

481. Ion-exchange and Ion-sieve Processes in Crystalline Zeolites.

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Ion-exchange properties of analcite and chabazite have been investigated and compared by using percolation, hydrothermal, vapour-phase, and melt methods. Analcite interchanged Na^+ freely for K^+ , NH_4^+ , Ag^+ , Tl^+ , and Rb^+ , but gave slight or negligible exchange of Na^+ for Li^+ , Cs^+ , Mg^{++} , Ca^{++} , or Ba^{++} . There was a complete ion-sieve effect between Rb^+ (radius 1.48 Å.) and Cs^+ (radius 1.65 Å.). Chabazite on the other hand exchanged freely among the ions Li^+ , Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , Ag^+ , Tl^+ , Ca^{++} , Sr^{++} , and Ba^{++} . Of ions tried only Mg^{++} failed to exchange.

The extent of hydration of ion-exchanged forms was determined, and also the extent to which lattice modification through exchange could be detected by X-ray powder photography. Minor changes from cubic to near tetragonal were often noted with ion-exchange analcites, but with chabazite there were no significant alterations. The ease of exchange is discussed in terms of the openness and character of the aluminosilicate framework; cationic radius and valency; ion-hydration and other factors. Recrystallisation was often found to supersede ion exchange, and the formation of several species including pollucite was examined.

CHABAZITE $[(\text{Ca}, \text{Na}_2)\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 6\text{H}_2\text{O}]$, mordenite $[(\text{Na}_2, \text{Ca}, \text{K}_2)\text{O}, \text{Al}_2\text{O}_3, 10\text{SiO}_2, 6\frac{2}{3}\text{H}_2\text{O}]$, and analcite $(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O})$ form a triad of crystals permeated by interstitial channels which become progressively less open in the order given. The character and the dimensions of these channels have been closely studied by molecular-sieve methods (Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195, 206; Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130T, 132T; Barrer and Belchetz, *ibid.*, 1945, **64**, 131T; Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555; Barrer and Riley, *J.*, 1948, 133). Some time ago an investigation was commenced of the ion-exchange properties of the three minerals, with a view to the production of modified molecular-sieve sorbents, and the study of ion-sieve behaviour among the species.

Part of this programme has been carried out. Mordenites modified by ion exchange show interesting gradations in molecular-sieve action (within limits set by the character of the

aluminosilicate framework) which lead to new possibilities of separating molecular mixtures (Barrer, *Trans. Faraday Soc.*, 1949, **45**, 363). A similar study of the effects of exchange on sorption equilibria has been made, by using some of the ion-exchange forms of chabazite to be described later (Barrer and Riley, *Trans. Faraday Soc.*, in the press). Ion-exchange processes involving analcite and chabazite will now be discussed and compared between themselves, and with those of mordenite (Barrer, *J.*, 1948, 2158). These three zeolites differ, as ion-exchange media, from clay minerals and amorphous or gel zeolites in that they are not subject to marked swelling and shrinking during exchange. Because they are based on non-shrinking aluminosilicate frameworks they are potentially capable of functioning as ion sieves just as they function as molecular sieves.

Previous work on exchange in crystalline zeolites is fragmentary. It includes, *inter alia*, studies on mordenite (Barrer, *J.*, 1948, 2158) and chabazite (Wiegner and Cernescu, *Trans. Internat. Congr. Soil Sci.*, 3rd Conf. Oxford, 1935, III, 5). Zoch (*Chem. Erde*, 1914, **1**, 219) has made measurements on several zeolites, finding the ease of entry of the ammonium ion in the order chabazite and stilbite > heulandite > harmotome > scolecite, and Gans (*Jahresb. Preuss. Geol. Landesanstalt, Berlin*, 1905, **26**, 188) had previously noted that chabazite, heulandite, and stilbite underwent exchange more readily than did analcite and natrolite. Clark and Steiger (*Amer. J. Sci.*, 1902, **13**, 27; *Z. anorg. Chem.*, 1902, **29**, 338; *U.S. Geol. Survey Bull.*, 1902, 207), Steiger (*Amer. J. Sci.*, 1902, **14**, 31), and Hey (*Min. Mag.*, 1930, **22**, 422; 1932, **23**, 51, 243; 1933, **23**, 421; 1934, **23**, 483; 1936, **24**, 227) have also made observations of ion exchange in a variety of crystalline zeolites. These data are difficult to compare. The crystal-chemical characters among the zeolites used are diverse; fibrous, laminar and robust framework crystals have all been used. Close comparisons like that now made between analcite and chabazite are essential for an understanding of ion exchange, and are a necessary preliminary to quantitative measurements suitable for testing and developing theories of ion exchange and of solid-state reactions.

EXPERIMENTAL.

Materials.—The chabazite crystals were naturally occurring white crystals from Kyogle, N.S.W., Australia, and pink crystals of Canadian origin. They were freed by hand picking from any rock matrix and ground before being used in ion-exchange studies. Analcite was grown hydrothermally as spheroidal and ikositetrahedral crystals small enough to be used as a rule without further grinding. They were formed by treating gels of approximate composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ with distilled water at $\sim 200^\circ$ in steel autoclaves (cf. Barrer, *J.*, 1948, 127, 2158; *Faraday Soc. Discussion*, No. 5, 1949, p. 326). The yields of analcite approached 100%.

The salts used were chlorides, carbonates, nitrates, nitrites, or sulphates of calcium, strontium, barium, lithium, sodium, silver, potassium, ammonium, thallium, rubidium, and caesium. Where possible they were of AnalaR quality.

