

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF THE RELATED ZEOLITES OFFRETITE AND ERIONITE¹

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ABSTRACT

New chemical analyses as well as optical and X-ray data show that offretite and erionite are closely related hexagonal zeolites. Offretite is alkaline earth rich and has a $\text{Si}/(\text{Al} + \text{Fe}^{3+})$ ratio of 2.48, whereas erionite is generally alkali-rich and has a $\text{Si}/(\text{Al} + \text{Fe}^{3+})$ ratio of 2.92 to 3.74. Ferric iron may substitute for aluminum in erionites from sedimentary deposits. The optic sign is negative for offretite and positive for erionite. Offretite characteristically has indices of refraction that are higher than those for erionite. A decrease in the indices of refraction and the cell volume of erionite can be correlated with an increase in the $\text{Si}/(\text{Al} + \text{Fe}^{3+})$ ratio.

INTRODUCTION

Offretite was described by Gonnard (1890) as a new zeolite in amygdaloidal basalt at Mount Simionse near Montbrison, Loire, France. Except for a probable occurrence in basalt from Palau Island, Caroline Islands (Dürfeld, 1911), no other occurrence of offretite has been reported.

Erionite was first described by Eakle (1898) from a rhyolitic welded tuff near Durkee, Oregon. No other occurrences had been found until 1959, when Deffeyes reported the zeolite in tuffaceous sedimentary rocks of Cenozoic age in Nevada, South Dakota, and Wyoming. Erionite has subsequently been identified from most of the western U. S., where it occurs chiefly in altered silicic tuffs of upper Cenozoic lacustrine deposits. The largest deposits of erionite seem to be in the desert areas of southern California, central Nevada, and southeastern Oregon.

The relationship between erionite and offretite was investigated by Hey and Fejer (1962), who concluded that the two zeolites gave identical X-ray powder photographs. Hey and Fejer suggested that only one name was necessary, and that the name offretite had clear priority. The identity of offretite had been misinterpreted earlier by Strunz (1956), who indicated that offretite was identical with phillipsite on the basis of X-ray study of material from Montbrison. Inasmuch as phillipsite is very abundant at Montbrison (Gonnard, 1890), Strunz probably examined phillipsite rather than offretite (Hey and Fejer, 1962).

Recently, Bennett and Gard (1967) and Harada *et al.* (1967) proposed a structural basis for distinguishing erionite from offretite. Electron diffraction and single-crystal X-ray studies showed that the *c* cell dimension of offretite is half that of erionite. Thus, erionite and offretite are different yet closely related zeolites, and both names should be retained.

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The present study complements these structural studies and provides further criteria for distinguishing the two zeolites. New chemical, optical, and X-ray data are given for offretite from Montbrison and for several erionites from the western United States.

CHEMICAL COMPOSITION

The original chemical analysis of offretite that was published by Gonnard (1890) does not accurately characterize the zeolite. The molecular ratio $\text{Al}_2\text{O}_3/(\text{Ca},\text{Mg},\text{Na}_2,\text{K}_2)\text{O}$ for zeolites should be unity; however, this ratio for Gonnard's analysis is about 1.5. Thus, the Al_2O_3 content of Gonnard's analysis is greatly in excess of his reported CaO and K_2O contents. Whether this excess was due to analytical error or due to contamination is unknown.

In order to have a better basis for a comparison of the composition of offretite with that of erionite, a new chemical analysis was prepared on offretite from the original locality near Montbrison, France. The analysis was prepared by Blanche Ingram on 80 milligrams of offretite that had been hand picked from material kindly supplied by Dr. Claude Guillemain.

The new analysis (Table 1, sample 1) of offretite shows that alkaline earths are greatly in excess of alkalis and that the molecular ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is about 4.97. Gonnard's analysis showed that potassium was the predominant cation and that the molecular ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 4.67. The total H_2O content in the new analysis is very close to that in Gonnard's analysis. The molecular ratio $\text{Al}_2\text{O}_3/(\text{Ca},\text{Mg},\text{Na}_2,\text{K}_2)\text{O}$ of the new analysis is about 1.1, much closer to unity than Gonnard's original analysis. Neither Gonnard's analysis nor the present one shows Na_2O . A microspectrochemical analysis on 1 milligram of offretite by C. L. Waring showed only 0.01 percent Na.

The meager published analyses of erionite as well as previously unpublished analyses (Table 1) indicate that this zeolite is more siliceous than offretite and that the molecular ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and cation contents are variable. Except for a specimen from Mazé, Japan (Harada *et al.*, 1967, p. 1787), the erionites are alkali rich. The molecular ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranges from 6.03 to 7.98.

