPERTIES

Phillipsites from the deep-sea sediments occur as elongated, prismatic crystals that are chiefly subhedral to euhedral (Fig. 2). Individual crystals range in length from less than 8 μm to about 250 μm; most, however, are 10–120 μm long. When viewed under crossed nicols, the "individual crystals" are shown to have a complex sector twinning that simulates single crystal forms. Cruciform twinning is relatively rare. The analyzed phillipsites are colorless to yellowish brown, depending on the abundance of minute isotropic inclusions. Inasmuch as the value (lightness) of the color can be correlated with the Fe_2O_3 content shown in Table 2, the inclusions are probably amorphous iron oxides. Large phillipsites commonly show a zonal distribution of the inclusions.

Index of Refraction. The mean index of refraction of the analyzed deep-sea phillipsites has a relatively narrow range, 1.477–1.486 ± 0.001 (Table 5), and the birefringence is low, about 0.002. Phillipsite from

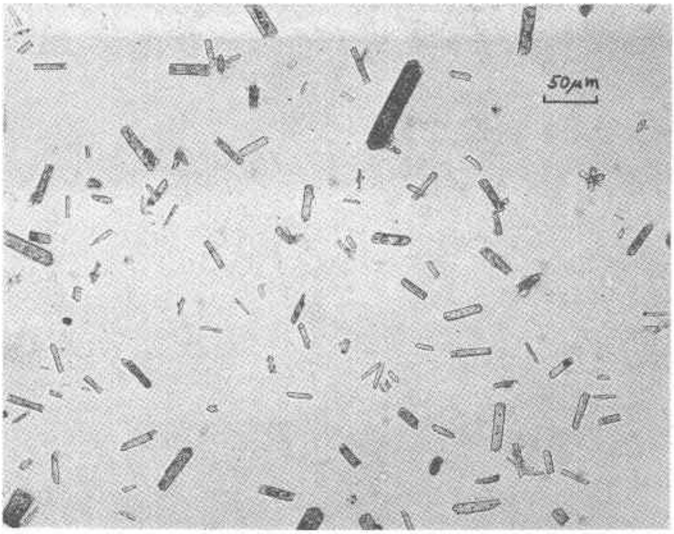

FIG. 2. Photomicrograph of a typical concentrate of prismatic phillipsite from core No. Ris 80G (sample No. 10). Unpolarized light.

various rock types and geologic environments show a range in the mean index of refraction of about 1.44–1.51. Hay (1964) found that the index of refraction of natural phillipsites decreases with an increase in the Si/Al ratio. Phillipsites with Si/Al ratios less than 2 commonly have indices of 1.48–1.51, whereas phillipsites with Si/Al ratios of 3 or greater have indices of 1.44–1.48. Thus, the deep-sea phillipsites fit this general

TABLE 5. MEAN INDEX OF REFRACTION AND CELL PARAMETERS FOR DEEP-SEA PHILLIPSITE

Sample No.	Mean index of refraction (±0.001)	*a* (Å)	*b* (Å)	*c* (Å)	$\overline{V}$ (Å^3)
1	1.482	10.003(2)	14.156(3)	14.260(2)	2019.4(5)
2	1.481	9.962(2)	14.169(2)	14.243(2)	2010.3(4)
5	1.485	9.928(6)	14.141(20)	14.221(6)	1996.6(26)
9	1.483	9.975(16)	14.182(19)	14.274(29)	2019.4(41)
10	1.484	9.981(6)	14.175(10)	14.198(6)	2008.7(13)
11	1.486	9.960(7)	14.133(10)	14.208(5)	1999.9(16)
14	1.477	9.974(6)	14.174(8)	14.307(17)	2.22.6(23)
15	1.478	9.970(14)	14.165(12)	14.264(9)	2014.4(30)
17	1.480	9.980(6)	14.161(6)	14.248(4)	2013.6(12)
18	1.485	10.005(3)	14.182(4)	14.282(4)	2026.7(7)
21	1.486	9.946(4)	14.125(8)	14.260(6)	2003.3(9)
22	1.483	9.974(4)	14.124(18)	14.290(4)	2013.3(23)

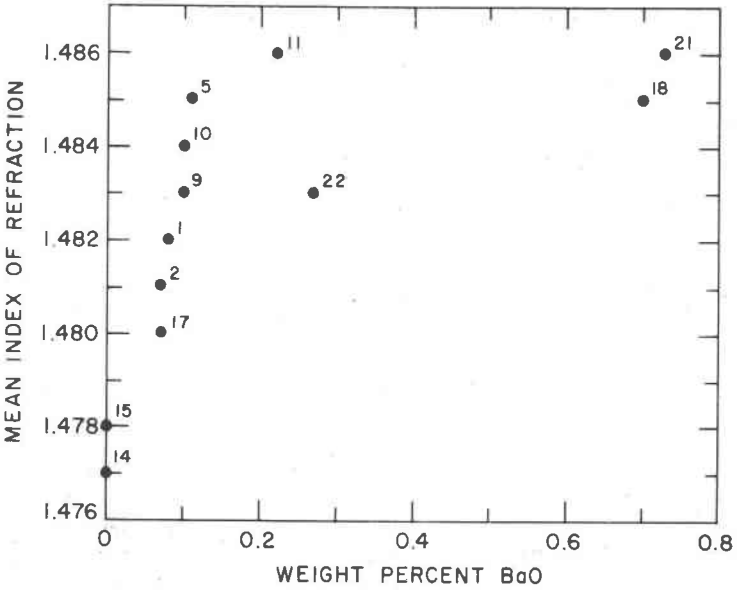

FIG. 3. Variation in the mean index of refraction versus the BaO content for deep-sea phillipsite. Numbers indicate samples listed in Tables 3 and 5.

pattern inasmuch as they have intermediate Si/Al ratios and intermediate indices of refraction.

