THE CHEMICAL COMPOSITION OF NOSELITE AND HAÜYNE

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R. Brauns in his important study of *die Mineralien der Niederrheinischen Vulkangebiete* (7) states that the composition of noselite is: $6(NaAlSiO_4) \cdot Na_2SO_4$, and of haüyne: $X(NaAlSiO_4) \cdot CaSO_4$. (Excerpt: "Allgemein also enthielte der Laacher Haüyn das Nephelinsilikat verbunden in nicht festem Verhältnis mit $CaSO_4$.")

These formulae are purely empirical and represent a logical conclusion arrived at by inspection of analyses of natural minerals.

In the present paper new experimental data will be discussed, partly verifying, partly clarifying the aforementioned formulae. A complete study of the crystal structures of noselite, haüyne, and sodalite has also been carried out, but only data pertinent to the chemistry of these minerals will be considered here.

NOSELITE ($Na_8Si_6Al_6O_{24} \cdot SO_4$)

There should be little doubt that the true formula for noselite is: $6(NaAlSiO_4) \cdot Na_2SO_4$. All analyses are in fair agreement with this formula, and nothing really supports the older view of a more highly sulfurated molecule: $3(NaAlSiO_4) \cdot Na_2SO_4$. In spite of this fact the latter formula is apparently the one enjoying general acceptance.

In order to establish the true formula definitely, syntheses were made by mixing glass of the composition $NaAlSiO_4$ with Na_2SO_4 corresponding to the ratios 6:1 and 3:1. Heated for *ca.* 150 hours around 800° the mixture corresponding to the ratio 6:1 became practically homogeneous (isotropic with $n=1.492$), whereas the mixture 3:1 was still nonhomogeneous. Thus in the first mixture the reaction product seemed to be only noselite, and this was also verified by an x-ray analysis of the powder whose diffraction pattern was almost identical with that of natural noselite. In the x-ray spectrogram of the second mixture all the lines belonging to the noselite structure were present, but in addition a few extra lines were encountered which could be identified as belonging to the high-temperature modification of Na_2SO_4. Beyond any possible doubt, therefore, the formula of noselite has been established as $Na_8Al_6Si_6O_{24} \cdot SO_4$.

It is proposed that the formula be written as above and not like a double salt, $6(NaAlSiO_4)\cdot Na_2SO_4$, for *x*-ray studies of the atomic arrangement have shown that the two Na-ions which in the double salt formula are united to the SO_4-group occupy positions which are structurally identical with those of the other Na-ions. This way of writing the formula does have mnemonic advantages but should be avoided because it might be construed as having a structural analogue.

Haüyne $[(Na, Ca)_{4-8}Al_6Si_6O_{24}\cdot(SO_4)_{1-2}]$

In the noselite molecule soda can be partly replaced by lime, and if the lime content exceeds *ca.* 6 per cent the mineral is called haüyne. Thus the natural haüyne is not a chemical compound but a mixed crystal with noselite as one end member and some Ca-bearing silicate, or silicates, as other end members.

A mixture of the constituent oxides will not, when heated under atmospheric conditions, combine to form haüyne, but the chief reaction products are usually noselite and anorthitic feldspar. No elaborate experiments for making haüyne (for instance, in bombs) were attempted, however, since it can be shown that *x*-ray diffraction data from natural haüyne suffice for establishing the true chemical formula.

X-ray diffraction data from noselite and haüyne are on record (8), (9), and new data were obtained during the course of this study. The two minerals exhibit very similar crystal structures. They both are isomorphous with the space group T_d^1; the lattice spacings are slightly larger in haüyne than in noselite, but otherwise they have practically the same atomic arrangement.

The length of the edge of the unit cube is, for noselite: $a_0=9.04$Å (artificial material); for haüyne: $a_0=9.11$ Å (*ca.* 10 per cent CaO).

These structures can be thought of as packings of large oxygen ions containing the smaller cations; the index of refraction of the crystal will depend upon how tightly the ions are packed. The unit of structure contains in the case of noselite 28 oxygen ions (and 21 cations). This is in agreement with the low index of refraction of noselite, and since haüyne has almost the same refractive index and lattice spacings, the unit of its structure also must contain nearly the same number of ions. For this reason, if for no other, the frequently postulated formula for haüyne: $6(NaAlSiO_4)\cdot 2CaSO_4$ (leading to 32 oxygen ions in the unit cube) has to be discarded. Furthermore, all analyses save one (4) show a decidedly lower content of CaO and SO_3 than this formula.

A possible formula for haüyne must fulfill the following two requirements:

(1) It should be derivable from a structure isomorphous with that of noselite. (2) It should lead to a unit of structure containing exactly or nearly the same number of ions.