Ferric iron may substitute for aluminum in erionite because the molecular ratio $\text{Al}_2\text{O}_3/(\text{Ca},\text{Mg},\text{Na}_2,\text{K}_2)\text{O}$ is closer to unity if the Fe_2O_3 content is added to the Al_2O_3 content. Five of the nine erionite analyses that report Fe_2O_3 show an improved ratio if the Fe_2O_3 is added. In his study of zeolites from saline lake deposits, Hay (1964, p. 1374) found that Al_2O_3 was deficient in phillipsite analyses but that the molecular ratio $\text{Al}_2\text{O}_3/(\text{Ca},\text{Mg},\text{Na}_2,\text{K}_2)\text{O}$ was near unity when the Fe_2O_3 content was added to the Al_2O_3 content. We noted a similar Al_2O_3 deficiency

TABLE 1. CHEMICAL COMPOSITION OF OFFRETITE AND ERIONITE

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|--------------------------------|------|-------|--------|-------|-------|--------|-------|-------|-------|-------|-------|--------|
| SiO ₂ | 53.0 | 54.72 | 57.16 | 57.40 | 57.24 | 60.81 | 59.07 | 59.51 | 58.89 | 59.16 | 60.39 | 60.67 |
| Al ₂ O ₃ | 18.1 | 15.24 | 16.08 | 15.60 | 13.93 | 13.59 | 13.75 | 14.20 | 14.23 | 13.44 | 13.32 | 12.90 |
| Fe ₂ O ₃ | — | 1.04 | — | — | 1.95 | 3.63 | 2.15 | .73 | .38 | 1.48 | 1.31 | 1.35 |
| FeO | — | — | — | — | 0.2 | — | .09 | .02 | .02 | .05 | — | .09 |
| MgO | 2.0 | 1.17 | .66 | 1.11 | .15 | .80 | .69 | .14 | 1.16 | .26 | .49 | 1.09 |
| CaO | 4.1 | 4.32 | 3.50 | 2.92 | .00 | 1.54 | .96 | .01 | 2.67 | .21 | 1.30 | .65 |
| Na ₂ O | — | 1.00 | 2.47 | 1.45 | 6.24 | 1.90 | 3.04 | 5.92 | .64 | 6.03 | 3.48 | 4.39 |
| K ₂ O | 3.6 | 2.46 | 3.51 | 3.40 | 4.10 | 7.17 | 4.86 | 3.64 | 4.85 | 3.29 | 4.33 | 4.09 |
| H ₂ O+ | 17.7 | 19.12 | 17.30 | 17.58 | 8.18 | 10.57 | 8.83 | 8.94 | 9.95 | 8.01 | 7.84 | 7.69 |
| H ₂ O- | 1.1 | | | | | | | | | | | |
| TiO ₂ | — | .00 | — | — | .32 | — | .17 | .05 | .09 | .15 | .09 | .09 |
| P ₂ O ₅ | — | — | — | — | .04 | — | .01 | — | .03 | .03 | — | .02 |
| MnO | — | .00 | — | — | .28 | — | .01 | — | .00 | .03 | — | .03 |
| CO ₂ | — | — | — | — | .44 | — | — | — | — | — | — | — |
| Cl | — | — | — | — | .02 | — | — | .01 | .02 | — | .02 | — |
| F | — | — | — | — | — | — | .01 | .01 | .01 | — | .05 | — |
| Total | 99.6 | 99.07 | 100.68 | 99.46 | 99.99 | 100.01 | 99.98 | 99.52 | 99.58 | 99.57 | 99.99 | 100.00 |

Offretite:

1. No. W-168588; new analysis; analyst, Blanche Ingram. Locality, Mount Simionse, Montbrison, Loire, France. $\omega=1.489$, $\epsilon=1.486$.

Erionite:

2. Harada *et al.* (1967, p. 1787); Fe₂O₃ contains FeO. Locality, Mazé, Niigata Prefecture, Japan. $\omega=1.477$, $\epsilon=1.480$.
3. Eakle (1898, p. 67). Locality, Durkee, Baker County, Ore.
4. Staples and Gard (1959, p. 272). Locality, Durkee opal mine, sec. 36, T. 11 S., R. 43 E., Baker County, Ore. $\omega=1.468$, $\epsilon=1.471$.
5. Hay (1966, p. 10); corrected for dolomite impurity. Locality, west side of Lake Natron, Tanzania. $\omega=1.464$, $\epsilon=1.468$.
6. Eberly (1964, p. 33). Locality, Rome, Malheur County, Ore.
7. No. D100748; new analysis; analyst, Christel L. Parker; corrected for calcite impurity. Locality, near Eastgate, SE $\frac{1}{4}$ sec. 28, T. 17 N., R. 36 E., Churchill County, Nev. $\omega=1.464$, $\epsilon=1.467$.
8. No. D101777; new analysis; analyst, George Riddle; Al₂O₃ contains P₂O₅. Locality, east of Pine Creek, NW $\frac{1}{4}$ sec. 20, T. 28 N., R. 52 E., Eureka County, Nev. $\omega=1.458$, $\epsilon=1.461$.
9. No. D101778; new analysis, analyst, George Riddle. Locality, east of Jersey Valley Wash., NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 9, T. 27 N., R. 40 W., Pershing County, Nev. $\omega=1.467$, $\epsilon=1.471$.
10. Sheppard *et al.* (1965, p. 246). Locality, southern flank of Cady Mountains, SW $\frac{1}{4}$ sec. 6, T. 8 N., R. 5 E., San Bernardino County, Calif. $\omega=1.463$, $\epsilon=1.467$.
11. No. D101779; new analysis; analyst, George Riddle; corrected for calcite impurity, Fe₂O₃ contains FeO, Al₂O₃ contains P₂O₅. Locality, east of Crooked Creek, NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 5, T. 32 S., R. 41 E., Malheur County, Ore. $\omega=1.464$, $\epsilon=1.467$.
12. Sheppard and Gude (1968, p. 15); corrected for calcite impurity. Locality, near Tecopa, Ne $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 20 N., R. 7 E., Inyo County, Calif. $\omega=1.461$, $\epsilon=1.465$.

