1. Chill the thin sections to 0° C. and lift off the cover glass with a razor blade.
2. Clean the surface of the thin section with acetone or alcohol. Do not cover the back of the section with Scotch Tape.
3. Prepare 400 ml. of stain solution (50 g. of sodium cobaltinitrite to 100 ml. of distilled water) and warm to hasten solution.
4. Cover the bottom of the polyethylene box with hydrofluoric acid.
5. Adjust the temperature of the water bath to 40° C.
6. Place the thin sections face down on the rack with the lead weight in position. Place the rack over the HF for 15 to 30 seconds.
7. Move the loaded rack from the HF fumes and suspend it in the stain solution for 30 seconds.
8. Move the loaded rack from the stain solution and suspend it in flowing tap water until the water runs clear.
9. Unload the rack and air dry the thin sections on paper towels. Coverglasses can be placed on the stained thin sections using permount.

Manuscript received May 16, 1963

STUDIES ON SOLID SOLUTION BETWEEN SODALITE, NOSEAN AND HAUYNE

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Introduction

It is reported in the literature that solid solution exists between sodalite, nosean and hauyne (Pauling, 1930; Barth, 1932b). Borgstrom (1930) stated that chemically analysed natural sodalite sometimes contains some sulphate but admitted that this may have been due to mechanical mixing with nosean. Barth (1932a) considered nosean and hauyne to be a chemically mixed crystal, writing the formula as nosean $Na_8Al_6Si_6O_{24}.SO_4$ and hauyne $(NaCa)_{4-8}Al_6Si_6O_{24}.(SO_4)_{1-2}$, although he considered sodalite as a separate species. Pauling (1930) claimed that sodalite and nosean are isomorphous, because sodalite may be converted into nosean by heating it in fused sodium sulphate, and he further showed that hauyne may be converted to sodalite by heating the former in fused sodium chloride. No details of temperatures of these reactions were given. Solid solution has never been demonstrated by analysis of natural minerals coupled with x-ray or optical studies. Lacking the natural specimens it was decided to attack the problem by means of a number of hydrothermal syntheses.

Experimental Methods

Stoichiometric mixtures of sodalite, nosean and hauyne were made up using the following formulae for end members:

Sodalite	$6NaAlSiO_4.2NaCl$
Nosean	$6NaAlSiO_4.Na_2SO_4$
Hauyne	$6NaAlSiO_4.2CaSO_4$

These compositions correspond to those of Winchell & Winchell (1951).[1] The compositions of these mixtures are shown in tables 1 and 2. The mixtures (usually about 20–50 mg. of sample plus 10–20 mg. of water) were loaded into the usual gold capsules and reacted at an elevated temperature of 600° C. for a duration of 140 to 160 hours under a pressure of 15,000 p.s.i. in test tube type bombs. The reacted materials were then removed from the bombs and mixed in the ratio of 3:1 weight per cent with a very pure quartz from Oliver, B.C. This mixture was *x*-rayed on a Norelco high angle diffractometer using Cu$K\alpha$ radiation with a Ni filter, the quartz being used as an internal standard.

TABLE 1. NOSEAN-HAUYNE, COMPOSITION OF EXPERIMENTAL RUNS

Composition of original charge in mineral mole per cent		
nosean	hauyne	Phases present
100	0	(nos-hauyne)*
90	10	(nos-hauyne)
66	33	(nos-hauyne)
66	33	(nos-hauyne)
50	50	(nos-hauyne)
50	50	(nos-hauyne)
33	66	(nos-hauyne)
33	66	(nos-hauyne)
33	66	(nos-hauyne)
33	66	(nos-hauyne)
	100	(nos-hauyne)

*(nos-hauyne) indicates a single phase of mixed composition.

All runs at 600° C and 15,000 p.s.i.

Since the nosean and hauyne diffraction patterns are identical except for minor shifts in *d* spacings (Van Peteghem & Burley, in press), the term nosean-hauyne will be used to describe them or any isomorphous mixture of them. In the case of the nosean-hauyne mixtures, two methods were used in the investigation of the synthetic products obtained.

[1]The formula for hauyne differs from that of Barth (1932a) mainly in being richer in O_2. This composition was chosen because of the ease of preparation. Any oxygen not taken up in the reaction should have no effect on the reaction, air always being present.

(1) The value of $2\theta_{10.1}$ (quartz) $-$ $2\theta_{211}$ (nosean-hauyne), hereafter referred to as $\Delta 2\theta$ were measured for varying mol. percentages of the mixtures.

(2) The unit cell dimensions of intermediate members of the series nosean-hauyne were obtained by graphical extrapolation after the method of Nelson & Riley (1945).