X-ray studies have established the fact that in noselite the ions occupy the positions shown in Table 1, line I. A possible chemical composition of the hypothetical end member of the noselite-haüyne series is given under II′ (Table 1). Any mixed crystal between I and II′ would then have the formula $(Na, Ca)_{4-8}Al_6Si_6O_{24} \cdot SO_4$. An inspection of the analyses of haüyne shows, however, that the calcium sulfate content usually is slightly higher than that demanded by this formula. It seems, therefore, as if to a limited extent, additional Ca and SO_4 ions can be built into the haüyne structure. The reason for this incorporation must be sought in the fact that haüyne crystals with considerable silicate II′ in them would display an extremely open structure. The pure noselite has also an open "framework" within which there are empty spaces and passages, and as seen from Table 1, the eight sodium ions in noselite, I, are replaced by only four calcium ions in II′, thus causing the open "framework" type of structure to become still more pronounced.

TABLE 1. COMPARISON OF THE CHEMICAL COMPOSITION OF NOSELITE, HAÜYNE, AND SODALITE

	1a	1b	4a				12f		12g+ 12g
Noselite I	—	S	O_4	—	Na_4	Na_4	Al_6	Si_6	O_{24}
II′	—	S	O_4	—	—	Ca_4	Al_6	Si_6	O_{24}
Haüyne II″		.... $(SO_4)_{1-2}$			$(Na,Ca)_{4-8}$		Al_6	Si_6	O_{24}
Sodalite III	Cl	Cl	—	—	Na_4	Na_4	Al_6	Si_6	O_{24}

Although there is room for two $(SO_4)^{--}$-ions in the unit cube of noselite (in analogy with the two Cl^+-ions in sodalite, see table), only one is actually present as there are in the structure no more electropositive valences available which could unite with an additional $(SO_4)^{--}$-ion. But in a calcium-bearing mixed crystal where Na^+ and Ca^{++} replace each other freely (because they have nearly the same ionic radius) the sum of the electropositive valences may be such that more than one $(SO_4)^{--}$-ion per unit of structure can be bound; the upper limit will be two, as there are not more than two positions available in the lattice. The general formula for the mixed crystal will thus be: $(Na, Ca)_{4-8}Al_6Si_6O_{24}(SO_4)_{1-2}$ where the number of the $(SO_4)^{--}$-ions depends upon how many electropositive valences are available, which again is determined by the Na:Ca ratio.

It should be added that only in this way can the atomic arrangement of haüyne be explained; no other chemical formula seems capable of explaining the observed intensities of the *x*-ray reflections.

It is noteworthy that the haüyne series in some respects is similar to the nepheline series, for if the silicates I and II′ are written: $3(Na_2Al_2Si_2O_8)\cdot Na_2SO_4$ and $3(CaAl_2Si_2O_8)\cdot CaSO_4$ respectively, it is seen that the molecule $Na_2Al_2Si_2O_8$ (nepheline molecule) is partly replaced by $CaAl_2Si_2O_8$ (anorthite molecule), just as has been found by Bowen (3) to be the case in crystals of nepheline. The same mechanism that conditions the unusual replacement of Na_2O by CaO in nepheline is therefore probably instrumental in haüyne also.

There is in all probability no complete series of solid solution between the silicates I and II′. Most natural haüynes carry about 60 per cent of silicate I (noselite silicate).

The following table gives the most recent analyses of haüyne recalculated in terms of the above-mentioned silicates.

TABLE 2. RECALCULATION OF HAÜYNE ANALYSES

	Haüyne from Monte Vulture (11)	Average value of haüyne from Laacher See (7)
	Mol. prop.	Mol. prop.
SiO_2	545	585
Al_2O_3	271	277
CaO	170	163
Na_2O	168	} 244
K_2O	58	
SO_3	100	} 152
Cl	11	
CO_2	10	
	$[Na_{5.0}Ca_{1.9}]Al_6Si_6O_{24}(SO_4)_{1.3}$ K_2O is reckoned with Na_2O and Cl and CO_3 are reckoned with SO_4	$[Na_{5.1}Ca_{1.7}]Al_6Si_6O_{24}(SO_4)_{1.5}$

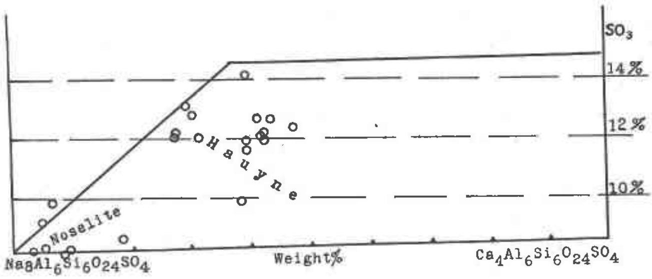

FIG. 1. Chemical composition diagram of noselite and haüyne [$(Na, Ca)_{4-8}Al_6Si_6O_{24}(SO_4)_{1-2}$]. Abscissa, ratio $Na_2O:CaO$. Ordinate, degree of sulfuration.

