

## AFGHANITE: NEW OCCURRENCES AND CHEMICAL COMPOSITION

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### ABSTRACT

Afghanite has been identified and analyzed by microprobe in lapis lazuli from Lyadzhuar-Darinsk, U.S.S.R. and Edwards, New York, U.S.A., bringing to five the number of known occurrences of this mineral. A new analysis of a specimen from the type locality, Sary-Sang, Afghanistan, leads to the idealized formula  $4[A_8B_{12}O_{24}X_3]$ , with  $A = \text{Na, Ca, K}$ ;  $B = \text{Si, Al}$ ;  $X = \text{SO}_4, \text{Cl, CO}_3$ . The role of H has not been established. Compared to other members of the cancrinite group, afghanites tend to be rich in Ca but depleted in K. They have  $\text{SO}_4:\text{Cl} \approx 1:1$ , but little  $\text{CO}_3$ . The relationship of natrodavynite and magnesium-cancrinite to established members of the cancrinite group is uncertain.

### SOMMAIRE

On a identifié et analysé à la microsonde l'afghanite du lapis lazuli de Lyadzhuar-Darinsk (U.R.S.S.) et d'Edwards, N.Y. (E.-U.), ce qui porte à cinq le nombre d'endroits où ce minéral a été repéré. De plus, une analyse nouvelle de l'afghanite faite sur spécimen de la localité-type, Sary-Sang (Afghanistan), mène à la formule idéalisée  $4[A_8B_{12}O_{24}X_3]$  avec  $A = \text{Na, Ca, K}$ ;  $B = \text{Si, Al}$ ;  $X = \text{SO}_4, \text{Cl, CO}_3$ . Le rôle de l'hydrogène demeure obscur. En comparaison des autres membres du groupe des cancrinites, les afghanites sont riches en Ca et pauvres en K, avec rapport  $\text{SO}_4:\text{Cl}$  proche de l'unité et faible teneur en  $\text{CO}_3$ . Quoique les autres membres du groupe aient aussi des compositions caractéristiques, leur relation avec la natrodavynite et la cancrinite magnésienne reste incertaine.

(Traduit par la Rédaction)

### INTRODUCTION

Afghanite is an uncommon mineral related to cancrinite, first described from a specimen of lapis lazuli from Sary-Sang, Afghanistan (Bariand *et al.* 1968) and later from lapis lazuli of the Lake Baikal region, U.S.S.R. (Ivanov & Sapozhnikov 1975). According to the Russian authors, afghanite was identified from the Tultui and Malo Bystrinski deposits by "further studies that showed that the mineral was

broadly distributed in occurrences of southwest Baikalia." Afghanite has recently been identified in silicified limestone ejecta in pumice from Pitigliano, Tuscany, Italy (Merlino & Mellini 1976, Merlino & Orlandi 1977b).

During a study of the petrogenesis of lapis lazuli, afghanite was positively identified in specimens taken from three different localities. Two of these (Edwards, New York and Lyadzhuar-Darinsk, Pamir, U.S.S.R.) are new localities for this mineral; Edwards is the first reported North American occurrence. The other specimen is from the type locality, Sary-Sang. Optical and chemical properties conform with afghanite but the final confirmation was made by X-ray diffraction photographs taken with a Gandolfi camera. The pattern closely matches that of type afghanite and include diagnostic lines with spacings of 6.05, 5.35 and 4.00 Å which belong to afghanite but not to cancrinite, davynite or microsommite (Bariand *et al.* 1968). In all specimens, the afghanite is rather fine-grained and too impure for single-crystal X-ray studies.

In addition, a mineral, very likely afghanite, was noted in other thin sections, but identifications rest on optical properties alone. These thin sections were cut from lapis lazuli of Lyadzhuar-Darinsk (2 additional specimens), Malo Bystrinski, Lake Baikal area, U.S.S.R. (1 specimen) and the main lapis lazuli occurrence, Lake Harbour, Baffin Island (1 specimen).

