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CATION EXCHANGE PROPERTIES OF WAIRAKITE AND ANALCIME

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Introduction

The problem of the relationship between wairakite and calcium-analcime is a recurring one. Barrer (1950) first reported the reaction of analcime with calcium cations to result in no appreciable calcium exchange for sodium at 25° C. Ames and Sand (1958) reported the synthesis of wairakite, as did Koizumi and Roy (1960), and Barrer and Denny (1961). Barrer and Denny also reported the synthesis of two calcium-analcimes, listing the wairakite as well under calcium-analcime. Both calcium-analcimes exhibited the 6.81 Å spacing usually associated with wairakite. Hoss and Roy (1960), however, obtained both wairakite and calcium-analcime in their alteration studies and differentiated the above-cited phases because of the absence of the 6.81 Å reflection in the calcium-analcime *x*-ray diffraction pattern. Barrer and Marshall (1964) reported a fifty per cent yield of strontium-analcime that did not exhibit the 6.81 Å wairakite reflection. The strontium-analcime synthesis could not be duplicated. Structural classification problems within the analcime group were discussed by Smith (1963).

During the present work, strontium and calcium-analcimes and wairakite were synthesized reproducibly and their ion exchange properties compared with natural wairakite and analcime. The results are presented here for possible use in clarifying the relationships between the various analcimes and wairakite.

Methods of Investigation

Calcium and strontium-based analcimes were made by a method similar to that reported by Hoss and Roy (1960). Sodium-based natural phillipsite from Nevada, approximately $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 5H_2O$, was based with calcium or strontium, placed in a 150 ml bomb with two grams of calcium or strontium hydroxide, and held at 15,000 psi hydrostatic pressure and 280° C. for seven days. Two such treatments were given the material in one case, but the *x*-ray diffraction pattern showed little change as a result of the extra hydrothermal treatment.

The wairakite was synthesized from Ludox SM silica suspension and calcined nitrates of aluminum and calcium in a 150 ml bomb for 30 days

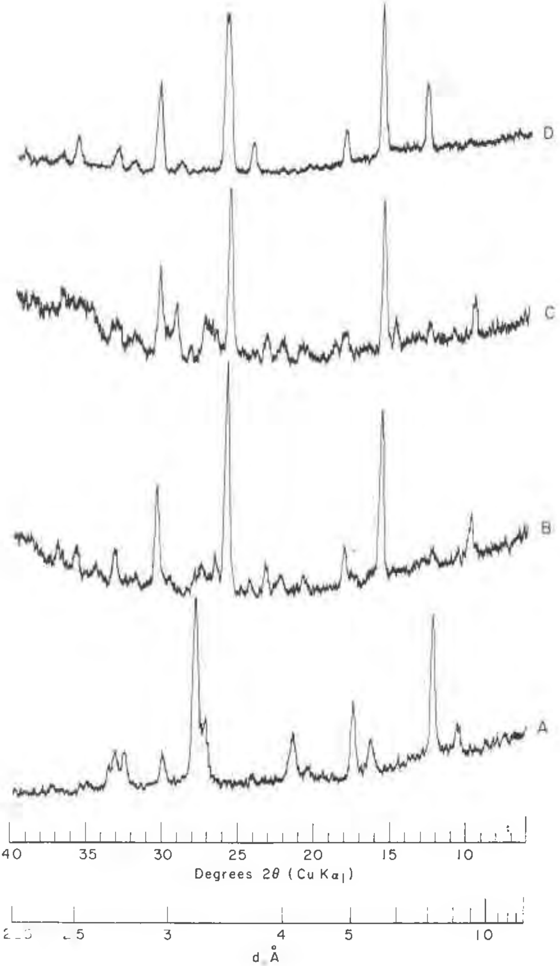

FIG. 1. *X*-ray diffraction tracings of: A) natural, calcium-based Nevada phillipsite; B) synthetic, calcium-based analcime derived from (A); C) synthetic, strontium-based analcime derived from strontium-based (A); D) natural wairakite used in this study.

at 315° C. and 15,000 psi hydrostatic pressure. The starting composition was $CaO \cdot Al_2O_3 \cdot 5SiO_2$.

The natural analcime was from Hector, California, and the natural wairakite from the 2750 foot level of Drillhole 218 at Wairakei, New Zealand. The wairakite occurrence at Wairakei was described by Steiner (1953, 1955). *X*-ray diffraction patterns of the wairakite and Nevada phillipsite used in this study are given in Fig. 1. The natural analcime was derived from a waterlaid tuff (Ames *et al.* 1958), and was eighty to ninety per cent pure analcime with calcite the major impurity. The wairakite was removed by hand from tuff surfaces, and was greater than 95 per cent wairakite.