Ion-exchange Methods.—Four procedures for effecting ion exchange were employed: percolation, hydrothermal, fusion, and vapour-phase methods. Percolation is a comparatively mild technique, being confined as a rule to low temperatures ($\leq 100^\circ$). Hydrothermal exchange reactions carried out in steel autoclaves were most commonly studied in the temperature range 150° to 310° . The autoclaves had about 20-c.c. capacity. 1–2 G. of powdered zeolite crystals were mixed with an excess of the exchanging salt, placed in the autoclave with 5–15 c.c. of water, and heated for periods between 12 hours and 5 days. The products were carefully washed free from entrained salts, and sometimes hydrothermally extracted with distilled water. They were then dried and stored.

Exchange by the fusion method, *i.e.*, by use of molten salts, required the m. p. of the salt to be low enough to eliminate danger of lattice collapse in the zeolite at the reaction temperature. Barium nitrite (m. p. 217°) was used successfully to introduce barium into chabazite,* and lithium nitrate (m. p. 255°) was also used in this way. Exchange *via* the vapour phase was limited to the use of ammonium salts and so to the introduction of ammonium ions, but the method was often remarkably efficient.† The method was used at 208° , 248° , 340° , and 350° , and easily produced NH_4 -analcite, -mordenite, and -chabazite. Both ammonium chloride and zeolite crystals were first outgassed to remove water and so prevent development of a high pressure of water vapour at the experimental temperature. Reaction was carried out in sealed glass tubes and, as before, all products were after reaction carefully freed from entrained and occluded salt.

Optical and X-Ray Examination of Products.—The crystalline reaction products were examined with a Leitz polarising microscope. Crystal form, birefringence, and refractive indices were observed normally in white light, but sometimes in sodium light. The optical method was very useful in demonstrating homogeneity or inhomogeneity of the products. X-Ray powder photographs were taken by using Hilger HRX equipment with 9-cm. cameras and filtered $\text{Cu-K}\alpha$ radiation. Exposures were of 6–8 hours duration. In subsequent measurements of the spacings from powder photograph intensities of the diffraction arcs were at the same time estimated visually. The X-ray method at once established the

* Hydrothermal exchange with barium chloride was equally successful.

† This procedure appears to have been originated by Clark and Steiger (*loc. cit.*).

close similarity between ion-exchanged forms and the parent mineral, or showed when recrystallisation had occurred.

Chemical Examination of Products.—In a number of reactions the amount of the ion characteristic of the zeolite displaced by exchange into the mother-liquor was carefully determined. This procedure was particularly useful when the ion-exchange products were needed intact for investigation as sorbents or for other purposes. In a further group of these ion-exchange reactions partial chemical analyses of the solids were made. Such analyses were confined to determinations of the cations present and so gave the extent of ion exchange. Both these methods of examination were supplemented by taking X-ray powder photographs to demonstrate that no recrystallisation of the aluminosilicate framework had occurred. Such a proof usually renders unnecessary a complete determination of $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratios. However, in a third group of the exchange products more complete chemical analyses were carried out, including determinations of $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratios. These analyses confirmed the assumption that in the experimental conditions cation interchange normally occurred without change in the molar ratios of silica to alumina. Standard analytical methods were employed for silicates and for the several cations, although in one or two cases special procedures were used. Ammonium was determined by decomposing the NH_4 -zeolite with boiling concentrated aqueous sodium hydroxide and absorbing the ammonia in standard acid. Water was determined by measuring the total loss in weight on ignition (ammonia and water) and then calculating from the NH_4^+ content previously found how much water had also been lost.

Results.—Some of the successful ion-exchange experiments are summarised in Table I. The mildest method used was the percolation procedure, which revealed a marked difference between analcite and chabazite. At 20° and 100° analcite gave, by percolation, no evidence of exchange with magnesium chloride and calcium chloride solutions and only slight exchange with aqueous potassium chloride. On the other hand, even at 20° prolonged percolation of sodium chloride and potassium chloride solutions through chabazite gave extensive exchange; only aqueous magnesium chloride still showed negligible interchange. These results accord with the more open diffusion paths permeating the chabazite crystals, compared with those in analcite, and with the less basigenic character of magnesium than of alkaline-earth and alkali metals.*

The more vigorous methods of effecting exchange (by use of fused salts, ammonium chloride vapour, or hydrothermal treatment) demonstrated further differences between chabazite and analcite. Chabazite readily exchanged with Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Ag^+ , Ca^{++} , Sr^{++} , and Ba^{++} . Mordenite (Barrer, *J.*, 1948, 2158) has previously been shown to exchange with Li^+ , Na^+ , K^+ , NH_4^+ , Ca^{++} , and Ba^{++} . In each case there was among these ions no critical factor of valency or of ionic radius. Crystals of both species may accommodate both uni- and bi-valent cations. Analcite on the other hand underwent exchange with Na^+ , K^+ , NH_4^+ , Ag^+ , Tl^+ , and Rb^+ ; but with Li^+ , Cs^+ , Ca^{++} , and Ba^{++} interchange occurred only to a limited or negligible extent even under extreme conditions (Table II). The crystal can readily accommodate only univalent cations, but not all univalent ions (see Discussion).

There appears to be one difference between mordenite and chabazite. Chabazite (see Table I) gives evidence of intracrystalline occlusion of salt in one or two instances, in addition to exchange. Mordenite (Barrer, *J.*, 1948, 2158) did not give evidence of this occlusion. This observation is in accordance with the more open channels in chabazite, as determined from its molecular-sieve properties. The channels in chabazite are able to contain simple species such as ammonium chloride in addition to the exchanging cations. The narrower channels in mordenite (and the still narrower ones in analcite) are unable to accommodate such species.