### OCCURRENCE

The Afghan specimen (no. 5) contains well-formed thin tabular crystals of afghanite (about 1% by volume) that cut through lazurite in several directions; at least two of these seem to be in a preferred orientation (Fig. 1) with {0001} laths of afghanite forming a dihedral angle of 60°. The laths do not extend beyond the lazurite grains. Common associated minerals are phlogopite, diopside and oligoclase.

Pamir specimen no. 4 contains approximately 13 vol. % afghanite. Crystals are stout to slender tabular; in some clusters, they are

## OPTICAL PROPERTIES

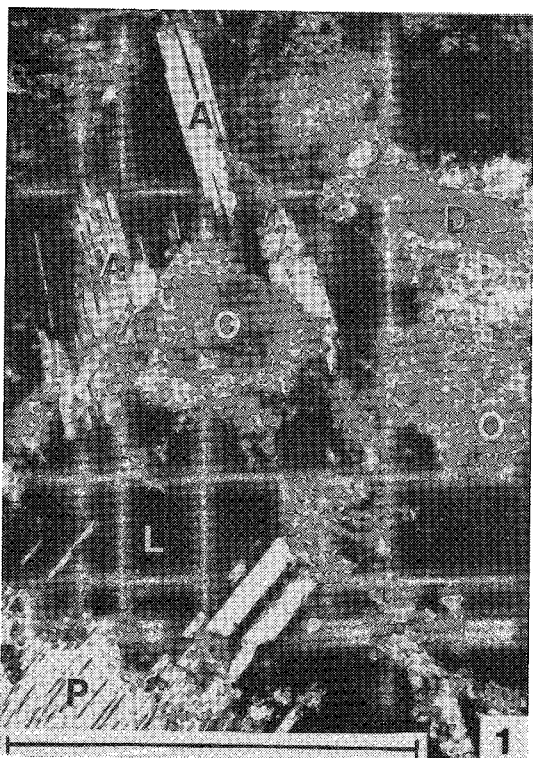


FIG. 1. Thin tabular afghanite (A) in lazurite (L). Other minerals are diopside (D), oligoclase (O) and phlogopite (P). Specimen 5 from Sary-Sang, Afghanistan. Crossed polars, bar scale = 1 mm.

present almost to the exclusion of lazurite. Afghanite and lazurite-afghanite clusters are surrounded by diopside.

Afghanite occurs in a similar crystal habit and mineral association in the two other Pamir specimens, but in very minor amounts. Tabular afghanite was identified (about 10% of the thin section) in a diopside-phlogopite-lazurite-calcite rock from Malo Bystrinski, Lake Baikal, U.S.S.R.

Lapis lazuli specimen no. 6 was collected from the D4 sphalerite orebody, Edwards mine (St. Joe Minerals Corporation), Edwards, New York. Major minerals are pargasite, diopside, oligoclase and lazurite. Afghanite amounts to about 1% by volume. Its habit is somewhat different than in the Pamir and Afghan sections: rounded grains lack crystal outline and are commonly separated from lazurite. A few grains of tabular afghanite are also present in the thin section.

The Baffin Island afghanite appears as rounded isolated grains in small amounts in nepheline, associated with diopside and lazurite.

Bariand *et al.* (1968) and Ivanov & Sapozhnikov (1975) have shown that, in thin section, afghanite is colorless, uniaxial positive, has low-order interference colors and low relief. It lacks good cleavage and may show conchoidal fracture. With such quartz-like properties the mineral could possibly be confused with quartz itself, particularly where isolated in diopside and present in anhedral grains as at the Edwards mine. This may, at least in part, explain reports of quartz-lazurite associations (*e.g.*, Fersman 1920, Voskoboinikova 1938); otherwise, a free silica-feldspathoid association is difficult to understand.