The analcime cation exchange capacities for different cations, such as sodium and strontium, were found to be markedly dissimilar. While a previously-employed, double-tracing, technique for zeolite capacity determinations may be satisfactory for the determination of a composite binary system capacity (Ames, 1964), it would be of value in the present study to know the absolute zeolite capacity for each cation. Hence another technique, that of isotopic dilution, was utilized. Isotopic dilution as applied to exchange capacity determinations can be summarized as follows (Meites and Thomas, 1958, p. 364):

$$N_0 = \frac{A_a \cdot N}{A_s} - N, \qquad \text{(a)}$$

where

N_0 = cation exchange capacity
N = milliequivalents of cation in the equilibrating solution,
A_a = original tracer counts in the equilibrating solution, and
A_s = final tracer counts in the equilibrating solution.

The zeolite sample is first based using the cation with which the capacity is to be measured. The zeolite is then washed clean of extraneous basing cations and contacted with a solution containing a known number of milliequivalents of basing cation plus the same radioactive tracing cation. In the case of sodium, for example, the zeolite is based with sodium washed until sodium-free wash water is obtained and contacted with a solution containing sodium plus sodium-22. The capacity for the given cation is determined by using the relationship given in equation (a).

The principal potential errors in exchange capacity determinations utilizing isotopic dilution are failure to wash the zeolite sample free of excess basing cation, resulting in a low capacity value, and failure to completely equilibrate the zeolite with the final solution containing the tracer. In the latter case, the resulting exchange capacity also would tend to be less than the actual capacity value. Equilibration time was three days in all cases.

The isotherms for calcium-based analcimes were obtained by a standard method described elsewhere (Ames, 1964). High purity sodium-22, strontium-85 and calcium-45 radiosiotopes were used in distilled water solutions of reagent grade chemical compounds.

RESULTS AND DISCUSSION

The x-ray diffraction patterns of calcium-based phillipsite, the resulting calcium-based analcime, a strontium-based analcime and natural wairakite are given in Fig. 1. Note the similarity between the calcium and strontium-based analcime patterns. The 9.1 Å reflection ordinarily would indicate a small amount of mordenite, but the absence of the other two main mordenite reflections at 3.48 Å and 3.22 Å indicate that the presence of mordenite is highly unlikely. The 6.81 Å reflection of wairakite is not represented on either the calcium or strontium-based patterns. Both of the synthetic analcimes are very likely noncubic (Coombs, 1955).

TABLE 1. THE EXCHANGE CAPACITIES OF THE VARIOUS ANALCIMES AND WAIRAKITES AS MEASURED BY AN ISOTOPIC DILUTION METHOD AT 25° C. THE SYNTHETIC ANALCIMES WERE MADE BY HYDROTHERMAL TREATMENT OF NATURAL PHILLIPSITE

Zeolite Sample	Cation Exchange Capacity, meq/g		
	Na^+	Ca^{2+}	Sr^{2+}
Hector analcime (natural)	1.7	0.5	0.3
Wairakei wairakite (natural)	nd	nd	nd
Calcium-based analcime (synthetic)	1.5	1.5	nd
Strontium-based analcime (synthetic)	1.1	1.1	nd
Wairakite (synthetic)	nd	nd	nd

nd = less than 0.03 meq/g.

The exchange capacities, as determined with sodium, calcium and strontium, of the analcimes and wairakites are given in Table 1. The exchange capacity of the natural analcime from Hector, California decreases steadily from 1.7 meq Na^+/g to 0.3 meq Sr^{2+}/g. The presence of 5 to 15 per cent finely disseminated calcite admixed with the Hector analcime results in an apparent calcium and strontium exchange capacity. The pure synthetic analcime, however, had a negligible calcium and strontium capacity, as reported previously by Barrer (1950). Cation diameter rises from 1.88 Å for Na^+ to 2.24 Å for Sr^{2+}. Cation size is not the whole explanation as potassium, ammonium, rubidium and thallium-based analcimes are known (Barrer, 1950), containing twice as many cations as a strontium-based analcime and often of larger diameter than Sr^{2+}.

According to Taylor (1930), the aperture size of analcime is 2.8 Å, certainly large enough to accommodate a 2.24 Å diameter strontium cation. Perhaps a combination of unfavorable cation size and cation spatial distribution is responsible for the low strontium capacity of natural analcime, as suggested by Barrer (1950). The results of this study suggest, in addition, that the cause of analcime having calcium capacity at all is the presence of calcium or strontium during the formation of the analcime.

Calcium-based analcime, on the other hand, shows the same sodium and calcium capacity but a negligible strontium capacity. Strontium-based analcime likewise has the same sodium as calcium capacity as well as a negligible strontium capacity (less than 0.03 meq/g). Assuming that the cation exchange behavior of the calcium and strontium-based analcimes also is influenced by a combination of cation size and spatial distribution in respect to the anionic sites, certain structural differences among the analcimes are apparent. The spatial positions of the calcium and strontium in their respective analcimes can be specifically "tailored" to hold those cations when synthesized with calcium or strontium only. This "tailoring" probably results in a distorted sodium-analcime structure.