Recrystallisation Reactions.—Recrystallisation reactions additional to exchange were observed with analcite and leucite under appropriate conditions using solutions of potassium hydroxide, sodium hydroxide, sodium fluoride, potassium fluoride, potassium carbonate, sodium carbonate, potassium chloride, sodium chloride, sodium sulphate, barium chloride, barium bromide, lithium chloride, and lithium nitrate. This led to a diversity of crystalline aluminosilicates and shows that analcite (or leucite), which is easily made in $\sim 100\%$ yield, is an excellent starting material for syntheses of geochemical as well as chemical significance. These reactions will, however, be described in another paper.

Chabazite also underwent several recrystallisation reactions of considerable interest. As noted in the previous section (see Table II) it was impossible to obtain pollucite (*i.e.*, Cs-analcite) from analcite or leucite by ion exchange, although the three species analcite, leucite, and pollucite are based upon nearly the same aluminosilicate framework (W. H. Taylor, *Repts. Prog. Physics*, 1939, 358) and leucite and analcite are readily interconvertible merely by ion exchange ($\text{Na}^+, \text{H}_2\text{O}$ interchangeable with $\text{K}^+ + \text{H}_2\text{O}$). Nevertheless the much more profound change of chabazite into pollucite occurred readily and unexpectedly under the conditions given in Table III.

Two additional recrystallisation reactions were obtained by using chabazite, each yielding species which have no natural counterparts but have previously been synthesised in the author's laboratory. These minerals were $\text{BaO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, n\text{BaCl}_2, m\text{H}_2\text{O}$ ($n = \sim 0.66$; $2 < m < 3$) (Barrer, *J.*, 1948, 127) and $\text{Ti}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ (H. F. W. Taylor, *J.*, 1949, 1253). The barium mineral was formed occasionally when chabazite was treated at $\sim 200^\circ$ with water and excess of barium chloride (Table III). This mineral has been grown readily from analcite, leucite, and gels (Barrer, *J.*, 1948, 127), and so its formation from chabazite was not studied further.

* Magnesium is not normally found in any naturally occurring zeolites. These contain as cations one or more of Na, K, Ca, Sr, and Ba. A similar experiment, in which chabazite was left in contact with aqueous copper sulphate for 18 months, gave no evidence of exchange of Na or Ca for feebly basigenic Cu. Only the *surfaces* of the chabazite crystallites became stained with a green basic copper sulphate.

TABLE I.

Successful exchange reactions with analcite and chabazite.

Ion.	Reaction conditions.	Observations.	Conclusion.
	(a) <i>Synthetic analcite</i> (refractive index, n , 1.48 ₆).		
K ⁺	Analcite given two treatments with aq. KCl (KCl in excess). Each treatment, 1 day at 216°.	X-Ray pattern identical with that of natural leucite. Na ₂ O : K ₂ O : Al ₂ O ₃ : SiO ₂ = 0.04 : 0.91 : 1.00 : 3.80; H ₂ O, 1.51%; n , 1.51.	Exchange nearly complete.
NH ₄ ⁺	Analcite heated with NH ₄ Cl vapour at ~340° for 16 hours.	X-Ray pattern rather similar to that of leucite, but with characteristic differences. (NH ₄) ₂ O, 11.1; H ₂ O, 1.5%; Na and Cl, trace. n , 1.52 ₄ .	Exchange complete.
Rb ⁺	Analcite and an equal volume of RbCl heated with 5 c.c. of H ₂ O for 48 hours at 182°.	X-Ray pattern characteristic, based on analcite and pollucite. n , 1.51. H ₂ O, 1.9%. Rb ₂ O : Na ₂ O = 0.85 : 0.15 (molar).	Exchange extensive.
Tl ⁺	Analcite (1 g.) + Tl ₂ SO ₄ (3 g.) heated with 10 c.c. of H ₂ O and 2 drops 2N-NaOH at 160° for 5 days.	X-Ray pattern identical with that of Tl-analcite crystallised hydrothermally from Tl ₂ O, Al ₂ O ₃ , 4SiO ₂ gel (Taylor, <i>J.</i> , 1949, 1253). Diffraction arcs remarkably similar in spacing to Rb-analcite. n , 1.64. H ₂ O, 0.5; Tl ₂ O, 49.3%.	Exchange nearly complete.
Ag ⁺	Analcite (1 g.) + AgNO ₃ (3 g.) heated with 10 c.c. of H ₂ O at 160° for 5 days.	X-Ray pattern very similar to that of analcite in spacings but not intensity. n , 1.56. H ₂ O, 8.6; Ag ₂ O, 20%.	Exchange considerable.
	(b) <i>Chabazite</i> (n , 1.49 ₂ *).		
Ba ⁺⁺	Chabazite heated with molten Ba (NO ₃) ₂ at 270° for 44 hours.	Analysis gave BaO : Al ₂ O ₃ : SiO ₂ = 0.70 : 1.00 : 4.13; also H ₂ O, 18.9%. †	Exchange considerable.
Sr ⁺⁺	Chabazite heated with aq. SrCl ₂ (salt in excess) for 2 days at 240°.	X-Ray pattern of chabazite with slightly modified intensities. H ₂ O, 19.3; CaO, 1.5%; SrO, 12.8%. Much occluded. SrCl ₂ removed (before X-ray and analysis made) by hydrothermal extraction twice at 248° for 2 days with distilled water. The SrCl ₂ could not be washed out at 100°.	Exchange considerable.
NH ₄ ⁺	(i) 4 G. of chabazite heated with solid NH ₄ Cl at 206° for 22 hours.	On heating of the product at 350°, copious NH ₄ Cl evolved from crystals previously thoroughly washed. Thus NH ₄ Cl had been occluded. 0.120 G. of CaO in mother-liquor from aqueous washings.	Partial exchange.
	(ii) Product from (i) heated with NH ₄ Cl at 248° for 1 day.	Again copious NH ₄ Cl evolved at 350° from crystals washed and dried. Washings contained 0.345 g. of CaO. X-Ray pattern of chabazite with modified intensities; n , 1.48 ₇ .	Exchange nearly complete.
Li ⁺	Chabazite heated with aq. LiNO ₃ (salt in excess) for 2 days at 248°. Two treatments given.	Considerable Ca displaced into washings. Chabazite pattern with modified intensities. n , 1.48. H ₂ O, 14.2; Li ₂ O, 2.0; CaO, 3.4% (<i>i.e.</i> , about 30% exchange).	Exchange partial.
Na ⁺	Chabazite (<200 mesh) treated with n-NaCl at 20° by continued percolation.	X-Ray pattern of chabazite (also similar to that of allied zeolite gmelinite). Initially zeolite gave CaO, 10.1; Na ₂ O, 2.1%. After exchange it contained 0.5% of CaO, 10.3% of Na ₂ O and 23.7% of H ₂ O and had n 1.47 ₇ .	Exchange extensive.
K ⁺	Chabazite (<200 mesh) treated with n-KCl at 20° by continued percolation.	X-Ray pattern of chabazite with modified intensities. Initially zeolite gave: CaO, 10.1 and Na ₂ O, 2.1%. After exchange it contained: CaO, 1.0; Na ₂ O + K ₂ O, 15.3; H ₂ O, 18%. n , 1.48.	Exchange extensive.
Rb ⁺	0.5 G. of chabazite + 1 g. of RbCl + 5 c.c. of H ₂ O heated for 2 days at 152°.	X-Ray pattern of chabazite with some modified intensities. 9% (by wt.) of CaO replaced by Rb ₂ O. H ₂ O, 11.2%. n , 1.48.	Exchange extensive.
Cs ⁺	1 G. of chabazite + 2 g. of CsCl + 5 c.c. of H ₂ O heated for 4 days at 151°.	X-Ray pattern of chabazite with some modified intensities. 5.5% (by wt.) of CaO replaced by Cs ₂ O. H ₂ O, 8.2%. n , 1.49 ₄ .	Exchange considerable.
Ag ⁺	1 G. of chabazite + 3 g. of AgNO ₃ heated with 10 c.c. of H ₂ O for 5 days at 160°.	X-Ray pattern of chabazite with some modified intensities. 11.2% (by wt.) of CaO replaced by Ag ₂ O. n , 1.49. H ₂ O, 11.6%.	Exchange complete.