These values were plotted against mol. per cent hauyne.

The synthetic products obtained from the sodalite-nosean and sodalite-hauyne mixtures listed in Table 2 were examined only qualitatively by x-ray powder diffraction. The detection of only one phase was considered as evidence for solid solution between the end members while if two phases occurred, it was assumed that solid solution did not exist.

TABLE 2. SODALITE-NOSEAN-HAUYNE, COMPOSITION OF EXPERIMENTAL RUNS

Composition of original charge in mineral mol. per cent of sodalite,	nosean,	& hauyne	Phases present
10	90		(nos-hauyne)*
10		90	(nos-hauyne)
90	10		sodalite & (nos-hauyne)
90		10	sodalite & (nos-hauyne)
50	50		sodalite & (nos-hauyne)
33	66		sodalite & (nos-hauyne)
66	33		sodalite & (nos-hauyne)
50		50	sodalite & (nos-hauyne)
33		66	sodalite & (nos-hauyne)
66		33	sodalite & (nos-hauyne)
19	81		(nos-hauyne)
23		77	(nos-hauyne)
80	20		sodalite & (nos-hauyne)
80		30	sodalite & (nos-hauyne)
75	25		sodalite & (nos-hauyne)
25	75		(nos-hauyne)
30	70		(nos-hauyne)
30		70	sodalite & (nos-hauyne)

*(nos-hauyne) means a single phase with a composition intermediate to the end members nosean and hauyne.
All runs at 600° C and 15,000 p.s.i.

Results

The synthetic product formed by using nosean and hauyne mixtures consisted of a single phase. The diffraction pattern of this phase was almost indistinguishable from the end members. The curve in Fig. 1 shows the relationship between $\Delta 2\theta$ (qtz $-$ nosean-hauyne) and mol. percentage of hauyne. The cell edge determinations made by the graphical method of Nelson & Riley are shown in Table 3. The cell volumes obtained from these measurements are plotted against mol. per cent hauyne in Fig. 2.

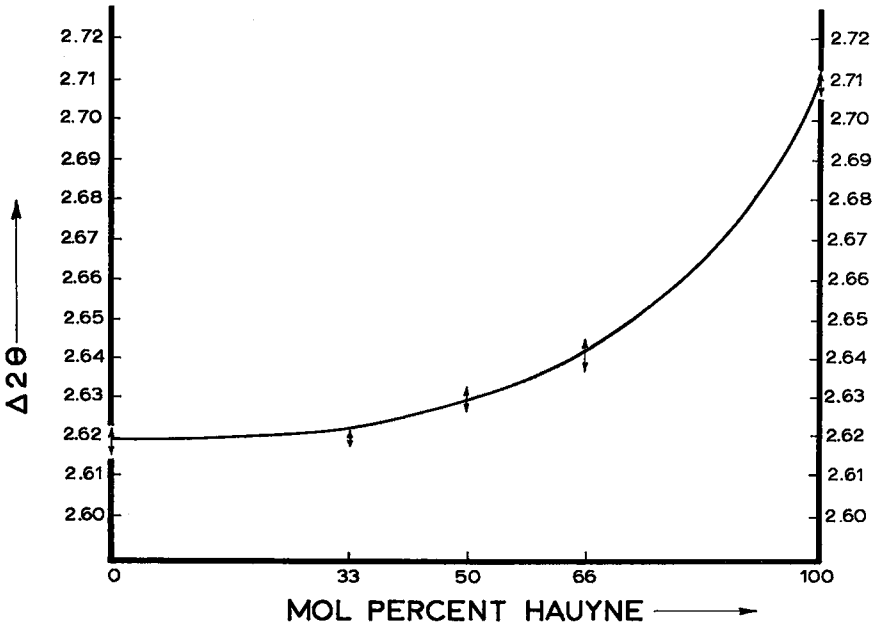

FIG. 1

TABLE 3. NOSEAN-HAUYNE, CELL VOLUMES

Composition of phase in mol %	$\Delta 2\theta$	Cell volume in cubic angstroms
$Nos_{100}Ha_0$	2.62±0.02	745±6
$Nos_{90}Ha_{10}$		745±6
$Nos_{66}Ha_{33}$	2.62±0.01	742±4
$Nos_{66}Ha_{33}$		743±2
$Nos_{50}Ha_{50}$	2.63±0.01	746±3
$Nos_{50}Ha_{50}$		743±6
$Nos_{33}Ha_{66}$		
$Nos_{33}Ha_{66}$	2.64±0.01	
$Nos_{33}Ha_{66}$		748±3
$Nos_{33}Ha_{66}$		750±2
Nos_0Ha_{100}	2.71±0.02	751±3

When synthetic mixtures of sodalite-nosean were run, only limited solid solution was found. From approximately 100–75 mol. per cent nosean and 0–25 mol. per cent sodalite, a single phase ("nosean-hauyne") type mineral was present, but with a lesser amount of nosean and a correspondingly greater amount of sodalite, two phases were encountered, (nosean-hauyne) and sodalite. The same situation exists for mixtures of hauyne-sodalite except that the two phases appear when a somewhat larger percentage of hauyne is involved (see Table 2).