and a similar improvement in the ratio by addition of Fe₂O₃ to the Al₂O₃ for analyses of clinoptilolite and phillipsite from deposits of Lake Tecopa, California, and of clinoptilolite, mordenite, and phillipsite from the Barstow Formation, Mud Hills, California. There is, therefore, a strong suggestion that ferric iron can substitute for aluminum in zeolites of sedimentary deposits. The analysis of erionite from Rome, Oregon (Eberly, 1964, p. 33), suggests that ferric iron can substitute for as much as about 15 percent of the aluminum.

The new analysis of offretite and all available analyses of erionite were

calculated into atoms per unit cell on the basis of 72 oxygen atoms and are plotted on Figures 1 and 2. The unit-cell content of offretite is half that of erionite but was doubled for ease of comparison. Figure 1 is a plot of $(Al+Fe^{3+})$ atoms per unit cell versus Si atoms per unit cell and shows that the analysis of offretite stands apart from the analyses of erionite. However, additional analyses of offretite or erionite could close the compositional gap. The $Si/(Al+Fe^{3+})$ ratio for offretite is 2.48, whereas

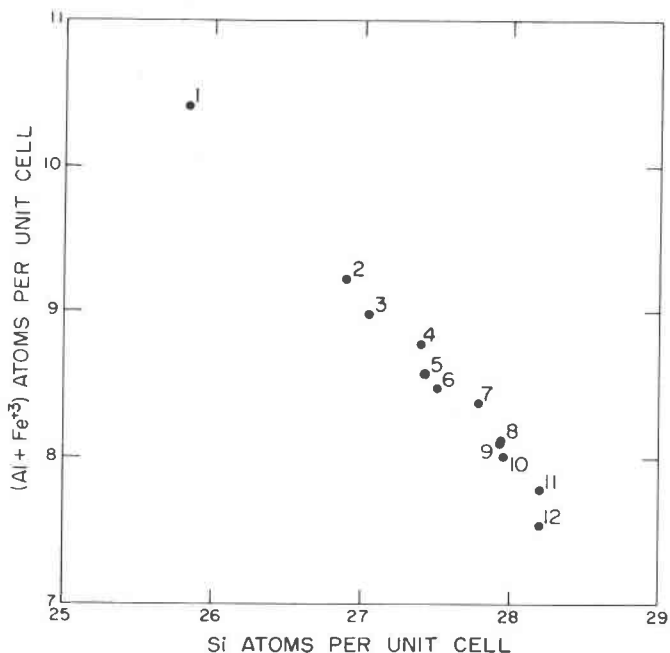


FIG. 1. Relation between $(Al+Fe^{3+})$ and Si atoms per unit cell for offretite and erionite, calculated on the basis of 72 oxygen atoms. Samples are same as those reported in Table 1.

the ratio for erionite ranges from 2.92 to 3.74. Only the erionite from Mazé, Japan (Harada *et al.*, 1967), has a $Si/(Al+Fe^{3+})$ ratio less than 3. It is interesting to note that this erionite from Japan occurs in basalt, but all the other analyzed erionites occur in much more silicic rocks. Two other erionites have been reported from basalt (Hey, 1959; Kamb and Oke, 1960, p. 87-90), but no chemical analyses were given.

