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THE CRYSTAL CHEMISTRY OF PHILLIPSITES

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ABSTRACT

Chemical analyses and crystallographic and physical data have been obtained for 22 samples of phillipsite. Samples were carefully selected so as to cover a wide range of chemical composition and similar data for 10 samples were taken from literature.

Si in tetrahedra varies from 57% to 74%; potassium is always present, whereas sodium and calcium may be abundant, but are sometimes very scarce. Cell parameters show the following ranges: $a = 9.871–10.007$, $b = 14.155–14.340$, $c = 14.207–14.415$ Å, and $\beta = 90°$. From correlation of these data a regression equation emerges which links chemical variables to cell parameters: an increase of aluminium percentage in tetrahedra has a positive correlation with b and c, but no influence on a, which in turn is the only cell parameter correlated to the content of exchangeable cations. The indices of refraction for 25 samples show the following ranges: $\alpha = 1.483–1.5052$, $\beta = 1.485–1.5106$, and $\gamma = 1.487–1.5132$. The mean index of refraction for all the phillipsites analyzed is 1.477–1.5094, and an increase in the index can be correlated with a decrease in both the $Si/(Si + Al + Fe^{3+})$ ratio and the monovalent/total exchangeable cations ratio.

INTRODUCTION

The zeolite "phillipsite" is very common both in sedimentary rocks and in fissures and cavities of magmatic rocks (mainly in basalts). The name was proposed for a mineral of Aci Castello, Sicily, by Lévy (1825) in honor of W. Phillips, the English mineralogist. For barian phillipsite the name "wellsite" (Pratt and Foote, 1897) is currently used.

There are many chemical analyses of phillipsite in the literature, but some are unreliable (see Fig. 1). Oddly enough, for such a common mineral, the occasions on which the cell parameters have been determined with confidence are few. Recently Sheppard *et al.* (1970) gave a new set of measurements on 12 phillipsites from deep–sea deposits, along with their chemical analyses; their research greatly enriches the conclusions that may be drawn from this paper.

The aims of this paper are to establish, for these minerals, the range of chemical variation and the correlation between their chemical formula and cell parameters. One of us (E.G.) was responsible for sample collection, X–ray diffraction work, density and optical measurements, and data processing; the other (A.G.L.G.) was responsible for the chemical analyses.

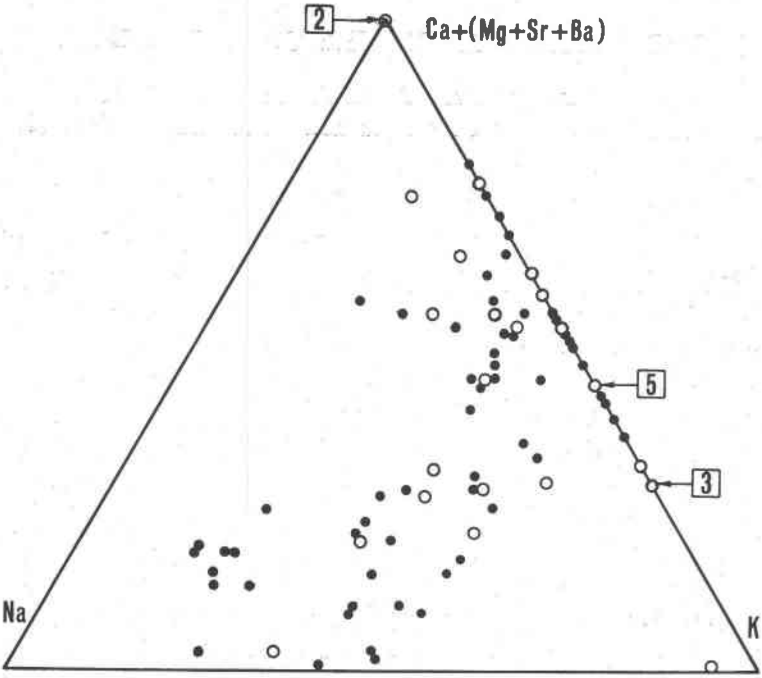

FIG. 1. Distribution of exchangeable cations reported in the literature, except those shown in Figure 2. Solid circles = analyses with a balance error of less than 10%; hollow circles = analyses with a balance error of more than 10%. The figure joined by an arrow to a circle indicates the number of analyses which overlap at that point. Sources of chemical analyses (the number in square brackets preceding the author's name indicates the number of chemical analyses taken from that literature source): [1] Barbieri and Penta (1969); [1] Billows (1920); [1] Caglioti (1927); [4] Des Cloizeaux (1862); [2] Di Franco (1942); [29] Doelter (1921); [1] Dunham (1933); [4] Hay (1964); [7] Hintze (1897); [1] Hoss and Roy (1960); [1] Iijima and Harada (1969); [1] Koch (1956); [2] Lacroix (1896); [1] Lacroix (1910); [1] Morbidelli (1964); [2] Pécsi-Donáth and Shimo (1966); [1] Regis and Sand (1966); [1] Rex (1967); [1] Sahama (1962); [2] Sheppard and Gude (1968); [1] Sheppard and Gude (1969); [5] Sheppard *et al.* (1970); [3] Shkabara (1950); [2] Tosto (1948); [1] Walker (1962); [8] Zambonini (1902); [3] Zambonini (1935).

ANALYSIS OF EXISTING DATA

An examination of all available chemical analyses of phillipsites enabled us to draw the triangular plot of Figure 1; each analysis was recalculated as a chemical formula with 32 oxygens along with its balance error (see Passaglia, 1970). For each formula atomic coefficients of exchangeable cations were multiplied by a suitable factor so as to make their sum equal to 100; they could then be inserted into the triangular plot, the small quantities of Mg, Sr, and Ba were added to Ca. From examination of Figure 1 it may be deduced that most phillipsites lie on a line joining the midpoints of sides Na—K and Ca—K, and thus the following observations may be made:

1) one–cation phillipsites have not yet been found;
2) phillipsites always contain a considerable amount of potassium;
3) many phillipsites are virtually lacking in sodium and many others in calcium; and
4) the most abundant cations in phillipsites are Na, K, or Ca.

EXPERIMENTAL AND METHOD OF CALCULATING CELL PARAMETERS

The new samples studied are listed in Table 1. Table 2 contains existing data (sometimes reprocessed by computer) also used in this research.

Chemical analyses were performed as follows: SiO_2 and H_2O gravimetrically, Al_2O_3 by complexometric titration; Na, K, Mg, Ca, Sr, and Ba by atomic absorption spectrometry using a Perkin-Elmer 303.

Density was measured using a torsion microbalance and toluene, according to Berman (1939), with fragments weighing about 80 mg.

Indices of refraction were measured on the U–stage by the Emmons double variation method.