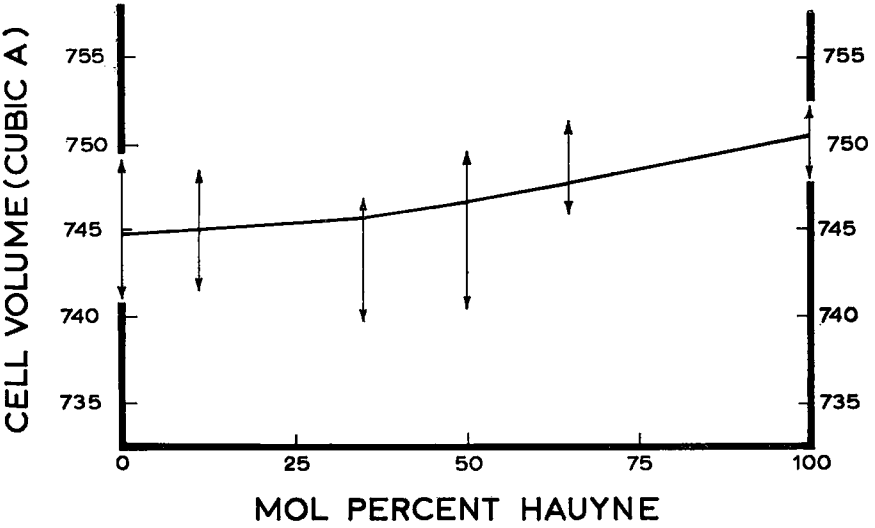

FIG. 2

Discussion

For the purpose of this investigation, solid solution was taken simply to mean that one phase only would be detected by x-ray investigation, and does not imply a structural connection between the pure hypothetical end members. In the case of nosean and hauyne a complete isomorphous series most probably exists between them since their structures are almost identical, both in addition possessing the same space group ($T_d^1 = P\bar{4}3m$). It is not necessary in a solid solution that the lattice parameters change in a linear fashion with the mol. fraction of the end members, but merely that the change be a continuous function. It appears that, since there are no breaks in the curves, Na^+ and Ca^{++} substitute easily for one another in the nosean-hauyne lattice, their respective ionic radii being 0.97 Å and 0.99 Å.

The formula of the series becomes more sulphated as Ca^{++} replaces Na^+ since the sulphate ion occupies every other cavity within the "cube-octahedral" cavities of the tetrahedral framework of nosean and nearly every cavity in that of hauyne (Barth 1932b).

On the other hand, Cl^- and $SO_4^=$ seem to substitute with much more difficulty.

Conclusions

Complete solid solution appears to exist between synthetic products of nosean and hauyne composition, but only limited solid solution occurs in synthetic products of sodalite-nosean and sodalite-hauyne compositions formed at 600° C. and 15,000 p.s.i. in the presence of excess water.

Acknowledgments

The authors are grateful to the National Research Council for a grant (A-612), and to the Research Corporation of America for a grant towards the purchase of *x*-ray equipment.

References

Barth, T. F. W. (1932a): The chemical composition of noselite and hauyne. *Am. Mineral.*, **17**, 466–471.

——— (1932b): The structure of the minerals of the sodalite group. *Zeit. Krist.*, **83**. 405–415.

Borgstrom, L. H. (1930): Chemismus der Mineralen der Sodalit under der Cancrinitgruppe. *Zeit. Krist.*, **74**, 113–130.

Nelson, J. B., & Riley, D. P. (1945): An experimental investigation of extrapolation methods in the derivation of accurate cell dimensions of crystals. *Proc. Physical Soc.*, **57**, 160–177.

Pauling, L. (1930): The structure of sodalite and helvite. *Zeit. Krist.*, **74**, 213–225.

Van Peteghem, J. K., & Burley, B. J. (1963): (in press).

Winchell, A. N., & Winchell, H. (1951): *Elements of optical mineralogy, part II—descriptions of minerals*, ed. 4, J. Wiley and Sons, New York.

Manuscript received January 16, 1963