The cation contents of offretite and erionite are shown in Figure 2. Although the paucity of analyses does not permit firm conclusions, two observations are worthy of mention: (1) offretite does not have a sufficiently characteristic cation content to distinguish it from the erionites

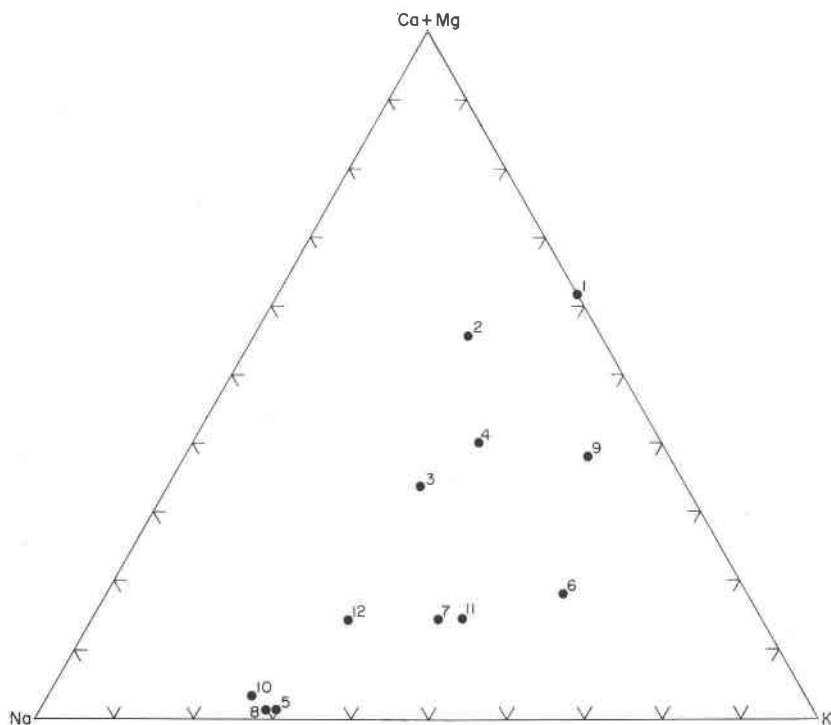


FIG. 2. Atomic percentages of Na, K, and (Ca+Mg) for offretite and erionite. Samples are same as those reported in Table 1.

and (2) the atomic percentage of potassium ranges from about 25 to 58, a narrow range compared to that of the other plotted cations. Cation exchange experiments on natural erionites (Eberly, 1964; Peterson *et al.*, 1965) have shown that much of the potassium cannot be exchanged. The relatively narrow range in potassium content, therefore, may be imposed by structural requirements. Offretite and the erionite from Mazé, Japan, show a predominance of alkaline earths. The composition of the host rock may have in part controlled the cation content of the zeolites because these two specimens are the only analyzed ones that occur in basalt.

OPTICAL PROPERTIES

Offretite and erionite are uniaxial but differ in optic sign; offretite is negative, whereas erionite is positive. Both are elongated parallel to the *c* crystallographic axis. Inasmuch as the sign of elongation in the uniaxial crystals is the same as the optic sign, offretite has negative elongation and

erionite has positive elongation. Thus, the sign of elongation, an easily determined property, seems sufficient to distinguish offretite from erionite.

The indices of refraction for offretite are higher than those for erionite. Indices for offretite are: $\omega = 1.489$ and $\epsilon = 1.486$; birefringence is 0.003. Indices of refraction for the analyzed erionites are: $\omega = 1.458$ – 1.477 and $\epsilon = 1.461$ – 1.480 ; birefringence is 0.003–0.005. All indices of refraction determined for this report are ± 0.001 . Sheppard and Gude (1968, p. 16) reported indices as low as $\omega = 1.455$ and $\epsilon = 1.459$ for an erionite from Lake Tecopa, California. Rare crystals from the Montbrison specimen

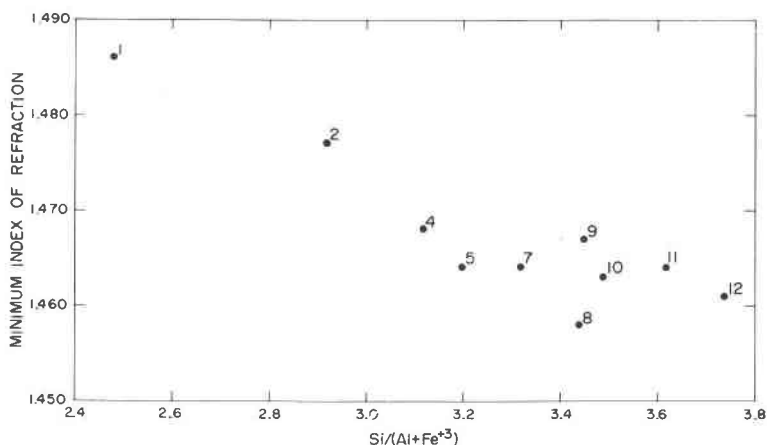


FIG. 3. Variation in the minimum index of refraction versus $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio for offretite and erionite. Samples are same as given in Table 1. Index for samples 2 and 4 from Harada *et al.* (1967, p. 1788) and Staples and Gard (1959, p. 264), respectively; all others are original. No available optical data for samples 3 and 6.

are zoned from offretite (negative elongation) at the interior to erionite (positive elongation) at the exterior. The offretite has the same indices of refraction as reported above, but the erionite has indices of refraction that are higher than those measured for the analyzed erionites: $\omega = 1.481$ – 1.484 and $\epsilon = 1.484$ – 1.487 . Except for this erionite from the zoned crystals, no erionite has an index of refraction higher than 1.48, and most erionites have indices below 1.47.