Powder tracings were recorded on a Philips diffractometer (1/4° per min), using a lead nitrate internal standard. Obtaining cell parameters from the powder data of phillipsite is an especially difficult task owing to its pseudosymmetry (see Černý, 1964); the monoclinic mineral is geometrically orthorhombic, ($\beta = 90° \pm 01'$) with $b \simeq c$, the difference often being less than 0.05Å. This finding is based on the measurements performed on single crystals quoted in the literature (Steinfink, 1962) and on 3 measurements performed on sample Nos. 6, 11, and 12 using precession photographs. Thus, many peaks are really unresolved doublets, and for many doublets two indexings are possible. Current least–square procedures with fixed indexing are unsuitable, and programs with re–indexing after each least–square cycle can also give questionable results. We chose the following procedure:

1) first approximate determination of cell parameters from few ($\simeq$ 12) powder lines;
2) generation of all d_{hkl}(calc);
3) indexing of the whole tracing taking into account the diffraction intensities of phillipsite as listed by Steinfink (1962); and
4) least square refinement of cell parameters using the indexing obtained in step 3.

Often steps 2, 3, and 4 were repeated.

RESULTS AND THEIR VARIABILITY

We found only 10 descriptions for phillipsite in the literature having "reliable" analyses (*i.e.*, with the balance error $E < 10\%$) and precise cell constants. Their analyses are listed in Table 3 with the 22 analyses performed by us. All data were processed to get atomic coefficients and

TABLE 1. LIST OF SAMPLES

No.	Locality of occurrence	Habit and paragenesis	Reference,if any
1	Acquacetosa(Roma,Italy).Abandoned quarry of "Casale San Sisto", near km 8.5 on Via Laurentina	Spherical radial aggregates(about 5 mm across)of vitreous twins with milky white chabazite and calcite, on leucitite	Caglioti(1927)
2	Capo di Bove(Roma,Italy)	Leucitite covered by a crust built up by vitreous twins; it is possible to detach good single crystals	Hintze(1897)
3	Casal Brunori(Roma,Italy).Quarry near km 4.5 on Via Pontina	As for No. 1	Zambonini(1902)
4	Civitella San Paolo(Roma,Italy)	As for No. 1 but with sharp scalenoedra of calcite	
5	Vallerano(Roma,Italy).Quarry of Via Laurentina	As for No. 1	Zambonini(1902)
6	Aci Castello(Sicilia,Italy)	Radial aggregates of vitreous twins; in cavities of the basalt	Di Franco(1901) Tosto(1948)
7	Cliffs facing the Rupe of Aci Castello(Sicilia,Italy)	Radial aggregates,crusts or vitreous twins in cavities of basalt; with natrolite and chabazite	Di Franco(1901) Tosto(1948)
8	Biggest "Faraglione" facing Acitrezza(Sicilia,Italy)	Radial aggregates or crusts in basalt; often with chabazite and natrolite	
9	Palagonia(Sicilia,Italy)	Large white twins about 1 cm across; in basalt	Di Franco(1901) Tosto(1948)
10	Poggio Rufo near Palagonia (Sicilia,Italy)	Spherical radial aggregates(about 3 mm across)of vitreous twins;with analcime, chabazite, and montmorillonite in basalt	
11	Pian di Celle(S.Venanzo,Perugia, Italy).Quarry of"Podere Pantano"	Crust coating and filling the cavities of "venanzite"	Morbidelli(1964)
12	M.Lungo near Montegalda(Monti Berici,Vicenza,Italy)	Small single crystals,milky or yellowish, in weathered pyroclastic breccia	Alietti and Galli(1965)
13	M.Calvarina(Verona,Italy). Near km 5 of Roncà-M.Calvarina road	Aggregates and single crystals in basalt; with calcedony,chabazite,analcime,albite	
14	Mont Semiol(Loire,France)	Aggregates(sometimes radial)of vitreous twins; with calcedony in basalt	
15	Perrier(Puy-de-Dôme,France)	Aggregates or crusts covering or completely filling the cavities in the basalt	Hintze(1897)
16	Vinařická hill near Kladno (Bohemia,Czechoslovakia)	Crust built up of milky radial aggregates of twins covering the basalt;with fine rhombohedra of calcite	Antonin(1942)
17	Zálésly near Ústí nad Labem (Bohemia,Czechoslovakia)	Aggregates of vitreous twins filling veins and cavities of the basalt	
18	Lubań(=Lauban),Poland.(Germany before second world war)	Aggregates of vitreous twins covering the surface of cavities in the basalt	Hintze(1897)
19	Limbacher Kopf near Asbach (Westerwald,Germany)	Crust of vitreous twins covering the surface of a large geode in the basalt;with a fine cluster of yellow natrolite	Hintze(1897)
20	Tellerhäuser near Schwarzenberg (Sachsen,Germany)	Crust of vitreous twins filling the veins and covering a free surface of the basalt	
21	Richmond near Melbourne (Victoria,Australia)	Single vitreous twins on a free surface of the basalt	Hintze(1897)
22	Moiliili quarry,Honolulu(Hawaii)	Crust of vitreous twins in the cavities of the nepheline-melilite-basalt	Dunham(1933)

TABLE 2. DATA FROM LITERATURE USED IN THIS RESEARCH (IN SOME CASES AFTER COMPUTER-PROCESSING)

Reference	Occurrence of phillipsite samples herein described	Code	Kind of data
Harada et al.(1967)	In a basalt of Mazé (Niigata Pref., Japan)	HIK	Chem.analysis, X-ray powder data, indices of refraction, density
Sheppard et al.(1970)	In the sediments of the Pacific and Indian Oceans	SG[a]	Chem.analyses, X-ray powder data(the latter received as personal comunication)
Galli(1971)	In a basalt of M.Calvarina(Verona, Italy)	G	Chem.analysis, unit cell dimensions, indices of refraction, density
Iijima and Harada(1969)	Lower Salt Lake Tuff (Oahu, Hawaii)	IH	Chem.analyses, unit cell dimensions

[a] The samples bear the number used by Sheppard et al. (1970), but are preceded by SG-code.

were then plotted on two diagrams. Figure 2 shows the variability in exchangeable cations in the manner of Figure 1. Careful comparison of these figures reveals that the "new" data confirm the main features of the cation–frequency in phillipsites as deduced from the "old" data. However, it must be emphasized that in the present research samples were analyzed which are richer in sodium (Nos. 6 and 8) than any specimen analyzed before; Nos. 2 and 11 represent a new record in potassium content, if one excludes one unreliable analysis; and sample G has a bivalent–cation content nearly as high as the highest previously reported. In many "old" analyses of Figure 1, the sodium content is exactly zero. Obviously this result is impossible, but many of the "new" data of Figure 2 show a very low sodium content. Intermediate compositions are also extensively represented in these "new" data.