An attempt was made, without success, to correlate the mean indices of refraction with the Si/Al ratios of the deep-sea phillipsites. However, the indices seem to be affected by the barium and sodium contents. A plot (Fig. 3) of mean index of refraction versus weight percent BaO suggests that an increase in the barium content can be correlated with an increase in the index of refraction. The effect seems most pronounced for BaO contents less than 0.2 percent. BaO contents greater than 0.2 percent seem to cause only a slight additional increase in the index. Figure 4 is a plot of the mean index of refraction versus weight percent Na_2O and suggests that an increase in Na_2O content correlates with a decrease in the index of refraction.

Cell Parameters. Cell dimensions and volume for the analyzed deep-sea phillipsites (Table 5) were obtained by a least-squares refinement of X-ray powder diffractometer data utilizing the U.S. Geological Survey's FORTRAN IV Computer Program W9214. The space group and initial orthorhombic cell parameters used were those of Steinfink (1962). Cell parameters for the analyzed phillipsites show the following ranges: $a=9.92$–10.06 Å, $b=14.11$–14.20 Å, $c=14.18$–14.32 Å, and $V=1994$–2027 Å^3.

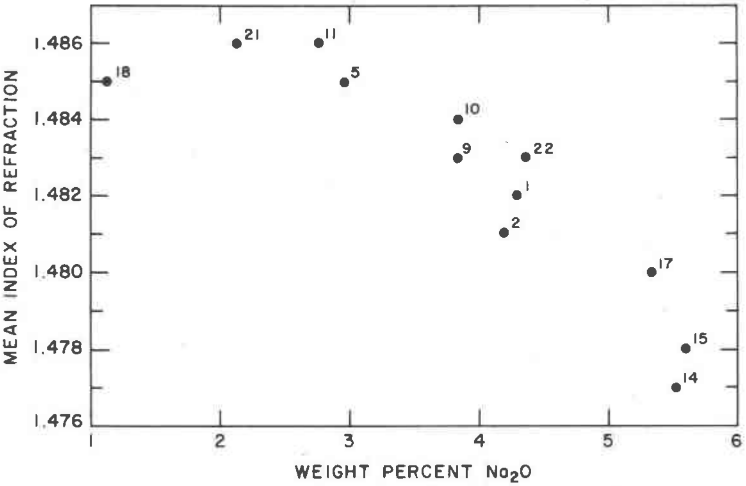

FIG. 4. Variation in the mean index of refraction versus the Na_2O content for deep-sea phillipsite. Numbers indicate samples listed in Tables 3 and 5.

There seems to be no correlation between the compositions of the deep-sea phillipsites and their cell parameters. Furthermore, alkalic phillipsites with Si/Al ratios of 3.2–3.3 (Toribio Manzaneres, Jr., oral commun., 1970) and a calcic phillipsite with a Si/Al ratio of 1.7 (Iijima and Harada, 1969) have about the same cell parameters as the deep-sea phillipsites. These data suggest that variations in chemical composition have slight or no effect on the cell parameters of natural phillipsite.

DISCUSSION

Phillipsite in the deep-sea deposits probably formed during diagenesis by the alteration of volcanic debris (Murray and Renard, 1891; Bonatti, 1963). Although basaltic glass was probably the ultimate precursor for the phillipsite, palagonite may have been an intermediate alteration product. The composition of the parent material is known to affect the composition of the zeolite (Mumpton, 1960). Thus, the difference in Si/Al ratios between authigenic phillipsite of deep-sea deposits and authigenic phillipsite of lacustrine deposits can be attributed to the difference in the composition of the parent materials. Most authigenic phillipsites in lacustrine deposits formed from silicic glass, chiefly of rhyolitic compsotion. These phillipsites have higher Si/Al ratios than the deep-sea phillipsites which are of basaltic parentage.

Phillipsites in both deep-sea and lacustrine deposits are alkalic, but the deep-sea phillipsites are generally more potassic than the lacustrine ones. Rhyolitic glass has a Na/K ratio of about 0.5, whereas basaltic glass (Moore, 1966; Hay and Iijima, 1968) has a Na/K ratio of about 2–3. Palagonite, however, has a Na/K ratio of about 0.3 (Moore, 1966). If phillipsite in the deep-sea deposits formed from palagonite, as Bonatti (1963) has suggested, its potassic character could have been inherited from the relatively potassic palagonite. The Na/K ratio of the fluid phase from which phillipsite crystallized should also influence the cation content of the phillipsite. Most of the phillipsites in lacustrine deposits formed in sodium carbonate-bicarbonate waters. These waters generally have a Na/K ratio greater than 30 (Hay, 1964 p. 1381). Sea water has a Na/K ratio of about 28 (Culkin, 1965), but interstitial water squeezed from modern oceanic sediments is more potassic and has an average Na/K ratio of about 20 (Siever *et al.*, 1965). Thus, there also seems to be a correlation between the sodic lacustrine phillipsites and relatively sodic waters and between the potassic marine phillipsites and relatively potassic waters.

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