Figure 3 is a plot of the minimum index of refraction versus the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio for offretite and those analyzed erionites for which sufficient optical data are available. Although there is much scatter for the erionites, the plot clearly shows a decrease in the index of refraction with an increase in the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio. Factors such as cation and water

contents are also known to affect the index of refraction of zeolites and probably account for the scatter of the erionites.

X-RAY POWDER DATA

The X-ray powder diffractometer patterns for offretite and erionite are similar; they differ sufficiently in detail, however, to be distinguishable.

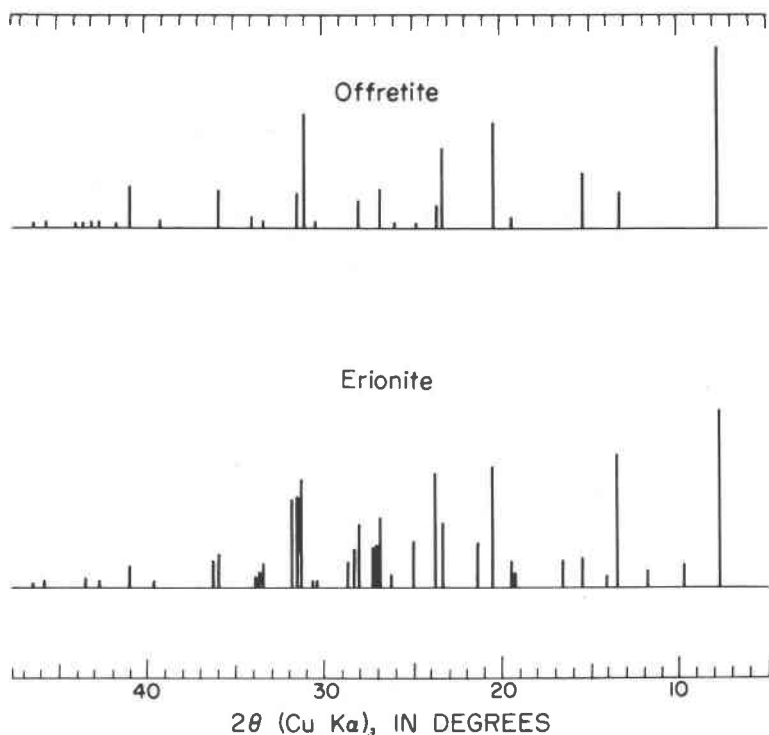


FIG. 4. Diagrammatic representation of X-ray powder diffractometer patterns for offretite and erionite. Intensities are indicated by height of lines above base line.

Figure 4 is a diagrammatic representation of the complete data given in Table 2. Differences in the number of observed lines and the intensity of lines are obvious. Differences in the position of lines are not so obvious in the figure but are measurable and are shown in Table 2. The X-ray data are consistent with a space group of $P\bar{6}m2$ for offretite (Bennett and Gard, 1967) and of $P6_3/mmc$ for erionite (Staples and Gard, 1959). Erionite characteristically has a more complex X-ray powder diffractometer record than offretite. Erionite commonly has double or triple lines where offretite has single or double lines. Observed lines at 9.07 Å, 7.51 Å,

