777. *Reactions and Stability of Chabazite-like Phases. Part II.*[1]
Ion-exchanged Forms of Some Synthetic Species.

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Thermal stability of cation-exchanged forms of a natural siliceous chabazite and of a range of synthetic chabazite-like phases tends to decrease the more aluminous the phases. There appears to be a family of at least four natural and synthetic zeolites of chabazite type.

When minerals or phases produced from the cation-exchanged forms were based on aluminosilicate frameworks of different type from chabazite, mineral growth was normally preceded by a structural breakdown to an amorphous or glassy phase. In other cases the chabazite lattice changed directly into the lattice of the new species.

IN the preceding paper we traced the rather regular influences of cation on the thermal stability and reactions of various cation-exchanged forms of chabazite with a constant $SiO_2 : Al_2O_3$ ratio of $1 : 5.05$. In the present paper we investigate, for a more limited series of cation forms, how systematic variations in the alumina : silica ratio influence the sintering reactions and stability of chabazite-like phases.

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[1] Part I, preceding paper.

EXPERIMENTAL

The methods of differential thermal analysis, thermogravimetry, and X-ray diffraction employed in Part I have also been used here, supplemented by ion-exchange and analytical data (methods previously discussed). The compositions of the phases investigated are given in Table 1. From these crystalline powders Li-, Na-, and Ca-rich cation-exchanged forms were

TABLE 1. *Synthetic phases structurally related to chabazite.*[2]

Specimen	Molar proportions			
	K_2O	Al_2O_3	SiO_2	H_2O
K-G1	1·03	1·00	4·15	4·51
K-G2	0·95	1·00	2·72	4·65
K-G3	0·99	1·00	2·65	3·75
K-G4	1·11	1·00	2·56	3·48
K-G5	0·92	1·00	2·30	3·65

also prepared, by two treatments with saturated aqueous chloride solutions, which ensure virtually complete exchange.[3,4] This treatment was followed by hydrothermal extraction with water, washing several times with acetone, and air-drying. All the products were equilibrated over saturated calcium nitrate solution. The water contents recorded in Table 1 refer to material treated in this way, so they do not necessarily represent the water contents of the crystals originally prepared.[2]

RESULTS

In Figs. 1—4 are shown the thermograms for the Li, Na, K, and Ca forms of each of the five phases of Table 1, and of the natural siliceous chabazite of Part I. With the successive curves is given the appropriate alumina : silica ratio for each experimental specimen. In every one of these diagrams there is a marked difference between the high-temperature end of the thermograms for the siliceous natural chabazite and the most siliceous of the synthetic chabazite-type phases. Moreover the aluminous phases also show some striking differences from either of the most siliceous phases, natural or synthetic.

The thermogravimetric curves for the Li, Na, and Ca forms of the six phases are shown in Figs. 5—7. In addition these curves were determined for most of the K-rich forms, but these all gave very smooth and similar curves, the water being completely lost by 400°. This similarity among the K-rich phases extends also in the lower-temperature range to the differential thermal analyses shown in Fig. 3. The endothermic sections of these curves all show a small sub-peak, towards the end of the region of water loss. In K-chabazite this sub-peak occurs at 325°, while in the synthetic phases it occurs at about 260—280°.

The differential thermal analysis curves of the Na forms (Fig. 2) resemble more closely those of the Ca-rich phases (Fig. 4) than those of the K phases shown in Fig. 3, except in the case of Na-G1. In the aluminous phases sub-peaks in the endotherms for water loss are strongly developed. The similarity between Na-G4 and Ca-G4 in this region is very marked. The thermogravimetric curves of the aluminous forms (Fig. 6) show some rather sharp changes in slope which suggest that the sub-peaks in the endotherms are associated with sudden releases of water.

The differential thermal analyses of the Li forms (Fig. 1) also show similarities with both the Na and the Ca phases, rather than with the K phases. The sub-peaks are often well developed, and are reflected in rather sudden changes in slope in the thermogravimetric curves (Fig. 5). Thus, as in the cases of the Na and the Ca phases (Figs. 6 and 7) these sub-peaks must also refer to sudden releases of water.