* In all cases mean values only of n are given. Crystals were birefringent, and among ion-exchange forms not always of uniform n .

† The water in barium chabazite was determined on a second preparation made hydrothermally, by using aqueous barium chloride.

TABLE II.

Experiments demonstrating difficulty of exchanging Na^+ in analcite for Li^+ , Cs^+ , Ca^{++} , or Ba^{++} .

Ion.	Reaction conditions.	Observations (including analysis).	X-Ray pattern (powder photograph).	Conclusion.
Li^+	Analcite heated with molten LiNO_3 for 2 days at 290° .*	Na_2O , 13.6; Li_2O , 0.84%.	—	Negligible exchange.
Ba^{++}	Analcite heated with molten $\text{Ba}(\text{NO}_3)_2$ for 44 hrs. at 270° .	Two expts. gave BaO , 6.5% and negligible, respectively. Some decomposition of analcite.	—	Exchange limited, and some decomposition.
	Analcite heated with aq. $\text{Ba}(\text{NO}_3)_2$ (salt in excess). Six treatments, each of 2 days, at 200° .	Na_2O (by diff.) : BaO : Al_2O_3 : SiO_2 : H_2O = 0.75 : 0.20 : 1.00 : 3.99 : 2.2.	—	Exchange limited.
	Analcite heated with aq. $\text{Ba}(\text{NO}_3)_2$ (salt in excess). Six treatments, each of 2 days, at 208° .	Na_2O : BaO : Al_2O_3 : SiO_2 : H_2O = 0.08 : 1.46 : 1.00 : 4.00 : 3.54.	Not analcite or harmotome. Some amorphous.	Decomposition and partial recrystallisation.
	Analcite heated with aq. $\text{Ba}(\text{NO}_3)_2$ (salt in excess). Four treatments, each of $2\frac{1}{2}$ days, at 310° .	BaO : Al_2O_3 : SiO_2 : H_2O = 0.98 : 1.00 : 4.00 : 2.08.	Largely amorphous.	Decomposition.
	Analcite heated with aq. $\text{Ba}(\text{NO}_3)_2$ (salt in excess). Five treatments, each of 1 day, at 176° .	Na_2O : BaO : Al_2O_3 : SiO_2 : H_2O = 0.95 : 0.04 : 1.00 : 3.98 : 1.06.	Analcite.	Negligible exchange.
Ca^{++}	Analcite heated with aq. CaCl_2 (salt in excess). Five treatments, each of 12 hours, at 200° .	CaO : Al_2O_3 : SiO_2 : H_2O = 0.36 : 1.00 : 4.03 : 1.80.	—	Partial exchange.
	NH_4 -analcite prepared as in Table I(a) heated with aq. $\text{Ca}(\text{NO}_3)_2$ (salt in excess). Four treatments, each of 3 days, at 220° .	$(\text{NH}_4)_2\text{O}$: CaO : Al_2O_3 : SiO_2 : H_2O = 0.33 : 0.41 : 1.00 : 3.32 : 1.63. Product still zeolitic sorbent to NH_3 , but some decomposition.	—	Partial exchange, with some decomposition.
	NH_4 -analcite as above heated with excess of $\text{Ca}(\text{OH})_2 + \text{H}_2\text{O}$ for 16 hours at 280° .	Material considerably altered.	Weak, and different from that of analcite.	Decomposition and recrystallisation.
Cs^+	NH_4 -analcite as above heated with aq. CsCl (salt in excess) at 220° for $3\frac{1}{2}$ days, then for 2 days at 290° with fresh CsCl (1 g.) + H_2O (15 c.c.).	Negligible NH_4^+ displaced into solution. n , 1.52 ₄ as in parent NH_4 -analcite. Cs_2O , 0.23%.	Identical with that of NH_4^+ -analcite.	Negligible exchange.
	K-analcite (leucite) of Table I(a) heated with aq. CsCl (salt in excess) for 2 days at 270° .	n still 1.50 ₆ , similar to that of original original leucite.	Identical with that of K-analcite.	Negligible exchange.
	Analcite heated with aq. CsCl (salt in excess) for 2 days at 270° .	n , 1.49 ₀ (cf. 1.48 ₆ for analcite, and 1.52 ₁ for pollucite).	Identical with that of analcite.	Negligible exchange.

