NEW DATA ON GALEITE AND SCHAIRERITE

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Abstract

Microprobe analyses of galeite, schairerite and galeite-schairerite polycrystals show that both phases are remarkably constant in Cl and F content, corresponding to the formula $Na_{15}(SO_4)_5F_4Cl$ for galeite and the formula $Na_{21}(SO_4)_7F_6Cl$ for schairerite. These formulas can be nicely reconciled with the cell dimensions of these and related phases.

Introduction

In their paper on galeite and related phases in the system Na_2SO_4-NaF-NaCl Pabst, Sawyer, and Switzer (1963, p. 485) stated that "The composition of galeite . . . may be represented by the formula that has been used for schairerite, $Na_2SO_4 \cdot Na(F,Cl)$." This formula had been used by Foshag (1931) when he named schairerite. He considered schairerite to be a mix crystal belonging to a series of which $Na_2SO^4 \cdot NaF$ is an end member. This compound was first described by de Marignac (1859). Wolters (1910) found only this double salt in the system Na_2SO_4-NaF-NaCl, but Foote and Schairer (1930) reported that "the double salt $Na_2SO_4 \cdot NaF$ has a limited part of its fluoride replaced by chlorine." They made no quantitative statement as to the substitution and gave only meager evidence in support of their assertion. Foshag, doubtless influenced by Foote and Schairer, attempted to refer morphological observations on schairerite and on the double salt to a common lattice.

Fleischer (1956), in reporting the preliminary description of galeite, wrote "Analysis . . . corresponding to $Na_2SO_4 \cdot Na(F,Cl)$. The mineral is therefore dimorphous with schairerite."

Pabst *et al.*, (1963) showed that the three phases, $Na_2SO_4 \cdot NaF$, schairerite, and galeite are morphologically and structurally distinct. In their Table 1 particular values of F:Cl were suggested for schairerite and galeite though the formula $Na_2SO_4 \cdot Na(F,Cl)$ was retained for both. The analyses reported for galeite at that time were in fair or good agreement with the proposed F:Cl ratio of 4:1 for this mineral, but the newly reported schairerite analysis as well as the analysis quoted from Foshag did not support the ratio 6:1 suggested for that mineral. The suggested ratios were based largely on physical properties and cell dimensions set forth in tables 2 and 3 and figures 7 and 9 (Pabst *et al.*, 1963). The existence of galeite-schairerite polycrystals for which a discontinuity in the *c* cell dimension could be predicted from morphology supported the view that there is a discontinuous change in composition between galeite and schairerite.

TABLE 1. AVERAGE ANALYSES OF GALEITE AND SCHAIRERITE
IN POLYCRYSTALS 1 AND 2

	Galeite			Schairerite		
	1	2	$Na_{15}(SO_4)_5F_4Cl$	1	2	$Na_{21}(SO_4)_7F_6Cl$
Na	36.4	36.5	36.82	36.7	36.8	37.00
SO$_4$	51.2	51.3	51.28	51.4	51.7	51.54
Cl	3.79	3.78	3.79	2.77	2.75	2.72
F	8.1	7.7	8.11	8.7	8.4	8.74
Total	99.49	99.28		99.57	99.65	

MICROPROBE STUDY

Several crystals of galeite, of schairerite, and of galeite-schairerite polycrystals were selected by morphology from the materials used in the earlier work it having been shown that these can be morphologically distinguished with assurance (Pabst *et al.*, 1963, figs. 3 & 5, tables 4 & 5).

Two of these crystals (designated polycrystals 1 and 2) which exhibit galeite morphology at one end, and schairerite morphology at the other, were analyzed with the electron microprobe. Average analyses were obtained using a large beam diameter (ca. 7 microns) and a sample current of ca. 0.05 microamperes. The standards used for analysis were sulfohalite ($Na_6(SO_4)_2FCl$), synthetic $Na_2SO_4 \cdot NaF$, and halite. Analyses were not available for these materials and they were assumed to be stoichiometric. The counts were corrected for background, but no other corrections (fluorescence, absorption, etc.) were made as the standards and unknowns are very similar in composition. Synthetic spinel was used to obtain background values. Average analyses of the two phases in the two polycrystals are given in Table 1. Other crystals of galeite and schairerite were also analyzed for fluorine and chlorine and yielded essentially the same values as the polycrystals.