The differential thermal analyses of the Ca phases (Fig. 4) are in some respects the most complex which were observed. The endothermic region of the curve for Ca-chabazite continues to nearly 800° and is associated with some weight loss even above 700°, as shown by the upper-most thermogravimetric curve of Fig. 7. In the thermograms of Ca-G2 and Ca-G5 the normal endothermic section associated with water loss at lower temperatures comprises a doublet

    [2] Barrer and Baynham, *J.*, 1956, 2882.
    [3] *Idem, J.*, 1956, 2892.
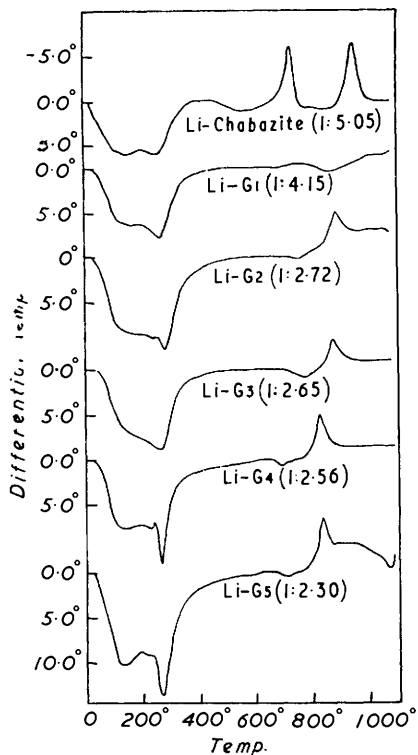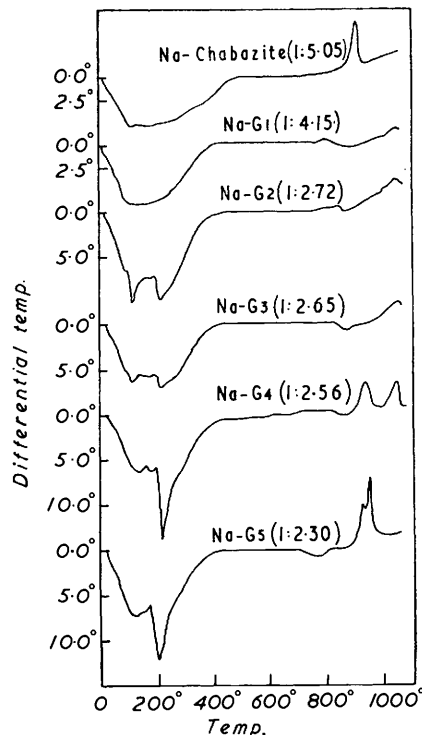   [4] Barrer and Sammon, *J.*, 1955, 2838.
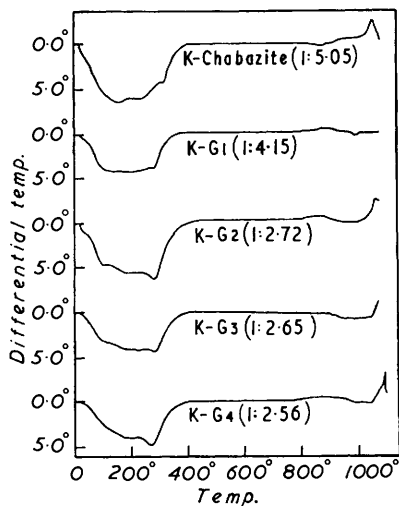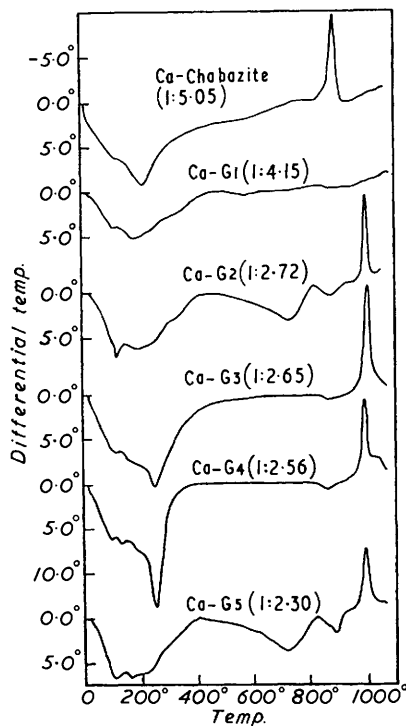
FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