* Hydrothermal methods were also used employing aqueous lithium chloride and lithium nitrate, with an excess of the salt. The analcite, however, recrystallised into several new lithium aluminosilicates.

TABLE III.

Exchange and recrystallisation of chabazite with CsCl, Tl_2SO_4 , and $BaCl_2$.

Reaction conditions.	Observations.	X-Ray pattern.	Conclusion.
Chabazite (1 g.) heated with 2 g. of CsCl and 5 c.c. of H_2O for 4 days at 151° (see Table I).	5.5% of CaO displaced into solution. Optical study showed no growth of pollucite.	Similar to chabazite.	Exchange, but no recrystallisation to pollucite.
Chabazite (1 g.) heated with 1 g. of CsCl and 5 c.c. of H_2O for 2 days at 182° .	6.1% of CaO displaced into solution. n , ~ 1.49 but not uniform. Small pollucite crystallites sometimes embedded in surface of larger chabazite crystals.	Similar to chabazite but with several, weak pollucite reflections.	Exchange, with some recrystallisation to pollucite.
Chabazite (1 g.) heated with 1 g. of CsCl and 10 c.c. of H_2O for 20 hrs. at 248° . Partial leak caused loss of some water.	Extensive recrystallisation to pollucite, n 1.522. Much CaO displaced into solution.	—	Recrystallisation to pollucite.
Product obtained above at 248° was further heated with 1 g. of CsCl and 10 c.c. of H_2O for 2 days at 248° .	Little further Ca displaced. Crystals, extracted several times with distilled water at 248° , liberated no Ca or Cl into mother-liquor.	Pollucite only.	Recrystallisation to pollucite complete.
Chabazite (1 g.) heated with 3 g. of Tl_2SO_4 and 10 c.c. of H_2O at 160° for 5 days. Twice extracted hydrothermally for 2 days at 220° until free from entrained Tl_2SO_4 .	Original chabazite crystals studded with spheroidal crystals. Extensive recrystallisation had occurred.	Pattern of species $Tl_2O, Al_2O_3, 4SiO_2$ analogous to those of analcite or leucite, and identical with Tl-analcite.	Recrystallisation to Tl-analcite.
Chabazite (2 g.) heated with excess of $BaCl_2$ and 5 c.c. of H_2O at 208° for 5 days.	Product extracted 5 times with boiling water. Considerable crystal regrowth.	Pattern of a synthetic Ba mineral previously grown hydrothermally.	Recrystallisation to species $BaO, Al_2O_3, 4SiO_2, nBaCl_2, mH_2O$ ($n = \sim 0.66$; $2 < m < 3$).*

* Barrer, *J.*, 1948, 127.

The thallium mineral was formed as spheroidal crystals when chabazite was heated at 160° with some water and an excess of thallium sulphate (Table III). H. F. W. Taylor (*loc. cit.*) has also grown it from gels, and it has been found that the X-ray powder photograph is identical with that of thallium analcite (Table IV). Taylor showed that this mineral can readily be converted into ordinary analcite by the reversible exchange of Na^+, H_2O with $Tl^+ + H_2O$. Accordingly one may at quite low temperatures convert chabazite into analcite by this procedure.

X-Ray Examination of Ion-exchanged Forms.—All ion-exchanged forms of chabazite and analcite were examined by X-ray powder photography. Within the closest limits it was possible to establish (i) the structural identity of leucite formed by ion exchange (*i.e.*, K-analcite) and a naturally occurring leucite, (ii) the identity of synthetic pollucite grown by recrystallising chabazite and of a naturally occurring specimen, and (iii) the identity of the mineral $TlAlSi_3O_8$ also grown from chabazite and Tl-analcite formed by ion exchange from analcite (Tables III and IV).

All the chabazite ion-exchanged forms, hydrothermally enriched in Li, Na, Ag, Sr, Ba, K, NH_4 , Rb, and Cs, were true chabazites with little or no observable variation in spacings from one another or from the parent chabazite crystals, although showing expected variations in relative intensities of some lines. It may be inferred that the chabazite aluminosilicate framework is open enough and rigid enough to accommodate all cations from Li^+ (the smallest; $r = 0.78$ A.) to Cs^+ (the largest; $r = 1.65$ A.), without significant alteration.