Traverses across the grains were made using a beam diameter of ca. 2 microns at a sample current of ca. 0.025 microamperes. Because of volatilization the data obtained during the traverses were used only qualitatively. The results of the traverses are depicted in Figure 1, where the number of counts accumulated in twenty seconds is plotted against the distance along the traverse. Fifty micron steps were taken between analyzed points in polycrystal 1, except near the boundary between schairerite and galeite where 20 micron steps were taken. Ten micron steps were taken across the galeite-schairerite boundary of polycrystal 2. One point near the boundary (represented by the barred line in Figure 1) gave two quite different numbers of counts when occupied two successive times. This may perhaps be explained by assuming that the point occupied was not *exactly* the same, but that the beam impinged on the crystal slightly on the galeite side of the boundary in the one case, and on the schairerite side of the boundary in the other case. If this is so, then the dashed lines in Figure 1 are perhaps more realistic than the solid line, and the transition is quite sharp, certainly being less than ten microns in width.

INTERPRETATION OF THE RESULTS

Figure 1 and Table 1 show that schairerite and galeite are remarkably constant in composition and that the F and Cl contents agree well with
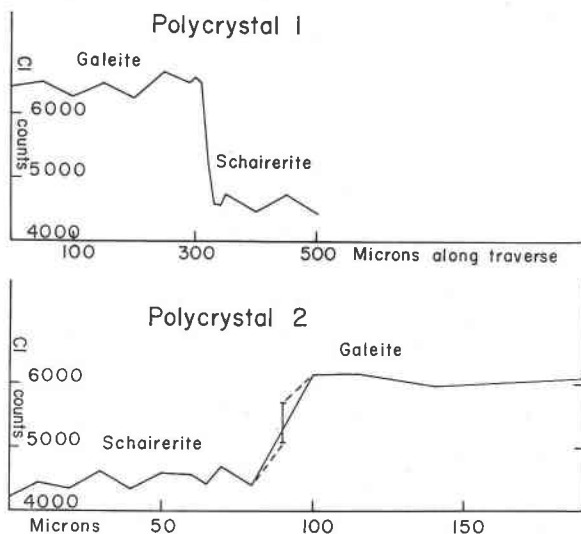
FIG. 1. Electron microprobe traverses across the schairerite-galeite boundary in two polycrystals.

the requirements of the F:Cl ratio 6:1 for schairerite and 4:1 for galeite. From these ratios it is possible to make close predictions of the c dimensions of schairerite and galeite from some very simple assumptions.

The cell dimensions of $Na_2SO_4 \cdot NaF$, schairerite, galeite and sulfohalite are given in Table 2. The structure of sulfohalite is here described in the hexagonal setting appropriate to cubic face-centering. This structure has recently been refined by Sakamoto (1968), confirming the old determinations by Watanabé (1934) and by Pabst (1934). As thus described the structure can be looked upon as consisting of alternating sheets of F ions and Cl ions between which lie sheets of Na_3SO_4. The distance between F and Cl sheets is $10.068 \times \sqrt{3}/6 = 2.906$.

It has been shown both from cell dimensions (Pabst et al., 1963, table 3 and fig. 7), a consideration of $hki0$ intensities (1963, table 6) and the topotaxy of Na_3SO_4F formed on heating of schairerite, galeite or sulfohalite (1963, p. 508–509) that the structures of the four phases are closely related. Na_3SO_4F has a marked subcell with $a_h' = a_h = 6.962$ Å. This subcell contains $9(Na_3SO_4F)$ and the distances between fluorine sheets in the structure may confidently be taken to be $24.50/9 = 2.722$ Å.