Quite possibly, some minerals in lapis lazuli, identified optically as natrodavynite, may also be afghanite. Thus "natrodavynite" from the Slyudyanka region gave  $\omega = 1.525$ ,  $\epsilon = 1.530$ ,  $\Delta = 0.0053$  (Smirnov 1928); the Lyadzhuar-Darinsk material gave  $\omega = 1.522$ ,  $\epsilon = 1.528$ ,  $\Delta = 0.005$  (Yudin *et al.* 1932). Type natrodavynite from Vesuvius has  $\omega = 1.5220$ ,  $\epsilon = 1.5267$ ,  $\Delta = 0.0047$  (Zambonini 1910). However, the quantities of certain chemical constituents reported by Zambonini are questionable. For example,  $\text{SO}_3$  was found by difference and  $\text{K}_2\text{O}$ , apparently, was not determined. The status of this mineral is therefore uncertain.

TABLE 1. CHEMICAL COMPOSITION OF AFGHANITE

	1	2	3	4	5	6
$\text{SiO}_2$	30.8	28.9	32.10	31.8	31.95	32.96
$\text{TiO}_2$	n.d.	n.d.	B.D.	n.d.	B.D.	n.d.
$\text{Al}_2\text{O}_3$	25	23.8	27.00	25.2	26.58	25.45
FeO	n.d.	n.d.	n.d.	n.d.	B.D.	B.D.
MgO	n.d.	n.d.	B.D.	0.03	B.D.	B.D.
CaO	16.5	17.4	12.34	11.7	11.66	11.98
$\text{Na}_2\text{O}$	12.6	(12.6)	12.43	13.3	13.26	12.52
$\text{K}_2\text{O}$	2.7	2.8	0.86	2.2	2.60	2.07
$\text{SO}_3$	8.5	8.3	9.68	10.5	10.99	10.82
Cl	4.6	5.5	4.54	3.6	4.35	3.98
F	n.d.	n.d.	0.035	n.d.	0.04	n.d.
$\text{CO}_2$	0.4	n.d.	0.76	n.d.	n.d.	n.d.
$\text{H}_2\text{O}$	0.7	n.d.	2.11	n.d.	n.d.	n.d.
	101.8	99.3	101.86	98.33	101.43	100.78
OnCl,F	1.0	1.2	1.05	0.81	1.00	0.90
	100.8	98.1	100.80	97.52	100.43	99.86
Ions based on 12 (Si + Al)						
Si	6.13	5.09	6.03	6.20	6.06	6.28
Al	5.87	12.00	5.97	5.97	5.94	5.72
Fe	—	—	0.00	—	0.00	0.00
Mg	—	—	0.01	—	0.00	0.00
Ca	3.52-9.07	3.93-9.83	2.48-7.21	2.45-8.04	2.37-7.88	2.45-7.83
Na	4.86	5.15	4.52	5.03	4.88	4.63
K	0.69	0.75	0.21	0.56	0.63	0.75
$\text{SO}_4$	1.27	1.31	1.36	1.54	1.55	1.55
Cl	1.55	1.96	1.44	1.19	1.40	1.28
F	—	2.93	3.27	—	2.73	—
$\text{CO}_3$	0.11	—	0.02	—	0.02	2.84
O	25.21	25.63	23.57	24.21	23.88	24.08
$\text{H}_2\text{O}$	0.46	—	1.32	—	—	—
$\omega$	1.523	—	1.528	—	—	1.522
$\epsilon$	1.529	—	1.533	—	—	1.529
$\Delta$	0.006	—	0.005	—	—	0.0055

1. Sary-Sang, Afghanistan; analysis on 150 mg by J. Fritsche (Bariand *et al.* 1968).

2. Sary-Sang, Afghanistan; microprobe analysis.  $\text{Na}_2\text{O}$  value from analysis 1.

3. Tultut deposit near Lake Baikal, U.S.S.R. E.A. Klepikova, analyst (Ivanov & Sapozhnikov 1975).

4. Lyadzhuar-Darinsk, Pamir, U.S.S.R.; microprobe analysis by W.L. Griffin, Oslo.

5. Sary-Sang, Afghanistan; microprobe analysis by P. Morton, Ottawa.

6. Edwards, New York; microprobe analysis by P. Morton, Ottawa.

B.D.: below detection; n.d.: not determined.