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR OFFRETITE AND ERIONITE^a

| Offretite, Montbrison, France | | | | Erionite, Tecopa, California | | | | Offretite, Montbrison, France | | | | Erionite, Tecopa, California | | | | |
|----------------------------------|---------------------------|--------------------------|----------|---------------------------------|---------------------------|--------------------------|----------|----------------------------------|---------------------------|--------------------------|----------|---------------------------------|---------------------------|--------------------------|----------------|----|
| <i>hkl</i> | <i>d</i> (calc) (Å) | <i>d</i> (obs) (Å) | <i>I</i> | <i>hkl</i> | <i>d</i> (calc) (Å) | <i>d</i> (obs) (Å) | <i>I</i> | <i>hkl</i> | <i>d</i> (calc) (Å) | <i>d</i> (obs) (Å) | <i>I</i> | <i>hkl</i> | <i>d</i> (calc) (Å) | <i>d</i> (obs) (Å) | <i>I</i> | |
| 100 | 11.51 | 11.50 | 100 | 100 | 11.44 | 11.41 | 100 | | | | | | 305 | 2.362 | — ^b | 3 |
| | | | | 101 | 9.11 | 9.07 | 11 | 113 | 2.362 | | | | 116 | 2.344 | — ^b | 3 |
| 001 | 7.58 | | | 002 | 7.52 | 7.51 | 7 | | | | | | 323 | 2.326 | | |
| 110 | 6.64 | 6.64 | 20 | 110 | 6.61 | 6.61 | 73 | 203 | 2.314 | | | | 206 | 2.296 | | |
| 101 | 6.33 | | | 102 | 6.28 | 6.28 | 5 | 500 | 2.302 | 2.300 | 5 | | 500 | 2.289 | — ^b | 3 |
| 200 | 5.76 | 5.76 | 35 | 200 | 5.72 | 5.72 | 16 | 402 | 2.292 | | | | 404 | 2.277 | | |
| | | | | 201 | 5.35 | 5.34 | 14 | | | | | | 501 | 2.263 | — ^b | 2 |
| 111 | 4.998 | | | 112 | 4.964 | | | | | | | | 413 | 2.235 | — ^b | 3 |
| | | | | 103 | 4.592 | 4.595 | 8 | 330 | 2.215 | 2.214 | 22 | | 330 | 2.202 | 2.200 | 11 |
| 201 | 4.584 | 4.581 | 4 | 202 | 4.554 | 4.551 | 12 | 501 | 2.203 | | | | 502 | 2.190 | | |
| 210 | 4.350 | 4.352 | 59 | 210 | 4.325 | 4.322 | 67 | | | | | | 315 | 2.183 | | |
| | | | | 211 | 4.157 | 4.156 | 24 | 213 | 2.185 | | | | 216 | 2.170 | | |
| 300 | 3.837 | 3.837 | 43 | 300 | 3.815 | 3.813 | 37 | 420 | 2.175 | 2.177 | 2 | | 420 | 2.164 | | |
| | | | | 203 | 3.771 | | | 322 | 2.167 | | | | 324 | 2.153 | | |
| 002 | 3.792 | | | 004 | 3.760 | | | | | | | | 421 | 2.141 | | |
| 211 | 3.773 | 3.774 | 11 | 212 | 3.749 | 3.746 | 65 | 331 | 2.126 | 2.126 | 4 | | 332 | 2.114 | — ^b | 2 |
| | | | | 301 | 3.698 | | | | | | | | 107 | 2.112 | 2.113 | 6 |
| 102 | 3.601 | 3.600 | 3 | 104 | 3.572 | 3.570 | 24 | 303 | 2.111 | 2.110 | 2 | | 306 | 2.095 | — ^b | 2 |
| 301 | 3.423 | 3.429 | 2 | 302 | 3.402 | 3.402 | 4 | | | | | | 503 | 2.082 | — ^b | 2 |
| 220 | 3.323 | 3.322 | 22 | 220 | 3.304 | 3.303 | 39 | 412 | 2.094 | | | | 414 | 2.080 | — ^b | 3 |
| | | | | 213 | 3.275 | 3.276 | 25 | 421 | 2.091 | 2.091 | 2 | | 422 | 2.078 | 2.079 | 5 |
| 112 | 3.293 | | | 114 | 3.268 | 3.271 | 25 | | | | | | 405 | 2.073 | — ^b | 1 |
| 310 | 3.192 | 3.190 | 17 | 310 | 3.174 | — ^c | | 510 | 2.067 | 2.068 | 2 | | 510 | 2.055 | — ^b | 2 |
| 202 | 3.166 | — ^c | | 204 | 3.142 | — ^c | | | | | | | 511 | 2.036 | — ^b | 2 |
| | | | | 311 | 3.106 | 3.106 | 12 | | | | | | 207 | 2.012 | — ^b | 1 |
| | | | | 303 | 3.036 | — ^b | 5 | 223 | 2.012 | | | | 226 | 1.997 | — ^b | 2 |
| 221 | 3.043 | | | 222 | 3.025 | — ^b | 5 | | | | | | 423 | 1.986 | — ^b | 2 |
| 311 | 2.942 | 2.942 | 3 | 312 | 2.924 | 2.923 | 10 | 511 | 1.994 | 1.995 | 2 | | 512 | 1.983 | 1.982 | 4 |
| | | | | 105 | 2.909 | 2.910 | 10 | | | | | | 325 | 1.978 | — ^b | 3 |
| 400 | 2.880 | 2.880 | 64 | 400 | 2.861 | 2.860 | 60 | 313 | 1.982 | | | | 316 | 1.967 | — ^b | 3 |
| 212 | 2.858 | 2.858 | 15 | 214 | 2.838 | 2.839 | 50 | 502 | 1.968 | 1.967 | 2 | | 504 | 1.955 | — ^b | 3 |
| | | | | 401 | 2.810 | 2.812 | 52 | | | | | | 217 | 1.924 | — ^c | |
| | | | | 313 | 2.682 | | | | | | | | 415 | 1.921 | — ^c | |
| 302 | 2.697 | | | 304 | 2.678 | 2.676 | 15 | 600 | 1.918 | | | | 630 | 1.907 | | |
| 401 | 2.690 | 2.693 | 3 | 402 | 2.674 | 2.680 | 12 | | | | | | 513 | 1.932 | — ^b | 1 |
| | | | | 205 | 2.663 | 2.673 | 8 | 332 | 1.913 | | | | 334 | 1.900 | | |
| 320 | 2.641 | 2.642 | 4 | 320 | 2.625 | | | | | | | | 601 | 1.892 | | |
| | | | | 321 | 2.586 | | | 403 | 1.899 | | | | 406 | 1.885 | — ^b | 1 |
| 003 | 2.528 | | | 006 | 2.507 | | | 004 | 1.896 | | | | 430 | 1.881 | 1.882 | 6 |
| 410 | 2.512 | 2.510 | 20 | 410 | 2.497 | 2.496 | 20 | 430 | 1.892 | 1.893 | 1 | | 008 | 1.880 | — ^b | 2 |
| | | | | 403 | 2.485 | | | 422 | 1.887 | | | | 424 | 1.875 | | |
| 222 | 2.499 | | | 224 | 2.482 | 2.480 | 17 | | | | | | 307 | 1.872 | | |
| 321 | 2.494 | | | 322 | 2.479 | | | | | | | | 431 | 1.867 | — ^b | 3 |
| | | | | 215 | 2.470 | | | 104 | 1.870 | | | | 108 | 1.855 | | |
| | | | | 411 | 2.464 | | | 601 | 1.860 | | | | 602 | 1.849 | | |
| 103 | 2.469 | | | 106 | 2.449 | | | 520 | 1.843 | 1.844 | 3 | | 520 | 1.832 | 1.834 | 8 |
| 312 | 2.442 | | | 314 | 2.425 | | | 431 | 1.836 | 1.838 | 5 | | 432 | 1.825 | — ^b | 2 |
| 411 | 2.384 | | | 412 | 2.370 | | | | | | | | | | | |