The lack of strontium-strontium exchange by even the strontium-based analcime probably indicates that the strontium cation is too large, considering the structural "tailoring" necessarily imposed on the normal analcime structure by synthesis from strontium cations only, to allow strontium self-diffusion and self-exchange. The smaller calcium and sodium cations can diffuse and exchange with the strontium. Wairakite is another structure, entirely adapted to accommodate divalent calcium ions only. Further, the calcium ions are not exchangeable—as indicated by lack of a measurable calcium or sodium cation exchange capacity. Wairakite, then, occupies a position in the alkaline earth metal cation series analogous to pollucite in the alkali metal cation series. Based on the *x*-ray data and apparently metastable character of Barrer and Marshall's strontium-analcime, it is doubtful that a stable strontium-analcime exists. The ion exchange character of strontium and calcium-based analcimes is apparent from the isotherms presented in Fig. 2. Note that while the sodium and calcium exchange capacities of the two analcimes are not the same, their exchange isotherms are quite similar when plotted on fractional scales as shown in Fig. 2. The strontium-analcime was exchanged to calcium-analcime before equilibration with sodium-calcium solutions. The preference of both zeolites for sodium is marked, indicating, in the author's opinion, that analcimes of this type are distorted sodium-analcimes that partially revert to the simple cubic structure of sodium-analcime when contacted with sodium cations. The occurrence of calcium or strontium-based analcimes in nature would be highly unusual because of their tendency to revert to a normal, but noncubic, sodium-analcime. These cation exchange results support the views of Steiner (1955) and

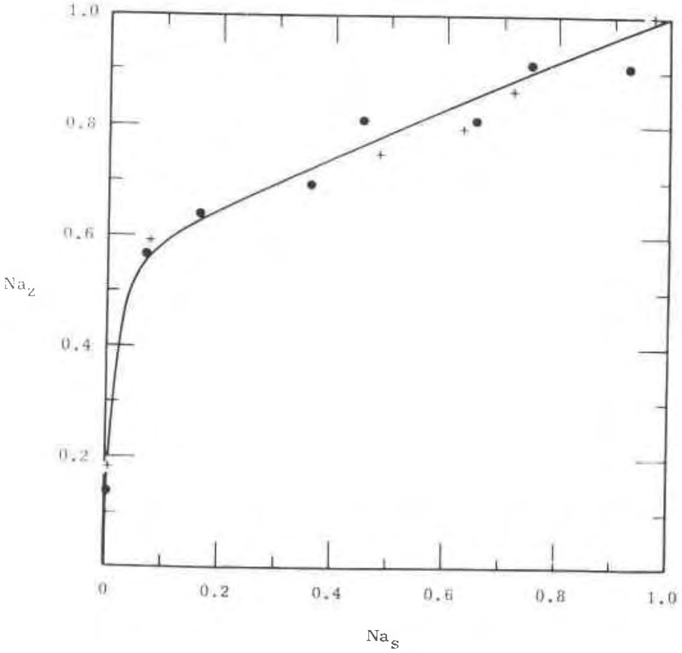

FIG. 2. The 25° C. isotherm for the reaction $Ca_z+2Na_s \leftrightarrows 2Na_z+Ca_s$. Total equilibrium solution normality was constant at one.

● = equilibrium compositions of calcium-based analcime and solution with the analcime made by hydrothermal treatment of calsium-based phillipsite; cation exchange capacity = 1.5 meq/g.

+ = equilibrium compositions of calcium-based analcime and solution with the analcime made from calcium exchange of strontium-based analcime, in turn made from hydrothermal treatment of strontium-based phillipsite; cation exchange capacity = 1.1 meq/g.

Na_z = the equivalent fraction of sodium on the zeolite.

Na_s = the equivalent fraction of sodium in the equilibrium.

Coombs (1955) who suggested that if an analcime-wairakite series existed, isomorphous substitutions of calcium for sodium were very limited.

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SILICA-RICH CHABAZITE FROM THE BARSTOW FORMATION, SAN BERNARDINO COUNTY, SOUTHERN CALIFORNIA[1]

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The Barstow Formation of middle and late Miocene age (Lewis, 1964) is a thick sequence of fluviatile and lacustrine rocks. Mudstones and sandstones are dominant, but locally more than 30 relatively thin tuffs are recognized. Recent work by the authors on the alteration of the tuffs has shown that much of the vitric material is replaced by zeolites, potash feldspar, opal and (or) montmorillonite. These authigenic minerals are generally so finely crystalline that positive identification can be made only by *x*-ray techniques. Routine examination of *x*-ray diffractometer traces of bulk samples of an altered tuff from the upper part of the formation indicated that some samples consist mainly of a zeolite having a diffractometer pattern similar to chabazite. Detailed study of the diffrac-

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