Refractive indices and birefringences of afghanite are listed at the bottom of Table 1.

#### CRYSTAL CHEMISTRY OF THE CANCRINITE GROUP

A review of the literature suggests that individual members of the cancrinite group have rather distinctive compositions. To explore these peculiarities further, the minerals were studied with respect to their *A* ions (Na, Ca, K) and plotted in Figure 2. Analyses of cancrinite and vishnevite taken from Deer *et al.* (1963) are supplemented with a number of analyses from the literature, two unpublished analyses from Kaminak Lake, Northwest Territories (kindly supplied by Dr. A. Davidson, Geological Survey of Canada) and three unpublished analyses of material from the Goulding-Keene quarry, Bancroft, Ontario (Reeve 1972). Analyses of davyne and microsommite are from Bariand *et al.* (1968), liottite from Merlino & Orlandi (1977a), franzinite from Merlino & Orlandi (1977b) and afghanite from Table 1 (analysis 2 omitted).

It can be seen that each member defines a rough compositional domain; vishnevites (including the sulfatic cancrinites of Deer *et al.* 1963), followed by cancrinites, tend to be most sodic; microsommites, davynes and liottite are

more potassic. However, note that whereas cancrinites and afghanites come from worldwide localities, microsommites and davynes are all from the Mount Vesuvius area and analyses are old, mainly of 1873-1878 vintage.

Two analyses warrant special mention. Numbers 8 and 9 are "magnesium-cancrinites" from St. John's Island, Egypt; they contain 8.71 and 9.90% MgO, respectively (Spencer 1923, El Shazly & Saleeb 1972). However, the high totals of *A* ions (8.72 and 9.09 atoms per formula) render these specimens somewhat suspect as members of the cancrinite group.

Members of the group may have a large deficit of *A* ions, commonly up to 25%. Thus Deer *et al.* (1963) list 6 to 8 Na, Ca, K atoms per formula unit.

A plot was also made to represent the *X* ions: S, C, Cl (Fig. 3). Here also, there is a suggestion that members tend to lie in characteristic compositional fields but some analyses used in Figure 2 have been omitted because they were incomplete; therefore, the domains are less well defined. Analyses 8 and 9 are at variance with cancrinite. In fact, number 9 lies rather close to afghanite in Figures 2 and 3 but its content of Mg and X-ray pattern distinguish it (El Shazly & Saleeb 1972). Afghanite has a ratio S:Cl of approximately 1:1, with little C.

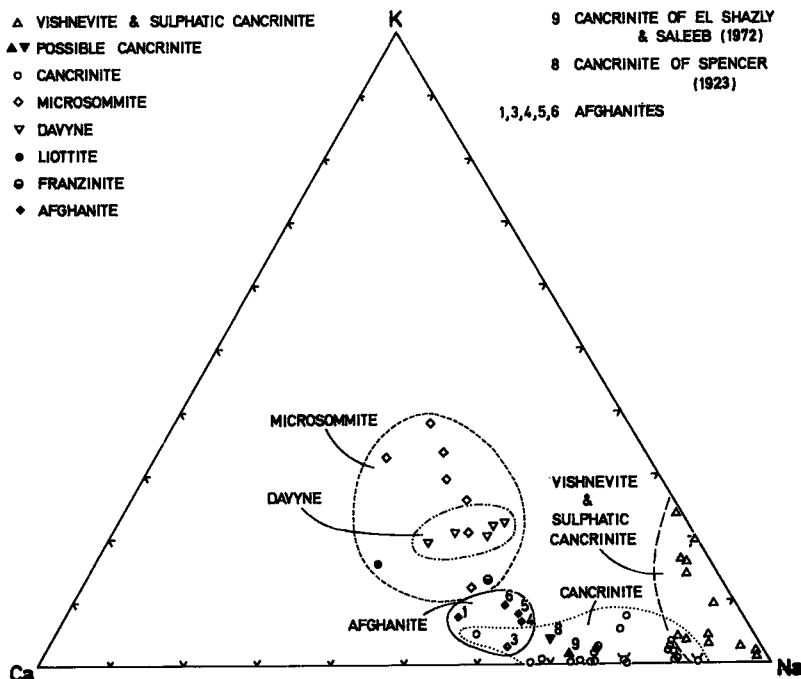


FIG. 2. Na-Ca-K diagram (atomic proportions) for minerals of the cancrinite group.