The differences in SiO_2 content are shown in the triangular mole plot of Figure 3, with $Si_{16}O_{32}$, $(Ca, Mg, Sr, Ba)_4Al_8Si_8O_{32}$, and $(Na,K)_8Al_8Si_8O_{32}$ at its vertices. The area where points crowd together has no particular shape or elongation, thus excluding any correlation between R and $M/(M+B)$ where

$$R = Si/Si + Al + Fe^{3+}, \qquad M = Na + K,$$

and

$$B = Ca + Mg + Sr + Ba.$$

TABLE 3. CHEMICAL ANALYSES AND UNIT CELL CONTENTS OF PHILLIPSITES

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	42.27	43.50	41.42	41.47	40.11	46.57	46.60	46.60	46.21	47.90	41.53
Al_2O_3	23.86	23.12	23.82	23.57	25.22	21.40	21.66	21.78	22.16	20.74	24.33
Fe_2O_3	0.10	0.08	0.07	0.08	0.13	0.06	0.07	0.05	0.04	0.06	0.08
MgO	0.02	0.06	0.03	0.02	0.04	0.08	0.05	0.03	0.03	0.02	0.05
CaO	7.37	2.70	8.50	8.00	8.20	1.08	2.70	1.75	5.64	2.30	2.10
SrO	0.23	0.08	0.28	0.21	0.27	0.04	0.05	0.03	0.08	0.02	0.03
BaO	0.03	0.06	0.09	0.06	0.33	0.06	0.30	0.06	0.60	0.23	0.08
Na_2O	1.43	2.40	0.65	0.94	1.01	9.64	7.80	9.80	2.32	8.33	3.16
K_2O	7.90	12.30	6.80	8.20	6.50	2.38	3.28	3.15	6.62	3.31	13.00
H_2O^+	12.43	10.35	15.32	15.70	15.29	14.71	9.73	12.87	11.93	13.75	10.07
H_2O^-	4.61	4.87	2.35	1.42	2.85	3.63	7.05	3.80	4.40	3.71	4.99
Total	100.25	99.52	99.33	99.67	99.95	99.65	99.29	99.92	100.03	100.37	99.42
Si	9.57	9.86	9.51	9.51	9.22	10.41	10.33	10.27	10.24	10.55	9.50
Al	6.37	6.18	6.45	6.37	6.83	5.64	5.66	5.66	5.79	5.38	6.56
Fe^{3+}	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.01	0.02	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.01	0.02
Ca	1.79	0.66	2.09	1.97	2.02	0.26	0.64	0.41	1.34	0.54	0.51
Sr	0.03	0.01	0.04	0.03	0.04	0.01	0.01	0.00	0.01	0.00	0.00
Ba	0.00	0.01	0.01	0.01	0.03	0.01	0.03	0.01	0.05	0.02	0.01
Na	0.63	1.05	0.29	0.42	0.45	4.18	3.35	4.19	1.00	3.56	1.40
K	2.28	3.56	1.99	2.40	1.91	0.68	0.93	0.89	1.87	0.93	3.79
O	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00
H_2O	12.87	11.51	13.54	13.09	13.91	13.67	12.41	12.25	12.06	12.82	11.49
R^a	0.60	0.61	0.60	0.60	0.57	0.65	0.65	0.64	0.64	0.66	0.59
E^b	-2.74	3.26	-1.76	-6.49	4.61	3.68	0.19	-4.57	1.83	-4.20	4.67

	12	13	14	15	16	17	18	19	20	21	22
SiO_2	54.97	50.65	52.13	46.30	43.26	49.91	45.67	46.20	45.67	47.12	40.55
Al_2O_3	16.24	18.80	17.77	21.39	23.27	19.38	21.67	22.01	21.88	21.68	24.73
Fe_2O_3	0.17	0.24	0.11	0.12	0.26	0.06	0.06	0.04	0.04	0.03	0.09
MgO	0.10	0.11	0.23	0.09	0.04	0.02	0.04	0.04	0.03	0.02	0.04
CaO	6.41	6.20	4.94	7.60	8.78	5.30	7.25	7.45	7.68	3.83	8.20
SrO	0.12	0.14	0.05	0.05	0.03	0.06	0.06	0.03	0.05	0.03	0.03
BaO	1.24	1.18	0.61	0.29	0.04	0.02	0.68	0.02	0.97	0.03	0.00
Na_2O	0.50	1.00	0.43	0.19	0.45	1.33	0.39	0.38	0.38	4.05	2.46
K_2O	2.49	4.03	6.64	6.43	6.24	6.06	6.47	6.58	6.80	6.50	5.30
H_2O^+	14.94	14.35	13.99	13.91	11.53	13.63	15.93	15.11	14.06	14.36	13.50
H_2O^-	2.94	3.95	2.88	3.36	5.65	3.59	0.84	1.46	2.43	2.26	4.51
Total	100.12	100.65	99.78	99.73	99.55	99.36	99.06	99.32	99.99	99.91	99.41
Si	11.85	11.13	11.40	10.34	9.76	11.01	10.27	10.27	10.19	10.41	9.30
Al	4.13	4.87	4.58	5.63	6.19	5.04	5.74	5.77	5.75	5.65	6.69
Fe^{3+}	0.03	0.04	0.02	0.02	0.04	0.01	0.01	0.01	0.01	0.00	0.02
Mg	0.03	0.04	0.07	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ca	1.48	1.46	1.16	1.82	2.12	1.25	1.75	1.77	1.84	0.91	2.01
Sr	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.00
Ba	0.10	0.10	0.05	0.03	0.00	0.00	0.06	0.00	0.08	0.00	0.00
Na	0.21	0.43	0.18	0.08	0.20	0.57	0.17	0.16	0.16	0.74	0.09
K	0.68	1.13	1.85	1.83	1.80	1.71	1.86	1.87	1.94	1.83	1.55
O	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00
H_2O	12.85	13.41	12.30	12.87	12.93	12.67	12.57	12.28	12.27	12.25	13.78
R^a	0.74	0.69	0.71	0.65	0.61	0.69	0.64	0.64	0.64	0.65	0.58
E^b	-0.10	2.57	-0.39	-0.42	-0.75	4.94	1.20	2.81	-3.57	4.53	-0.13

[a] $R = Si/(Si+Al+Fe^{3+})$

[b] E = Balance error (see Passaglia, 1970)

TABLE 3. (Continued)

	HIK	SG1	SG9	SG10	SG14	SG15	SG17	SG22	G	IH
SiO_2	46.03	55.23	53.78	53.46	52.05	54.03	52.54	53.89	49.30	43.95
Al_2O_3	21.43	17.57	17.44	18.13	18.09	17.70	17.87	18.50	18.97	22.42
Fe_2O_3	0.99	-	-	-	-	-	-	-	0.11	0.38
MgO	0.00	0.64	0.31	0.32	0.08	0.02	0.56	0.69	0.04	0.46
CaO	5.73	0.51	1.20	1.21	0.10	0.02	0.79	1.01	6.70	8.22
SrO	0.00	-	-	-	-	-	-	-	0.10	-
BaO	0.00	0.08	0.10	0.10	0.00	0.00	0.07	0.27	4.36	-
Na_2O	3.13	4.30	3.83	3.84	5.51	5.60	5.33	4.37	0.31	1.83
K_2O	5.59	7.02	7.50	7.54	7.30	7.33	6.45	6.72	2.50	2.17
H_2O^+	{17.22	{14.65	{15.84	{15.40	{16.87	{15.30	{16.39	{14.55	16.50	15.80
H_2O^-									0.90	4.28
Total	100.12	100.00	100.00	100.00	100.00	100.00	100.00	100.00	99.79	99.51
Si	10.24	11.65	11.58	11.46	11.38	11.56	11.39	11.40	11.02	10.00
Al	5.62	4.37	4.42	4.58	4.66	4.46	4.56	4.61	5.00	6.01
Fe^{3+}	0.17	-	-	-	-	-	-	-	0.02	0.06
Mg	0.00	0.20	0.10	0.10	0.03	0.01	0.18	0.22	0.01	0.15
Ca	1.37	0.12	0.28	0.28	0.02	0.01	0.18	0.23	1.60	2.00
Sr	0.00	-	-	-	-	-	-	-	0.01	-
Ba	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.02	0.38	-
Na	1.35	1.76	1.60	1.60	2.34	2.32	2.24	1.79	0.13	0.81
K	1.59	1.89	2.06	2.06	2.04	2.00	1.78	1.81	0.71	0.63
O	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00
H_2O	12.78	10.31	11.37	11.01	12.31	10.92	11.85	10.27	12.97	15.23
R[a]	0.65	0.73	0.72	0.71	0.71	0.72	0.71	0.71	0.69	0.62
E[b]	2.07	1.74	-0.05	3.29	4.28	2.72	-4.16	1.53	2.96	5.58