The analcite ion-exchanged forms, although retaining the analcite structure closely, suffered some small adjustments in the aluminosilicate framework. These changes are compatible with the view that the volumes occupied in the lattice by the units H_2O, Na^+ and Cs^+ are practically the same.† Thus both

* Ionic radii are taken from Evans, "Crystal Chemistry," Cambridge Univ. Press, 1938, p. 170. A similar set of radii is given by Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1937, p. 346, and by Slater, "Chemical Physics," McGraw-Hill, 1939, p. 383.

† Pollucite is often formulated as $(Na_2, Cs_2)O, Al_2O_3, 4SiO_2, H_2O$, *i.e.*, with half the water present in analcite. This water may be associated with the sodium, in which case a pure Cs-pollucite would be anhydrous; or it may be present in vacant sites in the crystal. W. H. Taylor (*Z. Kristall.*, 1930, **74**, 1) states that there are 24 sites per unit cell in analcite, occupied by only 16 Na^+ ions, and in pollucite which is isostructural with analcite an identical situation must arise. There are thus just enough vacant sites for water molecules to give the above formula; but these water molecules would *not* be associated with the Cs^+ ions. Moisture determination on a synthetic pollucite derived by recrystallising chabazite was not conclusive owing to the presence of a certain amount of the highly hydrated parent chabazite.

TABLE IV.
Identity of some natural and synthetic species.

Natural leucite.*		Synthetic leucite.		Natural pollucite.		Synthetic pollucite.		Ti ₂ O, Al ₂ O ₃ , 4SiO ₂ , prepd. by recrystallisation from chabazite.		Ti ₂ O, Al ₂ O ₃ , 4SiO ₂ , by ion-exchange from analcite.	
Spacing.	<i>I</i> .†	Spacing.	<i>I</i> .	Spacing.	<i>I</i> .	Spacing.	<i>I</i> .	Spacing.	<i>I</i> .	Spacing.	<i>I</i> .
5.37	s	5.40	ms	3.66	ms	3.65	ms	5.59	s	5.54	s
4.72	vw	4.72	vvw	3.41	s	3.41	s	3.63	vs	3.60	vs
3.40	vs	3.40	vs	2.90 ₆	ms	2.91 ₂	ms	3.35	vs	3.35	vs
3.23	vs	3.23	vs	2.60 ₈	vw	2.66 ₈	vvw	3.20	vw	—	—
3.03 ₁	vw	3.04 ₀	vvw	2.47 ₁	vw	2.49 ₈	vvw	3.00	vw	2.98	vw
2.88 ₀	s	2.90 ₀	s	2.40 ₈	ms	2.40 ₄	m	2.87 ₈	s	2.86 ₇	s
2.81 ₂	s	2.80 ₀	s	2.215	ms	2.209	m	2.651	vw	2.651	vw
2.60 ₄	mw	2.62 ₁	m	2.010	w	2.012	vw	2.446	w	2.431	vw
2.45 ₀	vvw	2.45 ₀	vw	1.969	w	1.974	vvw	2.391	ms	2.378	ms
2.33 ₇	ms	2.33 ₅	ms	1.905	vvw	—	—	2.175	m	2.163	ms
—	—	2.27 ₅	vvw	1.853	ms	1.858	m	1.978	w	1.966	w
2.112	m	2.112	m	1.730	s	1.730	ms	1.936	w	1.933	w
2.045	vw	2.036	vvw	1.699	w	1.701	vw	1.843	w	—	—
1.967	vw	—	—	—	—	1.628	vvw	1.812	m	1.810	m
1.913	w	1.908	vvw	—	—	1.587	vvw	1.726	mw	1.712	w
1.836	w	1.846	vvw	—	—	1.533	w	1.688	m	1.688	m
1.775	m	1.775	w	1.526	mw	1.523	w	1.664	vw	1.662	vw
1.716	m	1.717	w	1.469	w	1.473	vw	1.612	w	1.613	w
1.654	ms	1.654	ms	1.447	w	—	—	—	—	1.552	vw
1.623	w	1.621	w	—	—	1.410	vw	1.521	w	1.522	w
1.575	mw	1.583	w	1.349	mw	1.351	w	1.492	w	1.497	w
1.528	m	1.526	w	1.299	mw	1.303	w	1.460	w	1.457	vvw
1.476	m	1.478	w	1.279	vvw	—	—	1.440	vw	1.433	vvw
1.438	vw	1.442	vw	1.253	vw	1.256	vvw	1.381	vw	1.389	vw
1.406	w	1.410	vw	1.216	w	1.215	w	—	—	1.364	vvw
1.372	mw	1.374	w	1.177	w	1.180	w	—	—	—	—
1.355	mw	1.355	w	1.160	vvw	—	—	—	—	—	—
1.319	w	1.319	w	1.136	vw	1.139	vvw	—	—	—	—
1.295	mw	1.295	w	1.114	w	1.120	w	—	—	—	—
1.269	w	1.268	vw	1.037	vw	—	—	—	—	—	—
1.242	m	1.246	w	—	—	0.972	vw	—	—	—	—
1.201	vw	1.201	w	0.951	w	0.953	w	—	—	—	—
1.163	vw	1.163	w	—	—	—	—	—	—	—	—
1.140	vw	—	—	—	—	—	—	—	—	—	—
1.120	vw	1.126	vvw	—	—	—	—	—	—	—	—
1.084	vvw	—	—	—	—	—	—	—	—	—	—
1.064	vvw	1.061	vvw	—	—	—	—	—	—	—	—
0.996	vvw	—	—	—	—	—	—	—	—	—	—
0.984	vvw	—	—	—	—	—	—	—	—	—	—
0.968	vvw	—	—	—	—	—	—	—	—	—	—
0.969	vvw	0.909	vvw	—	—	—	—	—	—	—	—

* Supplied by Prof. Hawkes, Bedford College, Regent's Park, London, N.W.1.
† *I* = Intensity.