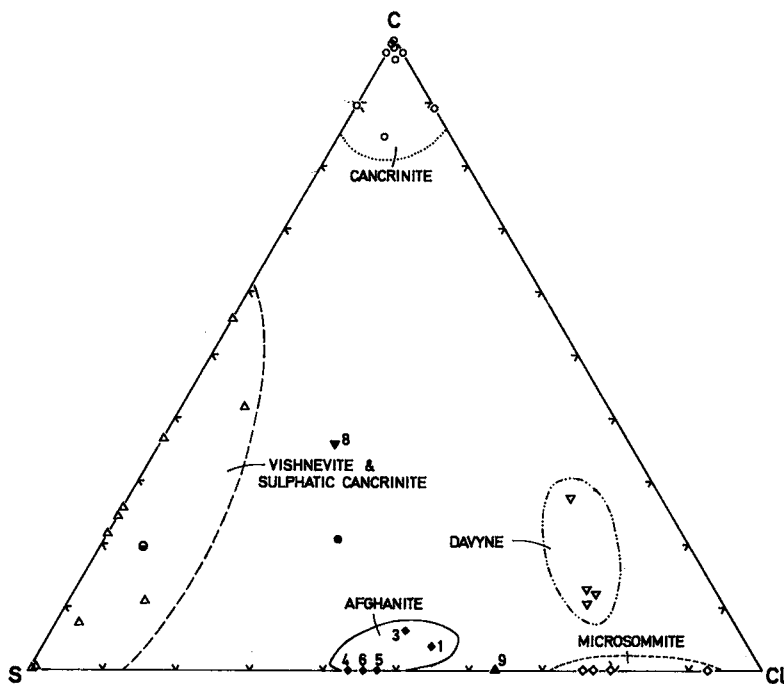


FIG. 3. S-Cl-C diagram (atomic proportions) for minerals of the cancrinite group. Symbols are the same as those in Figure 2.

The role of hydrogen is uncertain. Natural and synthetic cancrinites (Moenke 1974, Porotnikova & Derevyankin 1975) were shown to contain  $H_2O$  by infrared analysis. Weight-loss studies on type vishnevite (6.71%  $H_2O$ ) by Belyankin (1944) did not reveal hydroxyl or coordinated  $H_2O$  but suggested adsorbed water. However, IR and PMR analyses of synthetic hydrous cancrinite (4.03%  $H_2O$ ) by Sokolov *et al.* (1977) indicated two types of 'water', located as  $H_2O$  and  $H_3O^+$  in channelways parallel to *c*. This supports the conclusions of Barrer *et al.* (1970) who also placed water molecules in these channelways after detailed considerations based on X-ray diffraction data. Water was confirmed in afghanite from the Tultui deposit, U.S.S.R. (Table 1, Anal. 3) but OH seems precluded by IR and DTA studies. In addition, the X-ray pattern of a specimen heated for 1 hour at  $900^\circ C$  was identical with that of the unheated sample (Ivanov & Sapozhnikov 1975).