The content of H_2O does not show a large variation, ranging from about 15 percent to 17.5 percent.

Table 4 contains the cell parameters of all phillipsites listed in Tables 1 and 2. The cell parameters for the seven samples SG were calculated with the procedure used for all other samples starting from the powder data obtained from Richard A. Sheppard and Arthur J. Gude, 3rd. Although these constants are somewhat different from those published by Sheppard *et al.* (1970), the general conclusions drawn from the two sets of data are essentially consistent.

The best way to see the dispersion of cell parameters is to build a three-dimensional diagram in the space *a–b–c*, which is what we did. In view of the difficulty of including such an object in this journal, two projections in the planes *b/a* (Fig. 4 top) and *b/c* (Fig. 4 bottom) were prepared. A statistical test is not necessary to show a negative correlation between *b* and *a* and a positive correlation between *b* and *c*. In the space *a–b–c* the points are concentrated approximately in a cylinder, the axis of which joins points 4 and SG10. The harmotomes of Sadanaga *et al.* (1961), Černý and Povondra (1965), Sahama and Lehtinen (1967), and Black (1969) plot well outside this volume.

To show the variability of the X-ray diffractometer powder patterns we have listed in Table 5 the indexed powder patterns of four different samples: No. 3 with low *R*, rich in bivalent cations; No. 11 with low *R*, rich in monovalent cations; No. 12 with high *R*, rich in bivalent cations; and No. SG14 with high *R*, rich in monovalent cations. In Table 5 *d*(obs) values are listed in decreasing order in most cases; where exceptions occur, it is due to the order in which the indices appear in the first column.

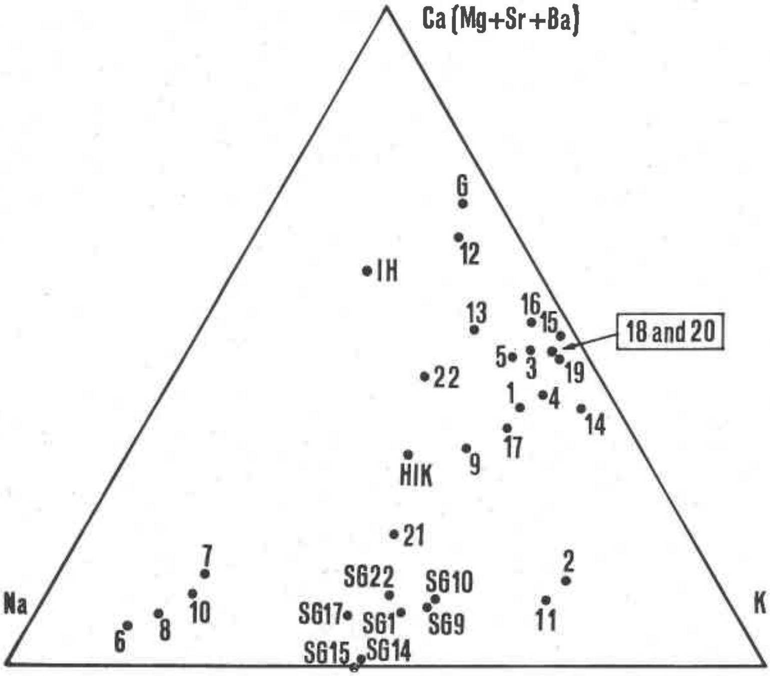

FIG. 2. Distribution of exchangeable cations in phillipsites here studied.

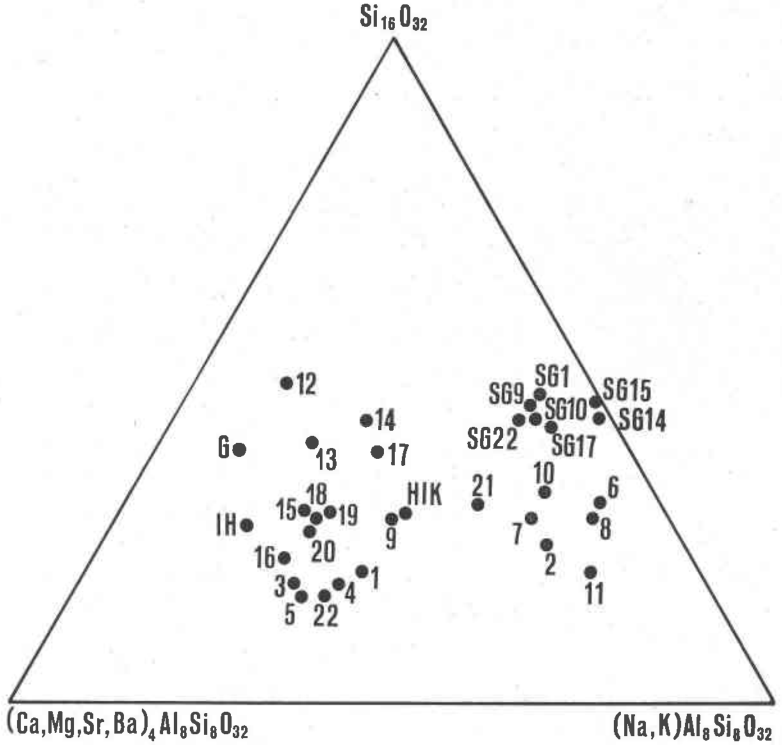

FIG. 3. Mole plot of $(Ca + Mg + Sr + Ba)_4Al_8Si_8O_{32}$–$(Na + K)_8Al_8Si_8O_{32}$–$Si_{16}O_{32}$

The measured and calculated densities are listed in Table 6. The indices of refraction α, β, and γ and the mean index of refraction of the analyzed phillipsites are reported in Table 7, from which it may be seen that for 25 samples α varies from 1.483 to 1.5052, β varies from 1.485 to 1.5106, and γ varies from 1.487 to 1.5132.