FIGS. 1—4. *Thermograms of* (*Fig.* 1) Li *phases,* (*Fig.* 2) Na *phases,* (*Fig.* 3) K *phases,* (Fig. 4) Ca *phases.*

extending from room temperature to about 420°. It is succeeded by additional endothermic regions, the first of which extends from about 430° to 830°. Then a second small, rather sharp peak extends from 830° to about 930°. Comparison of the curves for differential thermal analysis and thermogravimetry of Ca-G2 shows that the first endothermic region corresponds to the loss of 72·8% of the total water, the second to 25·5%, and the last to 1·7%. Thus there may be three types of water binding in this sample, and also in the specimen Ca-G5. From the viewpoint of the exothermal peaks the differential thermal analysis curves also fall into three categories. Ca-chabazite shows this peak at about 860°; Ca-G1 shows no peak; and the remaining four phases all show a similar peak at 1000°.

All the phases, for which curves are presented in Figs. 1—4, were X-rayed after separate specimens had been heated to each of a sequence of successively higher temperatures, as
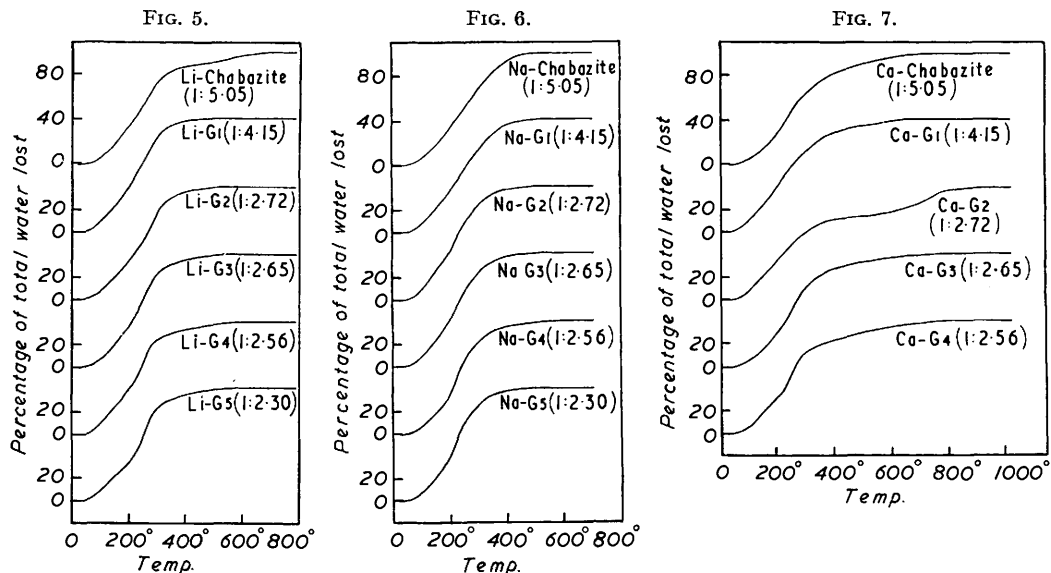
FIGS. 5—7. *Thermogravimetric curves for (Fig. 5) Li phases, (Fig. 6) Na phases, (Fig. 7) Ca phases.*

indicated in Part I. The Ca-zeolites, after being heated at 1090°, yielded felspars similar to, but not identical with, anorthite. This is preceded by formation of a glassy phase already present at 940°. On the other hand (Part I) the natural siliceous chabazite at 1090° produced quartz.

DISCUSSION

Recrystallisation Reactions.—The products of heat-treatment in the manner described in Part I are summarised in Table 2, for four of the chabazite-type phases of this paper and of Part I, in various cation-exchanged forms. The products formed are surprisingly numerous, including amorphous or glassy phases, quartz, β-eucryptite, a nosean-like phase, nepheline, α-carnegieite, leucite, kaliophilite, a hauyne-like phase, calcium felspar, and hydrogen chabazite.

Quartz was obtained only from the most siliceous phase, but in this one instance it was obtained from several of the cationic forms. The most siliceous K phases ($Al_2O_3 : SiO_2 = 1 : 5·05$ and $1 : 4·15$) yielded leucite as the only recrystallisation product. The two most aluminous phases, on the other hand, yielded only kaliophilite, and the two most aluminous Na phases yielded nepheline as final product. In the large majority of these reactions the appearance of a new crystalline phase is preceded by a temperature range in which the chabazite lattice becomes amorphous or glassy. This is the course taken when the structures of the new products differ very much from that of chabazite. The products

often differ considerably in $Al_2O_3 : SiO_2$ ratio from the original phase, so that the crystallisations involve not only nucleation from the amorphous or glassy breakdown product of the chabazites but at the same time disproportionation.