#### CHEMICAL COMPOSITION OF AFGHANITE

Table 1 lists available analyses of afghanite. Numbers 1 and 2 were made from the same

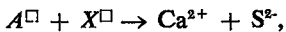
specimen. Bariand *et al.* (1968) used analysis 1 to derive their chemical formula;  $Na_2O$  was not determined in analysis 2, and analysis 1 was obviously considered the more reliable. The formula  $3[A_{12}B_{10}O_{34}X_4]$  was chosen over  $4[A_3B_{10}O_{24}X_3]$ . This preference was apparently guided mainly by a large total of *A* ions and a large amount of derived oxygen. However, the analyzed  $SiO_2$  and perhaps also  $Al_2O_3$  seem low compared to analyses 3 to 6. An increase in  $SiO_2$  would have the effect of lowering both *A* cations and oxygen in the formula. Furthermore, Bariand *et al.* state: "l'afghanite doit certainement contenir un peu de  $S^{2-}$ ." This would lower oxygen still further. Both formulae have numbers of atoms that can be accommodated in space group  $P6_3mc$  determined by Merlino & Mellini (1976).

In their description of the Tultui afghanite, Ivanov & Sapozhnikov give  $A_3B_{10}O_{24}X_3$  as an alternative formula; the agreement both in *B* ions and oxygen is better with this formula than with  $A_{12}B_{10}O_{34}X_4$ . A calculated density for this formula, using cell parameters supplied by Ivanov & Sapozhnikov and  $Z = 4$ , gives  $2.527 \text{ g/cm}^3$ . This compares well with the measured specific gravity of 2.517 quoted by the Russian authors and with the density calculated

from the Gladstone-Dale relationship ( $2.524 \text{ g/cm}^3$ ) using a geometrically weighted refractive index (1.530) and the specific refractive energies of Mandarino (1976).

Analyses 4, 5 and 6 are new microprobe analyses made at the Central Institute for Industrial Research (Oslo) and Carleton University (Ottawa) on ARL-EMX and Cambridge MK-5 microprobes, respectively. Values are averages of scans on several grains per thin section with a defocused beam. The sums of  $A$ ,  $B$  and  $X$  ions are in correct proportions for  $A_8B_{12}O_{24}X_3$ ;  $B:O$  is approximately 1:2. This formula is therefore preferred. It also resembles the cancrinite formula  $A_{8-2}B_{12}O_{24}X_{2-2}$  advocated by Jarchow (1965). In afghanite the ratio  $S:Cl$  approaches 1:1, suggesting some ordering in the  $X$  group.

Major cations in afghanite are relatively constant.  $K$  is depleted in the Tultui mineral (anal. 3, Table 1). Type afghanite is enriched in  $Ca$  compared to afghanite from other localities. The resulting charge surplus does not seem to be balanced by defects in  $A$  nor by coupled substitution involving  $Al$ . It must then be compensated by anion adjustment, perhaps by  $S^{2-}$  ions, with a replacement scheme of the type



where  $A^{\square}$  and  $X^{\square}$  represent vacant sites in  $A$  and  $X$ , respectively.

In conclusion, afghanite is a member of the cancrinite group that commonly occurs in lapis lazuli as oriented intergrowths in lazurite and rounded grains in diopside, nepheline and plagioclase. It has also been observed in limestone xenoliths in pumice. Afghanite has the general formula  $4[A_8B_{12}O_{24}X_3]$ , where  $A$  is mainly  $Na$  and  $Ca$ , with lesser  $K$ ;  $B$  represents  $Si$  and  $Al$  in approximately equal proportions;  $X$  is essentially  $SO_4$  and  $Cl$ , with little  $CO_3$ . The role of  $H$  is uncertain. Afghanite is uniaxial positive, with  $\omega$  about 1.52 and  $\Delta = 0.005$  to  $0.006$ .

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of specimens from Afghanistan and Edwards was defrayed by a National Research Council Operating Grant. Dr. W. L. Griffin kindly analyzed afghanite from Pamir. X-ray diffraction (Gandolfi) photographs were taken and interpreted by Miss Judith Baker at Carleton University. The manuscript was much improved after discussion with Drs. G. Y. Chao, A. Davidson and V. S. Papezik and the comments of the referees and the Associate Editor, Dr. J. A. Mandarino.

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Note added in proof: "Magnesium-cancrinite" from St. John's Island has been shown by W.L. Griffin (pers. comm.) to be a mixture of a Mg-free cancrinite-group mineral with calcite and spinel.