For a phillipsite from the Hawaiian Islands, the same locality as sample No. 22, Dunham (1933) gives $\alpha = 1.493$, $\beta = 1.497$, and $\gamma = 1.500$. For a phillipsite from Vesuvio (Italy) Larsen (1934) reports the values: $\alpha = 1.498$, $\beta = 1.500$, and $\gamma = 1.503$; furthermore he states that samples from Isle of Flanders, Annerode, and Habuhswald give similar results. For a phillipsite from Pian di Celle near San Venanzo (Perugia, Italy), the same locality as sample No. 11, Morbidelli (1964) gives $\alpha = 1.4998 \pm 0.0004$, $\beta = 1.5034 \pm 0.0004$, and $\gamma = 1.5076 \pm 0.0004$. All these values are very similar to the average of those phillipsites in Table 7 for which separate α, β, and γ values are given. The same table lists samples for which only the mean index of refraction and not separate α, β, and γ values is shown; it shows an overall variation of between 1.477 and 1.5094 in 39 samples.

RELATIONSHIP BETWEEN CHEMICAL COMPOSITION, CELL PARAMETERS, AND PHYSICAL PROPERTIES

The data in Tables 3, 4, and 7 were tested by searching for possible correlations using the BMD 02R stepwise multiple regression program by Sandi and Franchi (Centro Scientifico IBM, Pisa). The following chemical variables were chosen for the correlation test: 1) $R = \mathrm{Si}/(\mathrm{Si} + \mathrm{Al} + \mathrm{Fe}^{3+})$; 2) $M + B$, were $M = \mathrm{Na} + \mathrm{K}$, and $B = \mathrm{Ca} + \mathrm{Mg} + \mathrm{Sr} + \mathrm{Ba}$; 3) $M/(M + B)$; 4) H_2O (number of water molecules per unit cell); 5) $PCS = \sum$ [(atomic weight of an exchangeable cation) × (its coefficient in the chemical formula)]. The latter variable was taken into

TABLE 4. CELL PARAMETERS (Å) OF THE PHILLIPSITES. ERROR IN BRACKETS

No.	a	b	c	V(Å^3)
1	9.912(4)	14.332(5)	14.372(4)	2041.7(11)
2	9.945(3)	14.301(3)	14.411(3)	2049.6(8)
3	9.874(4)	14.306(7)	14.362(6)	2028.7(14)
4	9.899(2)	14.318(4)	14.395(4)	2040.3(8)
5	9.879(5)	14.340(7)	14.328(6)	2029.8(14)
6	9.955(3)	14.267(5)	14.329(4)	2035.1(10)
7	9.951(2)	14.278(5)	14.324(3)	2035.2(8)
8	9.974(2)	14.286(4)	14.298(3)	2037.3(7)
9	9.905(3)	14.272(6)	14.339(5)	2027.0(11)
10	10.003(3)	14.238(3)	14.285(3)	2034.5(8)
11	9.938(2)	14.321(3)	14.415(4)	2051.6(7)
12	9.907(3)	14.224(3)	14.297(2)	2014.7(7)
13	9.927(4)	14.263(6)	14.349(4)	2031.7(11)
14	9.940(2)	14.219(3)	14.299(2)	2021.0(6)
15	9.887(3)	14.271(4)	14.322(3)	2020.8(8)
16	9.883(3)	14.314(6)	14.311(6)	2024.5(12)
17	9.944(3)	14.232(5)	14.331(3)	2028.2(9)
18	9.875(2)	14.294(4)	14.313(3)	2020.3(7)
19	9.874(3)	14.282(4)	14.335(4)	2021.5(9)
20	9.871(4)	14.273(7)	14.305(5)	2015.4(13)
21	9.911(1)	14.279(3)	14.352(2)	2031.1(5)
22	9.891(3)	14.312(4)	14.324(4)	2027.7(9)
HIK	9.930(8)	14.306(11)	14.334(10)	2036.3(23)
SG1	9.926(7)	14.155(8)	14.207(8)	1996.1(19)
SG9	10.007(3)	14.220(7)	14.246(5)	2027.2(12)
SG10	9.975(3)	14.187(5)	14.247(3)	2016.2(9)
SG14	9.999(4)	14.205(4)	14.278(3)	2028.0(9)
SG15	9.951(3)	14.191(4)	14.255(3)	2013.0(8)
SG17	9.980(2)	14.203(2)	14.254(2)	2020.4(5)
SG22	9.994(4)	14.181(8)	14.255(5)	2020.3(13)
G	9.909(2)	14.246(3)	14.327(2)	2022.5(6)
IH	9.960(10)	14.300(10)	14.300(10)	2036.7(25)

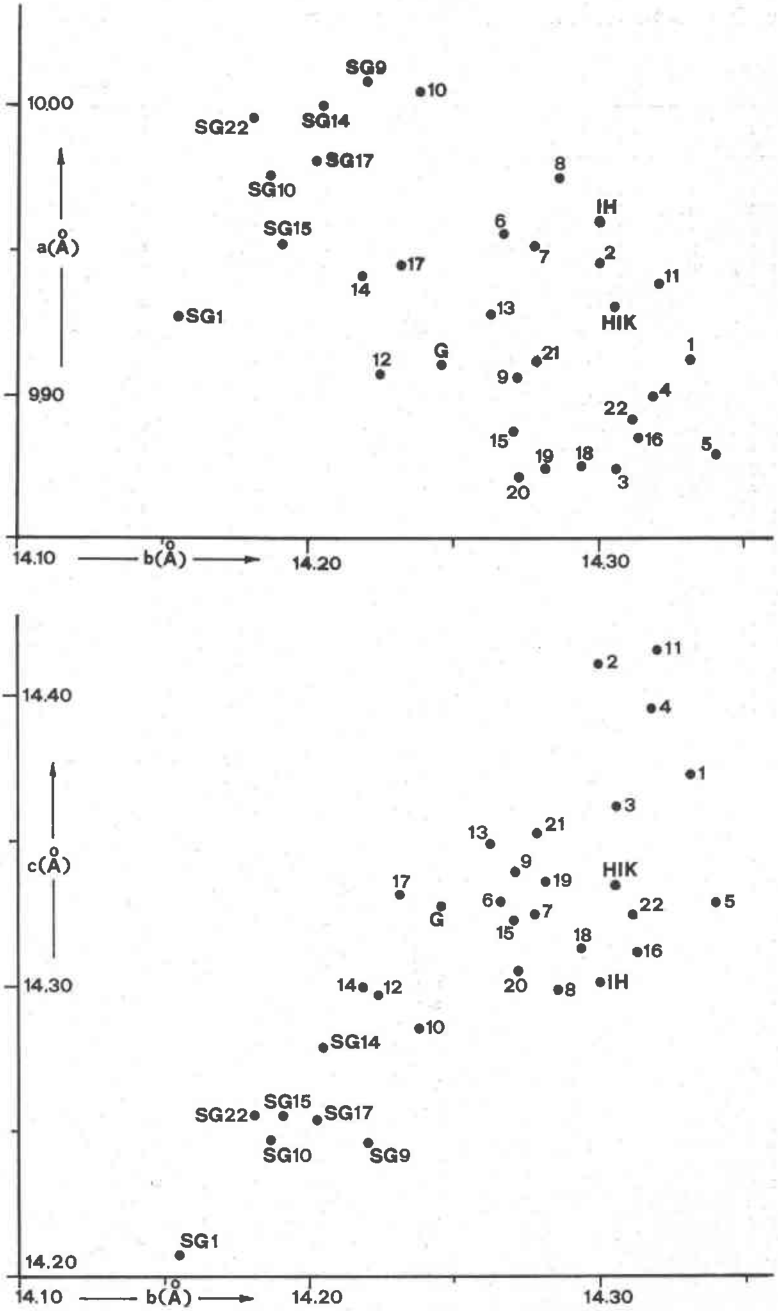

FIG. 4. Variation of cell constants of phillipsites. (a): *a*/*b* plot. (b): *c*/*b* plot.