If the F:Cl ratios of schairerite and galeite are 6:1 and 4:1 respectively the structures must involve one chlorine sheet to every 6 fluorine sheets in schairerite and one chlorine sheet to every four fluorine sheets in galeite. The c dimension of schairerite may then be expected to correspond to 2

TABLE 2. CELL DIMENSIONS OF MULTIPLE SALTS IN THE
SYSTEM Na_2SO_4-NaF-NaCl

	Sulfohalite	Galeite	Schairerite	$Na_3(SO_4)F$
a	10.068 Å[a]			
a_h	7.119 $(a/\sqrt{2})$	12.17	12.17	27.85
		$(7.026 \times \sqrt{3})$	$(7.026 \times \sqrt{3})$	(6.962×4)
c_h	17.44 $(a \cdot \sqrt{3})$	13.94	19.29	24.50
c_h predicted		13.98	19.42	
Cell content[b]	$Na_{18}(SO_4)_6F_3Cl_3$	$Na_{15}(SO_4)_5F_4Cl$	$Na_{21}(SO_4)_7F_6Cl$	$Na_{27}(SO_4)_{18}F_9$
ρ(obs.)	2.505	2.605	2.616[c]	2.67
ρ(calc.)	2.503	2.610	2.627	2.674

[a] a of sulfohalite from Sakamoto (1968); other dimensions from Pabst et al. (1963).

[b] Cell content of sulfohalite for the hexagonal cell, the volume of which is $\frac{3}{4}$ that of the cubic cell. Cell content of $Na_3(SO_4)F$ is for the prominent subcell with a_h 6.962 Å (6.912 in table 3, Pabst *et al.* (1963) is a misprint), and those of galeite and schairerite are for the prominent subcells with a_h 7.026 Å.

[c] The observed density given for schairerite in 1963, 2.612, was taken from Foshag (1931). Trial of many crystals by Berman balance with check on temperature and zero point before and after each determination yielded values in the range 2.59–2.62. One crystal weighing 17.31 mg. upon five trials gave 2.615, 2.616, 2.618, 2.612, 2.617, average 2.616-, σ ca. 0.002.

F-Cl intersheet distances and 5 F-F intersheet distances, $2 \times 2.906 + 5 \times 2.722 = 19.42$ Å, whereas that of galite should correspond to 2 F-Cl and 3 F-F intersheet distances, $2 \times 2.906 + 3 \times 2.722 = 13.98$ Å. The results are summarized in Table 2.

In view of the discrepancy between observed and calculated density of schairerite, the density relations of schairerite, galeite, and polycrystals were checked by suspension in a bromoform-ethanol mixture tested with a Westphal balance calibrated at 2.65 by means of a quartz crystal at 25°C. Several smaller, clean, schairerite crystals, galeite crystals, and polycrystals, too small for Berman balance measurements, were compared with the reference schairerite of density 2.616 (footnote in table 2), the density of the solution being varied only slightly by adjusting the temperature. In this way the crystals could be moved up and down at will, only slightly distributed by convection currents. The effect of the small density difference between schairerite and galeite was readily apparent and two of the three polycrystals when quietly suspended always had the galeite end upward. Also, one of the smaller schairerite crystals descended more quickly than the reference crystal, indicating its density to be slightly greater than 2.616. Evidently all but the smallest and most perfect schairerite crystals are affected by voids or imperfections and

perhaps galeite intercalations reducing the observed density, a condition visible in some larger crystals as veils or milkiness.

Conclusion

Finally we wish to emphasize that galeite and schairerite are not members of a mix crystal series as was implied by the formula previously assigned to them. Rather, these two minerals together with $Na_3(SO_4)F$, which has been described by Kogarko (1961) as "chlorine-free schairerite," and sulfohalite constitute a series comparable to the bastnaesite-parisite-roentgenite-synchisite series (Donnay and Donnay, 1953, also McConnell, 1960) comprising a number of discrete phases among which syntaxic intergrowths are common. In the case of the bastnaesite-synchisite series all but one of the possible pairs have been observed as polycrystals. In the Na_3SO_4F-sulfohalite series polycrystals have been observed only between the two intermediate members here discussed.

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