TABLE 2. *Effects of heating upon chabazite-type phases.*

$Al_2O_3 : SiO_2$ ratio	Cation form	Products and heating temperatures
1 : 5·05	Li	Li-Ch * (200°) Li-Ch (400°) Li-Ch (600°) *quartz* (850°) *β-eucryptite* (1070°)
	Na	Na-Ch (200°) Na-Ch (400°) Na-Ch (600°) modified Ch (820°) *quartz* (1070°)
	K	Modified Ch (200°) modified Ch (500 and 700°) unidentified (1000°) *leucite* (1100°)
	NH_4	Modified Ch (240°) modified Ch (410°) H-*Ch* (560 and 650°) *quartz* (800 and 1095°)
	Ca	Ca-Ch (200°) Ca-Ch (500°) modified Ch (810°) *quartz* (1090°)
1 : 4·15	Li	Li-Ch (200°) modified Ch (550°) mainly glassy (820°) *β-eucryptite* (1070°)
	Na	Na-Ch (160°) Na-Ch (500°) Na-Ch (700°) *glassy* (920°) *glassy* (1070°)
	K	Modified Ch (200°) modified Ch (550°) modified Ch and *amorphous* (700°) *glassy* (970°)
	Ca	Ca-Ch (200°) modified Ch (500°) modified Ch (700°) *glassy* (940°) Ca-*felspar* (1090°) *leucite* (1100°)
1 : 2·65	Li	Modified Ch (200°) modified Ch and *amorphous* (550°) *glassy* (820°) *β-eucryptite* (1060°)
	Na	Na-Ch (160°) modified Ch and some *nosean* (500 and 700°) *nosean* (940°) *nepheline* (1080°)
	K	Modified Ch (200°) modified Ch and *amorphous* (500 and 700°) *glassy* (980°) *kaliophilite* (1080°)
	Ca	Ca-Ch (200°) modified Ch and some *hauyne* (550°) *glassy* (940°) Ca-*felspar* (1090°)
1 : 2·30	Li	Li-Ch (200°) *amorphous* (550°) *β-eucryptite* (900 and 1080°)
	Na	Na-Ch (170°) *nosean* (300°, 500°, and 840°) *α-carnegieite* (950°) *nepheline* (1080°)
	K	Modified Ch (200°) *largely amorphous* (500°) *glassy* (700 and 950°) *kaliophilite* (1090°)
	Ca	Modified Ch (200°) *hauyne* (500°, and 820°) *glassy* (900°) Ca-*felspar* (1080°)

* Ch denotes parent chabazite-like phase.

There are exceptions. First are minor changes in line intensity and position associated with heating and water loss, in which the chabazite-type of structure is preserved in a slightly modified form. These changes may involve, not only water loss, but also rearrangement of cations and small adjustments of the anionic framework. The " modified chabazites " and hydrogen chabazite of Table 2 are of this kind. There is another somewhat more extensive change which also does not involve the preliminary transformation into a glassy phase. This is the change from structures related to chabazite to structures like those of nosean–hauyne minerals. The change in this case involves alteration in crystal symmetry from rhombic to cubic. Nosean felspathoids and chabazite zeolites were thought to be based on the same arrangement of polyhedra in 8-fold co-ordination.[5] Each polyhedron of the former is, or approximates to, a regular cubo-octahedron built from $(Al,Si)O_4$ tetrahedra, and has six faces circumscribed by rings of four tetrahedra and eight faces circumscribed by six-membered rings. But a new structure, different from that of the nosean–sodalite felspathoids, has been suggested [5a] for chabazite, thus making the observed transformation of interest. The transformation of chabazites at low temperatures into nosean-type structures has been noted previously in this laboratory:[3] it is confined to the more aluminous chabazite-type phases. This appears to reflect the limitation in composition of the nosean–sodalite felspathoids where the ratio $Al_2O_3 : SiO_2$ is close to the value 1 : 2. Thus for a siliceous chabazite to be converted without disproportionation into a nosean felspathoid would require a gross departure from the alumina : silica ratio characteristic of these felspathoids. A novel feature of the nosean- and hauyne-like structures formed in the present work is that there cannot be any of the