TABLE 5. X-RAY DIFFRACTION POWDER DATA OF SAMPLES Nos. 3, 11, 12, AND SG14

	3		11		12		SG14	
h k l	I^a	d_{obs}(Å)	I^a	d_{obs}(Å)	I^a	d_{obs}(Å)	I^a	d_{obs}(Å)
1 0 1	w	8.140	w	8.192	w	8.150	m	8.195
0 0 2	vs	7.180	s	7.189	s	7.136	vs	7.140
0 2 0	vs	7.158	s	7.150			vs	7.105
0 1 2	m	6.425	mw	6.430	w	6.390	ms	6.385
1 2 1	m	5.379	m	5.391	m	5.362	ms	5.362
0 2 2	m	5.071	mw	5.082	w	5.045	ms	5.036
2 0 0	ms	4.936	m	4.970	mw	4.960	m	5.000
1 0 3	m	4.303	mw	4.327	w	4.293	m	4.295
1 1 3	s	4.119	s	4.136	ms	4.106	s	4.112
1 3 1								
2 0 2	m	4.065	mw	4.089	d	4.069	ms	4.092
2 2 0								
0 3 2	–	–	w	3.979	vw	3.952	m	3.948
2 1 2	–	–	–	–	–	–	m	3.938
1 2 3	vw	3.691	–	–	w	3.677	mw	3.677
0 1 4	w	3.483	w	3.494	vw	3.468	mw	3.461
1 4 1	s	3.276	s	3.282	m	3.258	s	3.254
3 0 1	vs	3.205	vs	3.211	m	3.213	ms	3.245
0 2 4					vs	3.186	vs	3.177
0 4 2								
1 3 3								
3 1 1	vs	3.134	s	3.148	m	3.138		
2 3 2	w	3.094	w	3.106	vw	3.089	vw	3.099
3 2 1	ms	2.930	s	2.942	ms	2.936	m	2.948
2 0 4	w	2.900	m	2.912	–	–	–	–
2 4 0					–	–	–	–
0 3 4	vw	2.870	m	2.875	–	–	–	–
2 1 4	vw	2.848	–	–	–	–	–	–
1 0 5	s	2.754	s	2.764	s	2.747	s	2.743
1 4 3							s	2.738
1 1 5	vs	2.706	s	2.718	ms	2.695	s	2.690
1 5 1	vs	2.700	vs	2.703	s	2.685		
2 2 4	s	2.693					s	2.683
2 4 2	s	2.688	s	2.694	ms	2.670		
3 1 3	ms	2.660	s	2.679			–	–
3 3 1			s	2.673			–	–
0 5 2			–	–	–	–	–	–
1 2 5	w	2.573	m	2.581	m	2.563	w	2.559
3 2 3	mw	2.537	m	2.547	w	2.534	vw	2.548
0 4 4	mw	2.532	m	5.539	m	2.523	w	2.515
4 0 0	w	2.470	w	2.487	vw	2.476	–	–
3 4 1	–	–	m	2.396	m	2.387	w	2.392
2 5 2	m	2.340	m	2.347	w	2.333	w	2.333
4 1 2	w	2.298	w	2.318	w	2.306	–	–
2 4 4	–	–	–	–	m	2.250	w	2.246
0 5 4	w	2.238	mw	2.240	mw	2.225	w	2.220
3 4 3	mw	2.158	mw	2.170	w	2.158	vw	2.162
2 1 6	–	–	w	2.138	–	–	–	–
3 2 5	vw	2.076	–	–	w	2.068	mw	2.074
1 6 3	–	–	w	2.091	–	–		
2 2 6	vw	2.056	mw	2.067	mw	2.055	mw	2.056
2 6 2					mw	2.049	mw	2.050
1 0 7	vw	2.006	w	2.017	mw	1.9986	w	1.999
5 0 1	vw	1.9540	mw	1.9684	mw	1.9635	w	1.9776
1 7 1	–	–	–	–	mw	1.9721	w	1.9655
3 5 3	–	–	–	–	–	–		
4 2 4	–	–	–	–	–	–		

TABLE 5. (Continued)

	3		11		12		SG14	
h k l	I^a	d_{obs} (Å)	I^a	d_{obs} (Å)	I^a	d_{obs} (Å)	I^a	d_{obs} (Å)
3 6 1	w	1.9107	w	1.9199	w	1.9060	–	–
5 2 1	vw	1.8851	vw	1.8974	w	1.8904	–	–
0 5 6	vw	1.8352	m	1.8405	m	1.8252	w	1.8236
0 0 8	s	1.7885	ms	1.8014	m	1.7864	mw	1.7845
0 8 0			ms	1.7904	m	1.7774	mw	1.7751
4 4 4	–	–	s	1.7752	w	1.7668	m	1.7730
3 1 7	–	–	m	1.7323	–	–	–	–
3 5 5	–	–			–	–	m	1.7227
3 7 1	–	–			–	–		
4 0 6	m	1.7196	ms	1.7262	s	1.7178		
4 6 0	m	1.7143	ms	1.7226	s	1.7148		
0 6 6	m	1.6842	m	1.6926	ms	1.6802	m	1.6780
0 3 8			w	1.6856	m	1.6724	–	–
4 2 6	m	1.6680	–	–	–	–	–	–
4 6 2	m	1.6654	–	–	–	–	–	–
6 0 0	vs	1.6444	s	1.6550	ms	1.6512	–	–
1 5 7	–	–	ms	1.6500	ms	1.6369	–	–
3 6 5	s	1.6034	mw	1.6088	m	1.5975	–	–
6 2 2	–	–	–	–	w	1.5700	–	–
3 4 7	–	–	w	1.5700	–	–	–	–
3 8 1	–	–	–	–	mw	1.5570	–	–
0 9 2	–	–	w	1.5539	s	1.5438	w	1.5384
4 7 2	m	1.5387	mw	1.5426	mw	1.5336	–	–
1 2 9			w	1.5445	mw	1.5313	–	–
1 9 3	m	1.4890	ms	1.4929	vs	1.4828	–	–
3 5 7							–	–
6 2 4	w	1.4654	m	1.4721	s	1.4664	–	–
6 4 2							–	–
5 6 3	–	–	w	1.4564	–	–	–	–
1 4 9	vw	1.4415	w	1.4456	ms	1.4343	–	–
3 1 9	–	–	m	1.4329	ms	1.4245	–	–
0 1 10	–	–			ms	1.4223	–	–
5 0 7	–	–					–	–
0 2 10	m	1.4090	w	1.4124	m	1.4014	–	–
0 10 2	mw	1.4036	w	1.4045	vw	1.3945	–	–
6 4 4	w	1.3799	ms	1.3866	s	1.3818	–	–
0 3 10	m	1.3755	vw	1.3803	m	1.3694	–	–
3 9 3	ms	1.3720	mw	1.3784	s	1.3664	–	–
6 0 6	–	–	vw	1.3658	vw	1.3572	–	–
6 6 0	–	–	w	1.3616	vw	1.3553	–	–
3 4 9	–	–	mw	1.3374	–	–	–	–
0 4 10	–	–			–	–	–	–
0 10 4	–	–	w	1.3307	–	–	–	–
3 9 5	–	–	m	1.2841	ms	1.2751	–	–
2 4 10	m	1.2841	–	–	–	–	–	–
7 0 5	–	–	mw	1.2735	–	–	–	–
7 5 1	–	–	m	1.2668	–	–	–	–
0 8 8	–	–	–	–	ms	1.2604	–	–