TABLE V.
Water content of ion-exchanged forms.

	H ₂ O found, %.	H ₂ O, %, calc. for M ₂ O (or MO), Al ₂ O ₃ , 4SiO ₂ , <i>m</i> H ₂ O (<i>m</i> = 6 for chabazite and 2 for analcite).		No. of moles of H ₂ O per unit of M ₂ O (or MO), Al ₂ O ₃ , 4SiO ₂ .
<i>Chabazites rich in</i>				
Ca	19.8		21.4	5.6
Sr	19.4		19.3	6.0
Ba	18.9		17.9	6.3
Na	23.7		21.1	6.7
K	18.0		19.8	5.5
Ag	11.6		15.8	4.4
Rb	11.2		17.0	4.0
Li	14.2		22.5	3.8
Cs	8.2		14.8	3.3
<i>Analcites rich in</i>				
Na	8.1		8.2	2.0
Ag	8.6		5.9	2.9
K	1.5		7.6	0.40
NH ₄	1.5		8.4	0.36
Tl	0.5		4.4	0.23
Rb	1.9		6.4	0.60

analcite and pollucite gave cubic unit cells with $a = 13.6_s$ and 13.6_s Å. for analcrite (determinations on two different synthetic specimens) and $a = 13.6_s$ Å. for pollucite. W. H. Taylor (*Z. Kristall.*, 1930, **74**, 1) gives $a = 13.67 \pm 0.04$ Å. in the case of analcrite. It was further found that Ag-analcrite prepared hydrothermally was hydrated, like Na-analcrite (Table V), and gave a cubic unit cell with $a = 13.7$ Å. This would be expected since the units H_2O, Na^+ and H_2O, Ag^+ should have similar volumes (for Na^+ , $r = 0.98$ and for Ag^+ , 1.13 Å.). However, K-, NH_4^+ , Rb-, and Tl-analcrites proved to be anhydrous so that the increased ionic radii make the units H_2O, M^+ (where $M^+ = K^+, NH_4^+, Rb^+$, or Tl^+) too large to occupy the interstices which previously contained H_2O, Na^+ , H_2O, Ag^+ , or anhydrous Cs^+ . The relevant ionic radii are: K^+ , 1.33; NH_4^+ , 1.43; Rb^+ , 1.48; Tl^+ , 1.49; and Cs^+ , 1.65 Å. On the other hand, the *unhydrated* ions K^+ , NH_4^+ , Rb^+ , and Tl^+ do not fully occupy the interstices, whereas the larger Cs^+ does. From the powder photographs one observed slight distortion in K-, NH_4^+ , Rb-, and Tl-analcrites which transformed the crystals, by a minor contraction of the a -axis and expansion of the c -axis, from cubic into approximately tetragonal forms, with an axial ratio c/a slightly greater than unity. Tl^+ and Rb^+ have nearly identical radii, and it was notable that the spacings corresponding to their powder photographs were almost indistinguishable.

The results thus interpreted indicate a smaller interstitial volume associated with each cation site in analcrite than in chabazite. This conclusion was supported in another decisive way. Li-, Ba-, and NH_4^+ -chabazites were investigated as sorbents and shown, like the parent chabazite crystals, to have excellent sorptive properties towards small molecules.* Among the analcrites, however, dehydrated synthetic Na-analcrite was found to sorb small polar gases only (H_2O , NH_3 , HCl), and the sorptive properties of K- and NH_4^+ -analcrites were negligible.

Interstitial Water.—The water contents of the various ion-exchanged crystals were determined as total water (in addition to intracrystalline water there may thus be small amounts of adsorbed water). The results are summarised in Table V. Col. 2 gives the total water content found, col. 3 that calculated for a formula M_2O (or MO), Al_2O_3 , $4SiO_2$, $6H_2O$ on the assumption of complete exchange, and col. 4 gives the number, n , of moles of water per unit M_2O (or MO), Al_2O_3 , $4SiO_2$.

Among the analcrites, only the Na^+ - and Ag^+ -ion-exchanged forms are hydrated. As noted in the previous section, the anhydrous character of the other ion-exchanged forms depends more on the small interstitial volume available than on the affinity between water molecules and ions. On the other hand, owing to the greater available interstitial volume in chabazite, all the ion-exchanged forms are hydrated, and there are several water molecules per cation. The extent of hydration under ordinary conditions of humidity of the atmosphere is compatible with the hydration series of the ions.† Full saturation of the crystals corresponds to six water molecules per cation for Ca^{++} , Sr^{++} , and Ba^{++} -chabazites, and three water molecules per ion for at least some univalent cations. If as is considered for some of the fibrous zeolites (W. H. Taylor, *Proc. Roy. Soc.*, 1934, *A*, **145**, 80) the water molecules are grouped directly around the cation, there would be a co-ordination shell of six water molecules per bivalent cation, and of three for a univalent cation. In the limited interstitial environment the co-ordination number 6 seems high, and some water molecules may be displaced away from the first hydration shell into vacant sites. Vacant sites can arise in a crystal in which all positions are occupied by univalent ions when these ions are replaced by half their number of bivalent ions. Another aspect of this replacement is considered below (see Discussion).

DISCUSSION.