^a Diffractometer: nickel-filtered $\text{CuK}\alpha_1$ radiation, tube at 35 kv and 20 ma, 1° divergence slit, 0.01 inch receiving slit, scanning speed $\frac{1}{2}$ 2° per minute, fluorite internal standard.

^b Reflection observed but not accurately measurable.

^c Reflection obscured by the reflection of the internal standard.

and 5.34 Å seem to distinguish erionite from offretite. Bennett and Gard (1967) reported that offretite can be distinguished in intergrowths with erionite by electron diffraction. We have found that the two zeolites can be distinguished in mixtures by an X-ray powder diffractometer technique using a slow scanning speed of $\frac{1}{2}$ degree 2θ per minute.

Cell dimensions and volume for offretite and most of the analyzed erionites (Table 3) were obtained by a least-squares refinement of the X-ray powder diffractometer data utilizing the U.S. Geological Survey's FORTRAN IV Computer Program W9214. The space group and initial cell parameters used for offretite and erionite were those of Bennett and Gard (1967) and Staples and Gard (1959), respectively. The cell di-

TABLE 3. CELL PARAMETERS FOR ANALYZED OFFRETITE AND ERIONITE^a

| | a (Å) | c (Å) | V (Å ³) |
|----|--------------|--------------|-----------------------|
| 1 | 13.291±0.002 | 7.582±0.006 | 1,159.9±1.0 |
| 2 | 13.24±0.02 | 15.12±0.02 | 2,295.5±0.2 |
| 4 | 13.254±0.006 | 15.100±0.010 | 2,297.4±3.0 |
| 5 | 13.227±0.004 | 15.062±0.012 | 2,281.9±2.0 |
| 7 | 13.225±0.001 | 15.066±0.005 | 2,282.1±0.7 |
| 8 | 13.217±0.002 | 15.049±0.007 | 2,276.6±1.0 |
| 9 | 13.218±0.003 | 15.060±0.010 | 2,278.6±1.0 |
| 10 | 13.214±0.003 | 15.048±0.004 | 2,275.5±1.0 |
| 11 | 13.212±0.002 | 15.042±0.005 | 2,274.0±0.9 |
| 12 | 13.214±0.002 | 15.041±0.004 | 2,274.4±0.8 |

^a Samples as in Table 1. Except for samples 2 and 4, all data are original. Cell volume for sample 2 was calculated by computer from cell dimensions given by Harada *et al.* (1967, p. 1793). Cell parameters for sample 4 were calculated by computer from d values given by Staples and Gard (1959, p. 269-270). No available data for samples 3 and 6.

mensions for offretite are $a=13.29$ Å and $c=7.58$ Å. Cell dimensions for the analyzed erionites show the following ranges: $a=13.21$ – 13.25 Å, and $c=15.04$ – 15.12 Å. Thus, the a dimension of offretite is larger than that of the erionites, and the doubled c dimension of offretite is larger than the c dimension of the erionites.