All data were obtained with diffractometer method (CuKα_1, Ni-filter): Nos.3, 11, and 12 by the authors, with lead nitrate as internal standard (Cubic, a = 7.8568 Å, card 6-0151 of the JCPDS); SG14 by Sheppard and Gude, with fluorite as internal standard.

[a] vs, very strong; ms, medium to strong; m, medium; mw, medium to weak; w, weak; vw, very weak.

TABLE 6. DENSITIES ($g.cm^{-3}$) OF PHILLIPSITES

No.	D(meas)	D(calc)[a]	No.	D(meas)	D(calc)[a]
1	2.21(1)	2.218	17	2.19(1)	2.156
2	2.21(2)	2.196	18	2.18(1)	2.198
3	2.20(2)	2.242	19	2.18(1)	2.178
4	2.21(2)	2.234	20	2.20(1)	2.208
5	2.24(1)	2.258	21	2.17(1)	2.168
6	2.16(1)	2.182	22	2.22(1)	2.242
7	2.18(1)	2.158	HIK	2.19	2.182
8	2.17(1)	2.156	SG1	n.d.	2.108
9	2.19(1)	2.180	SG9	n.d.	2.118
10	2.15(1)	2.168	SG10	n.d.	2.120
11	2.20(1)	2.212	SG14	n.d.	2.152
12	2.12(1)	2.136	SG15	n.d.	2.120
13	2.15(1)	2.170	SG17	n.d.	2.140
14	2.14(1)	2.154	SG22	n.d.	2.090
15	2.17(1)	2.198	G	2.21(1)	2.200
16	2.14(1)	2.212	IH	2.25	2.218

[a] *D*(calc) was obtained on the basis of 64 oxygens per unit cell

account only in the case of the indices of refraction, for the likelihood of its having any effect on cell dimension was ruled out.

The correlation between cell and chemical parameters, as given in Table 8, shows a close correlation between a and $M/(M + B)$, and also between b and c and $R = \mathrm{Si}/(\mathrm{Si} + \mathrm{Al} + \mathrm{Fe}^{3+})$. The same table also shows the regression equations with the greatest significance (level of probability higher than 99 percent) of cell parameters as functions of R and $M/(M + B)$, and vice versa. The significance of the regression equations is given by the F–ratio values (= ratio between mean square of regression and mean square of residual). In order to give a comprehensive yet simple picture of the reliability of these correlations Figure 5 has been drawn, which is a diagram with R as the abscissa and $M/(M + B)$ as the ordinate. Each specimen is represented by two points joined by a bar; the coordinates of one point are deduced from

TABLE 7. INDICES OF REFRACTION OF PHILLIPSITES. ERRORS IN BRACKETS

No.	α	β	γ	Mean index
1	1.5006(5)	1.5029(5)	1.5132(5)	1.5055
2	1.4902(5)	1.4930(5)	1.4980(5)	1.4937
3	1.4984(5)	1.5042(5)	1.5085(5)	1.5037
4	1.4992(5)	1.5033(5)	1.5095(5)	1.5040
5	1.5000(5)	1.5030(5)	1.5102(5)	1.5044
6	1.4902(5)	1.4930(5)	1.4980(5)	1.4937
7	1.4937(5)	1.4988(5)	1.5013(5)	1.4979
8	1.4936(5)	1.4989(5)	1.5001(5)	1.4975
9	1.4959(5)	1.4992(5)	1.5024(5)	1.4991
10	1.4929(5)	1.4945(5)	1.5001(5)	1.4958
11	1.4966(5)	1.5020(5)	1.5072(5)	1.5019
12	1.4958(5)	1.4979(5)	1.5050(5)	1.4995
13	1.4962(5)	1.4989(5)	1.5058(5)	1.5003
14	1.4864(5)	1.4890(5)	1.4952(5)	1.4902
15	1.4986(5)	1.5014(5)	1.5073(5)	1.5024
16	1.5052(5)	1.5090(5)	1.5111(5)	1.5084
17	1.5000(5)	1.5034(5)	1.5046(5)	1.5026
18	1.5023(5)	1.5064(5)	1.5133(5)	1.5073
19	1.5002(5)	1.5034(5)	1.5046(5)	1.5027
20	1.5049(5)	1.5106(5)	1.5128(5)	1.5094
21	1.4952(5)	1.4986(5)	1.5008(5)	1.4982
22	1.5043(5)	1.5072(5)	1.5122(5)	1.5079
HIK	1.483(2)	1.485(2)	1.487(2)	1.485
SG1	-	-	-	1.482
SG9	-	-	-	1.483
SG10	-	-	-	1.484
SG14	-	-	-	1.477
SG15	-	-	-	1.478
SG17	-	-	-	1.480
SG22	-	-	-	1.483
G	1.4978(5)	1.5026(5)	1.5047(5)	1.5017
IH[a]	1.493	-	1.495	1.494

[a] Iijima and Harada (1969) give the values: $\alpha = 1.486–1.500$, and $\gamma = .1.488–1.502$

the chemical analysis, the coordinates of the other point are deduced from the cell parameters by means of the regression equations of Table 8. For two–thirds of the specimens the bar is short enough to guarantee reasonable accuracy in the deduction of chemical composition from X–ray diffractometer powder data. For one–sixth of the specimens the bar is somewhat longer, and for the remaining sixth it is very long in comparison with the whole area. It is worth noting (see Table 4) that the three specimens with more uncertain parameters (error > 0.007 Å) are HIK, SG1, IH, which all belong to the group with a long bar in Figure 5. This does not mean, however, that parameter error is the only cause of the error in the chemical variables. In the case of a large difference, it should be pointed out that the error in ordinate is always larger than the error in abscissa, or, in other words, the accuracy for R(calc) is better than that for $M/(M + B)$ (calc), as already shown by the standard error given with the regression equation in Table 8. It is clear, therefore, that data deduced from cell parameters (and hence from X–ray diffractometer powder data) are no substitute for chemical analysis, although they can be usefully applied for a rough determination of the chemical composition or for the selection of specimens with extreme composition.