The crystal structure of these minerals requires that the composition lie within the blocked area, and the actual analyses (small circles in the diagram) confirm this.

SUMMARY

Noselite can be regarded as a chemical compound the composition of which can be expressed by the following formula: $Na_8Al_6Si_6O_{24}\cdot SO_4$.

Haüyne is a mixed crystal produced by the sodium in noselite being partly replaced by calcium and extra $(SO_4)^{--}$-groups simultaneously being built into the crystal lattice. The general formula for such a mixed crystal is: $(Na, Ca)_{4-8}Al_6Si_6O_{24}\cdot (SO_4)_{1-2}$.

REFERENCES
(With informatory notes)

1890.

(1) BRÖGGER, W. C., AND BÄCKSTRÖM, H., Die Mineralien der Granatgruppe: *Zeitschr. f. Krist.*, **18,** 209–276, 1890.

Formulae for noselite and haüyne as proposed by Rammelsberger, Clarke, Groth, and others were discussed. New formulae were set forth: noselite: Na_4 $Al(NaSO_4)$ $Al_2\cdot(SiO_4)_3$ and haüyne: Na_2Ca $Al(NaSO_4)$ $Al_2(SiO_4)_3$. These formulae are still generally accepted. The crystallographic relationship to helvite, which at that time seemed utterly fortuitous, was suggested; this was later verified through my x-ray studies (*Norsk Geol. Tidsskr.* **9,** 40, 1926) and can now be explained as a consequence of the radius ratios of the constituent ions. All these minerals were regarded as belonging to the garnet family.

1899.

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The correct formula for noselite, $6(NaAlSiO_4)\cdot Na_2SO_4$, was established based on synthetic studies; the same formula has since been confirmed by various investigators (6), (7), (8), (10); but owing to the conservatism peculiar to the science of mineralogy it has failed, so far, to become generally accepted. M. further explained haüyne as a mixed crystal of noselite and the silicate

$2(CaAl_2Si_2O_8)CaSO_4$, which is indeed very close to the truth. It is unfortunate that this fine piece of work has received so little attention. References to the earlier literature are given.

1912.

(3) Bowen, N. L., The binary system $Na_2Al_2Si_2O_8$ (nephelite-carnegieite)-$CaAl_2Si_2O_8$ (anorthite): *Am. J. Sci.*, **33**, 551, 1912.

The existence of mixed crystals between $Na_2Al_2Si_2O_8$ and $CaAl_2Si_2O_8$ was established.

1912.

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1920.

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The old formulae by Brögger and Bäckström were maintained.

1921.

(6) Gossner, B., Zur chemischen Konstitution der Silikate: *Centralblatt f. Min.*, **1921**, p. 513; **1922**, p. 193 ff.

Morozewicz's formula for noselite was re-established. Brögger and Bäckström's formula for haüyne was maintained.

1922.

(7) Brauns, R., Die Mineralien der Niederrheinischen Vulkangebiete, *Stuttgart*, **1922.**

Morozewicz's formula for noselite was re-established; to haüyne was given the formula as stated in the beginning of the present paper.

1927.

(8) Barth, T. F. W., Die Pegmatitgänge im Seilandgebiete: *Vid. Akad. Skr. Oslo*, **1927**, No. 8.

The section: "Zur Konstitution der Sodalitmineralien" (p. 75 ff.) is a preliminary note on the results given in the present paper. Based on X-ray studies Morozewicz's formula for noselite was re-established, and haüyne was regarded as a mixed crystal of noselite and the silicate: $3(CaAl_2Si_2O_8)\cdot CaSO_4$.

1929.

(9) Jaeger, F. M., Constitution and Structure of Ultramarine: *Akad. Amsterdam Versl.*, **32**; *Trans. Faraday Soc.*, **25**, 320, 1929.

X-ray data on noselite and haüyne.

1930.

(10) Borgström, L. H., Chemismus der Mineralien der Sodalith- und der Cancrinitgruppe: *Zeitschr. f. Krist.*, **74**, 117, 1930.

Morozewicz's formula for noselite was re-established. Brögger and Bäckström's formula for haüyne was maintained.

1931.

(11) Rittmann, A., Gesteine und Mineralien von Monte Vulture: *Schweiz. Min. Petr. Mitt.*, **11**, 250, 1931.

New analysis of haüyne.