[5] Pauling, *Proc. Nat. Acad. Sci.*, 1930, **16**, 453; *Z. Krist.*, 1930, **74**, 213; Bragg, " Atomic Structure of Minerals," Oxford Univ. Press, 1937, p. 265; Wyart, *Bull. Soc. franç. Mineralog.*, 1933, **56**, 81.
[5a] Dent and Smith, *Nature*, 1958, **181**, 1794.

included species (NaOH, Na_2CO_3, NaCl, Na_2SO_4, $CaCO_3$, etc.) which are normally present within cavities in other natural and synthetic felspathoids.

The products of reaction from chabazite include four species which Buerger[6] has termed " stuffed " derivatives of crystalline silica. Thus eucryptite[7] is based on a high-quartz structure in which $Al^{3+} + Li^+$ replace half of the Si^{4+} atoms of the framework. The Li^+ ions are present in interstices in this anionic framework. Eucryptite was obtained from every Li-chabazite phase whatever the $Al_2O_3 : SiO_2$ ratio. Nepheline is another stuffed derivative based this time on a tridymite structure slightly collapsed by a distortion of the framework. Kaliophilite is also regarded as a stuffed derivative of tridymite although its detailed structure is not known. Finally, α-carnegieite[8] is a stuffed derivative of cristobalite. Both carnegieite and nepheline are different forms of $NaAlSiO_4$, nepheline being the stable form below 1248°.[9] Thus the α-carnegieite obtained in this work has appeared in a range of temperature in which it is metastable.

Stability of Chabazite-type Phases.—We have now examined the stability to heat of chabazite-like phases covering a wide range in alumina : silica ratios and for a series of cation-exchanged forms of each phase. For any given cation-exchanged form loss of crystallinity or recrystallisation of the parent phase occurs at a lower temperature the more aluminous the phase becomes. In a zeolite structure, in which the ratio base : alumina is always 1 : 1, the more aluminous the mineral the greater are its framework charge, cation density, and cation-exchange capacity. It may then be this high framework charge which modifies the stability of the aluminous minerals. A number of other variations in properties have been traced in relation to changing $Al_2O_3 : SiO_2$ ratios for these chabazite-type phases.[2,3]

In Part I[1] we have shown that for a series of ion-exchanged forms the thermal stability of a siliceous natural chabazite increases in the sequence Li < Na < K < Rb < Cs. The situation among the more aluminous phases for the more restricted series of ions Li^+, Na^+, and K^+ is less well defined. However, the Na and K forms are of comparable stability. The Ca form also, among the siliceous phases, is of considerable stability.

Classification of Chabazite-type Phases.—Earlier investigations,[2,3] and especially those in Part I and in the present paper, provide evidence that there are various members of what may be termed the chabazite family of zeolites. These members differ sufficiently from one another to be regarded as separate species, in the way in which chabazite and gmelinite are already so considered. Nevertheless there are similarities in the alumino-silicate frameworks.

As noted above, the curves in Figs. 1—4 are of three distinct types. The siliceous natural chabazite is well distinguished from the most siliceous synthetic phase, which is equally well distinguished from the remaining synthetic phases having $Al_2O_3 : SiO_2$ ratios from 1 : 2·72 to 1 : 2·30. There are also variations in X-ray diffraction patterns, gas-sorbing properties, and refractive indices which have in part been traced elsewhere.[2,3] Among the synthetic phases there is some evidence of a discontinuity between those with Al_2O_3/SiO_2 less than 3 and those in which this ratio exceeds 3.

On the basis of such studies we suggest the following classification of members of the chabazite family: (i) chabazite, (ii) gmelinite, (iii) synthetic K-species[2,3] with $Al_2O_3/SiO_2 > 3$, (iv) synthetic K-species[2,3] with $Al_2O_3/SiO_2 < 3$.

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[6] Buerger, *Amer. Mineralog.*, 1954, **39**, 600.
[7] Winkler, *Acta Cryst.*, 1948, **1**, 27.
[8] Bowen and Greig, *Amer. J. Sci.*, 1925, **10**, 204.
[9] Barrer and Bultitude, unpublished work.