Strangely enough, although harmotomes were not included in the correlation tests, these regression equations apply to them fairly well. For instance, the minerals of Černý and Povondra (1965) with R(obs) = 0.72, $M/(M + B)$ (obs) = 0.32, a = 9.83, b = 14.17, and c = 14.34 (Å) gives R(calc) = 0.75 and $M/(M + B)$ (calc) = 0.33.

In our personal opinion the correlation between cell parameters and chemical variables as evidenced by our data appears worse than it really is. This is due both to the difficulty of obtaining precise data from natural specimens, which are never completely homogeneous, and to the difficulty, already mentioned, of obtaining accurate powder patterns.

Hay (1964) found that a decrease in the index of refraction of natural phillipsites is accompanied by an increase in the Si/Al ratio. Gude and Sheppard (1966) reported that the optical parameters of

TABLE 8. CORRELATION MATRIX BETWEEN CELL AND CHEMICAL PARAMETERS (TOP), AND REGRESSION EQUATIONS (BOTTOM)

	$\underline{R}$	$\underline{M}+\underline{B}$	$\underline{M}/(\underline{M}+\underline{B})$	H_2O
$\underline{a}$	0.538	0.230	0.722	-0.361
$\underline{b}$	-0.932	0.370	-0.443	0.637
$\underline{c}$	-0.730	0.336	-0.317	0.404
$\underline{R}$	1.000	-0.521	0.305	-0.533
$\underline{M}+\underline{B}$		1.000	0.627	-0.115
$\underline{M}/(\underline{M}+\underline{B})$			1.000	-0.638
H_2O				1.000

$\underline{a} = 9.82945 + 0.14540[M/(M+B)]$ F-ratio = 32.684

$\underline{b} = 14.87928 - 0.93798(R)$ F-ratio = 197.395

$\underline{c} = 14.78758 - 0.71836(R)$ F-ratio = 34.218

$13.71030 - 0.96198\ \underline{b} + 0.04662\ \underline{c} = \underline{R} \pm 0.0182$

$-34.91578 + 3.58600\ \underline{a} = [\underline{M}/(\underline{M}+\underline{B})] \pm 0.1454$

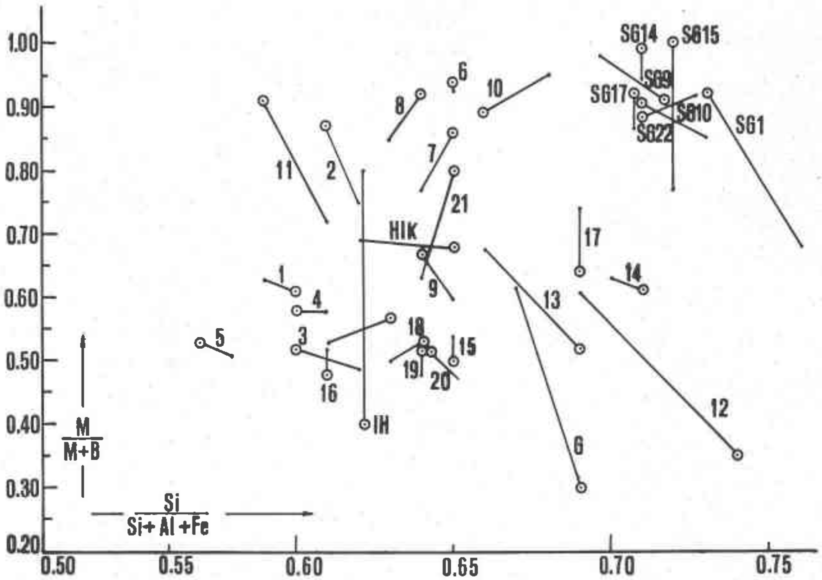

FIG. 5. The correspondence between observed and calculated values of R and $M/(M + B)$ is shown. The observed values, deduced from chemical analyses, are shown as pointed circles; the calculated values, deduced from cell parameters a, b, and c by means of the regression equation of Table 8, are shown as points; the two marks for the same specimen are joined by a solid bar.

zeolites depend on the Si/Al ratio, on exchangeable cations and on the degree of hydration. Sheppard *et al.* (1970) wrote that "an attempt was made, without success, to correlate the main indices of refraction with the Si/Al ratio of the deep-sea phillipsites." Furthermore, they showed that a decrease in the indices of deep-sea phillipsites is accompanied by an increase in Na_2O and suggested that an increase in the barium content can be correlated with an increase in the index of refraction.

The α, β, and γ and mean indices of refraction of phillipsites listed in Table 7 were correlated with the above-mentioned chemical variables. The correlation matrices obtained for α, β, and γ and the mean indices are given in Tables 9 and 10, respectively. From the comparison of these two correlation matrices the following deduction can be made: no significant correlation was found (Table 9) in the case of the 25 samples for which separate α, β, and γ values are available. We measured the indices of refraction for all 25 samples with the exception of HIK and IH. Analysis of the mean index of refraction, extended to include those samples for which only this value is available, revealed (Table 10) that it is negatively correlated with *R* and $M/(M + B)$ and positively correlated, albeit less markedly, with H_2O. None of these seven new measurements was made by us.

The regression equation with the greatest significance (level of probability higher than 99 percent) for the mean index of refraction is:

$$\text{Mean index} = 1.58408 – 0.10798(R) – 0.02457[M/(M + B)]$$

$$F\text{–ratio} = 41.490$$

Comparison of the two matrices also shows the close negative correlation of *R* with *PCS*. An attempt to correlate α, β, and γ and the mean index with weight percent BaO and Na_2O, respectively, was unsuccessful.

TABLE 9. CORRELATION MATRIX BETWEEN INDICES OF REFRACTION α, β, AND γ AND CHEMICAL PARAMETERS FOR 25 SAMPLES

	R	M+B	M/(M+B)	H_2O	PCS
α	-0.374	-0.148	-0.496	0.233	0.260
β	-0.398	-0.092	-0.449	-0.169	0.313
γ	-0.413	-0.092	-0.476	0.273	0.354
R	1.000	-0.684	-0.204	-0.129	-0.868
M+B		1.000	0.830	-0.205	0.634
M/(M+B)			1.000	-0.391	0.202
H_2O				1.000	-0.209
PCS					1.000

TABLE 10. CORRELATION MATRIX BETWEEN MEAN INDEX OF REFRACTION AND CHEMICAL PARAMETERS FOR 32 SAMPLES

	R	M+B	M/(M+B)	H_2O	PCS
Mean index	-0.702	-0.008	-0.689	0.551	0.533
R	1.000	-0.521	0.305	-0.533	-0.837
M+B		1.000	0.627	-0.115	0.604
M/(M+B)			1.000	-0.638	-0.086
H_2O				1.000	0.122
PCS					1.000

CONCLUSION

These results point to the existence of a wide variation in the chemical composition of the phillipsite mineral group. The percentage of Si in tetrahedra ranges from 57 percent to 74 percent, the exchangeable cations being exclusively monovalent in some samples (deep-sea phillipsites), but up to 70 percent bivalent in other samples. Phillipsite is one of the few zeolites where potassium may be the most abundant exchangeable cation. Some feature of the chemical composition can be deduced from the cell parameter; the degree of confidence of this deduction is sufficient for a rough determination of the chemical composition of the phillipsite under examination.

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