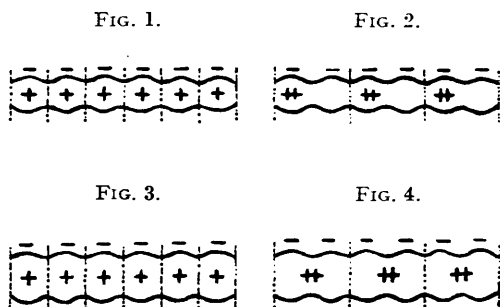
Reference has been made (p. 2344) to the observation that although analcrite, leucite, and pollucite are based on virtually the same aluminosilicate framework, so that analcrite and leucite are readily interconvertible simply by ion interchange (Na^+, H_2O interchangeable with $K^+ + H_2O$), nevertheless neither analcrite nor leucite will give pollucite by ion exchange. This is a very good example of ion-sieve action. The ions Na^+ , Ag^+ , K^+ , NH_4^+ , Tl^+ , and Rb^+ , with radii 0.98, 1.13, 1.33, 1.43, 1.49, and 1.48 Å. respectively, can diffuse into analcrite crystals, but Cs^+ (radius = 1.65 Å.) cannot. It follows that Na^+ - K^+ exchanges of the above type (*i.e.*, analcrite \rightleftharpoons leucite) are easily established, but that the Na^+ - Cs^+ and K^+ - Cs^+ equilibria cannot be established. In the synthesis of pollucite the Cs^+ cations are accordingly locked within the crystal once and for all during its growth and can be released only by its recrystallisation or decomposition. The correctness of this view was further demonstrated by hydrothermal treatment of powdered pollucite with a series of saline solutions (sodium chloride, lithium chloride, sodium carbonate, ammonium chloride, and barium chloride) at high temperatures ($\sim 300^\circ$).‡ These treatments effected no observable change in the refractive index of the pollucite such as ion exchange normally produces (*cf.*, for example, Table Ia).

* This work, carried out with Dr. Riley, is described elsewhere (*Trans. Faraday Soc.*, in the press).

† The energy of interaction of a permanent dipole of moment μ with a charge ϵ is $E_1 = -\mu\epsilon \cos \theta / r^2$. Taking the diameter of a water molecule as 2.8 Å. and a fixed orientation, θ , of the dipole axis relative to the line joining the charge and the centre of the dipole, and assuming that r = the radius of a dipolar molecule + the radius of the cation, one finds that E_1 decreases in the sequence $Ca^{++} > Sr^{++} > Ba^{++} > Li^+ > Na^+ > Ag^+ > K^+ > NH_4^+ > Rb^+ > Cs^+$. Again, for the polarisation energy of the molecule by the cation, $E_2 = -a\epsilon^2 / r^4$, where a is the polarisability of the molecule, one finds the same sequence in the ion series. With the exception of Li^+ , this series recalls the extent of hydration in ion-exchange chabazites shown in Table V.

‡ These treatments were carried out by Dr. H. F. W. Taylor.

Another aspect of the ion-sieve effect may help to explain the difficulty of obtaining Ca- and Ba-rich analcites (Table II). In analcite crystals, the interstitial channels suffer periodic restrictions sufficient to prevent diffusion of caesium. In these periodically restricted channels the replacement of uni- by bi-valent ions is shown by the change from Fig. 1 to Fig. 2, which give schematically the charge distributions. The bivalent cations cannot easily occupy positions at the restrictions in the channels for steric reasons; on the other hand, their presence in only half of the sites normal for univalent cations leads to a state of local disbalance of cationic and anionic charge. Since neither configuration is then very stable, exchange of uni- for bi-valent cations in analcite will be limited in extent. On the other hand, in chabazite and mordenite the restrictions in the interstitial channels are less marked, as demonstrated by their sorptive and molecular-sieve behaviour (cf. Barrer, *Ann. Reports*, 1944, **41**, 31, for a summary of these properties). There is now adequate room for bivalent cations to occupy intermediate positions along the channel, the configuration shown in Fig. 3 becoming that in Fig. 4 when univalent are replaced by bivalent cations; local neutralisation of anionic charge is much more nearly effected, and exchange proceeds easily either way.



Local balance or disbalance of anionic and cationic charges shown diagrammatically, in relation to interstitial channel dimensions.

Other factors are also considered to contribute to the extent of exchange. Very small ions such as Li^+ and Mg^{++} do not interchange freely, but this may be associated with a high energy of hydration in solution and with changes in the degree of hydration during exchange.* Wiegner and Cernescu (*loc. cit.*) who compared the behaviour of Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ in ion exchange in chabazite, emphasised the hydration factor, which they considered to be connected with the ease of entry (stated to be in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$). However, the direction in which the hydration factor would operate is not certain; much must depend upon the ion being displaced.

The basigenic character of the element is also of significance. Magnesium is comparatively weakly basigenic and its salts are hydrolysed fairly easily to basic salts. Hydrolysis may be augmented under hydrothermal conditions. Silver ions, on the other hand, are not strongly hydrated but the salts are not hydrolysed under comparable conditions. Silver, in fact, replaces other cations in chabazite and analcite surprisingly easily, but magnesium does not do so. It is thus clear that a diversity of factors may operate in controlling ion exchange. The factor of swelling and shrinking present in clay minerals and in gel exchangers has, however, been largely avoided in the present study by using clay crystals where shrinking and swelling are negligible, and these results may be to this extent simplified.

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* Hydration cannot, however, control exchanges occurring from a melt, and the same difficulty arises when Na^+ is replaced by Li^+ by this method (Table II) as in hydrothermal exchange. Hydrolysis also cannot affect the results of exchange by fusion.