Figure 5 is a plot of the cell volume versus the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio for the analyzed erionites. Offretite (sample 1) is also included on the plot; however, the doubled c dimension was used to calculate the cell volume for convenience of comparison. On this basis, offretite has a cell volume that is significantly larger than that of the erionites. Although there is much scatter among the erionites, the plot clearly shows that a decrease in the cell volume can be correlated with an increase in the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio. There is about a 2 percent decrease in cell volume from offretite to

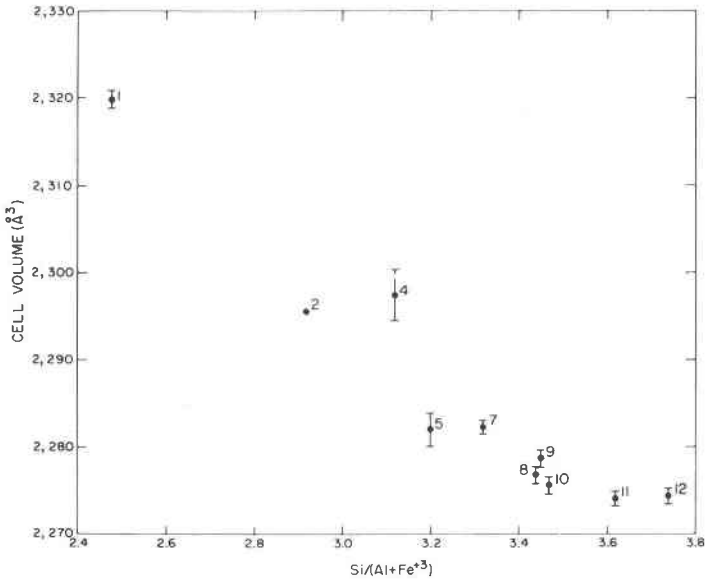


FIG. 5. Variation in the cell volume versus $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio for offretite and erionite. Standard error in cell volume is represented by bar. Samples are same as given in Table 1. No available data for samples 3 and 6.

the most siliceous analyzed erionite. Among the analyzed erionites, the decrease is about 1 percent. An unanalyzed erionite collected near Rome, Oregon, has a cell volume of $2,268 \text{ \AA}^3$ and indicates a $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio even higher than that of the most siliceous analyzed erionite. Erionite of the zoned offretite-erionite crystals from Montbrison has a cell volume of $2,301 \text{ \AA}^3$ which is slightly larger than that of the analyzed erionites. This large cell volume coupled with relatively high indices of refraction suggest that this erionite has a $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio close to that of offretite. Recent study of chabazites (Gude and Sheppard, 1966, p. 914) showed that siliceous varieties have a cell volume that is as much as 2.7 percent smaller than that of aluminous varieties.

DISCUSSION

In addition to the halved c dimension of offretite that was recognized by Bennett and Gard (1967) and Harada *et al.* (1967), optic sign, relatively high indices of refraction, and distinctive X-ray powder diffractometer pattern can be used to distinguish offretite from erionite. Offretite is also relatively aluminous compared to the analyzed erionites. A compositional gap in the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio seems to exist between offretite and the most aluminous erionite; however, the gap may only

seem to exist because of the paucity of analyses. Although most of the analyzed erionites have an excess of alkalis over alkaline earths as contrasted to offretite, cation content is not an adequate basis for distinguishing the zeolites.

The indices of refraction and cell volume of erionite can be correlated with the $\text{Si}/(\text{Al} + \text{Fe}^{3+})$ ratio. Siliceous erionites have relatively low indices of refraction and small cell volumes. Similar relationships have been found for analcime (Saha, 1959), chabazite (Gude and Sheppard, 1966), and phillipsite (Hay, 1964).

The chemical compositions of offretite and erionite seem to have been controlled, at least in part, by the compositions of the host rock. Siliceous and alkalic members occur in rhyolitic tuffs, whereas aluminous and alkaline earth-rich members occur in mafic lavas. Offretite and the most aluminous erionite from Mazé, Japan (Harada *et al.*, 1967), are the only analyzed specimens that occur in basalt. Kamb and Oke (1960) have also described erionite from basalt near Wenatchee, Washington. Although this erionite was not analyzed, its reported index of refraction (1.474) is high and indicates a relatively low $\text{Si}/(\text{Al} + \text{Fe}^{3+})$ ratio. Thus, if additional offretites or erionites are found to fill the apparent compositional gap, they will probably be found in basaltic rocks.

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