

MINERALOGICAL NOTES

THE X-RAY SPECTROGRAPHIC DETERMINATION OF SULFUR COORDINATION IN SCAPOLITE

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INTRODUCTION

The coordination state of sulfur in the silicate mineral scapolite has been a subject of discussion in recent years (Lovering and White, 1964; Schwarcz and Speelman, 1965). In this paper, the coordination of sulfur is determined by comparing the wavelengths of sulfur K_{α} radiation produced by fluorescent excitation of calcium sulfide, calcium sulfite and calcium sulfate (gypsum), with the wavelengths of the fluorescent radiation emitted by two samples of sulfur-rich scapolite, one from Laacher See in Germany and the other from Delegate, Australia.

DISCUSSION OF PREVIOUS ATTEMPTS TO DETERMINE COORDINATION

In 1914, Brauns showed that sulfur was an important component of scapolite in inclusions from the Laacher See volcanic rocks. He suggested that the sulfur-bearing component of the scapolite (end member) had the formula $\text{CaSO}_4 \cdot 3[\text{CaAl}_2\text{Si}_2\text{O}_8]$ and he named this 'silvianite.' Other authors followed Brauns in recording the sulfur in scapolite analyses as SO_3 , thus implying that the sulfur occurred as the sulfate radicle (*e.g.* Smirnov, 1926; Serdyuchenko, 1955).

Lovering and White (1964) suggested the possibility that sulfur was present as a divalent ion S^{2-} and that there was a sliding equilibrium between metal sulfides and the silicate phase scapolite. This suggestion was put forward because high sulfur scapolites, such as those in the inclusions from Laacher See (Brauns, 1914) and Delegate (Lovering and White, 1964), are low in chlorine, indicating that the sulfur probably occupies the chlorine sites; it is notable that S^{2-} and Cl^- have similar ionic radii, whereas SO_4^{2-} is much larger and may as a result be too large to be accommodated in the chlorine sites.

Schwarcz and Speelman (1965) compared the infrared absorption spectra of sulfur-rich and sulfur-poor scapolites in an attempt to distinguish absorption maxima corresponding to frequency modes for SO_3^{2-} . Unfortunately, these are largely obscured by SiO_4^{4-} bands although there is some indication of the presence of faint SO_3^{2-} bands.

EXPERIMENTAL PROCEDURE

The measurements were made using a Philips PW1220 spectrograph, operating under the following conditions:

X-ray tube: chromium (55kV, 36mA)

Primary collimator: 160 μ m

Analyzing crystal: pentaerythritol

Detector: flow proportional counter, fitted with a 3 μ m Mylar window and filled with P10 gas

Pulse height selector: 1-2 volt window

The samples were prepared following the procedure of K. Norrish and J. T. Hutton¹ (see also Norrish and Chappell, 1967, p. 204-206), giving pelleted samples with a boric acid back and edge. Approximately 0.5 gm of sample was used in each case.

The 2θ position of each line was determined by averaging the goniometer settings at which the same intensity was measured on either side of the peak (approximately 90% of the peak intensity). This method should give good relative values between various samples since, as Wilbur and Gofman (1966) have shown, the sulfur K_{α} line shows no noticeable structure changes with bonding, whereas changes in the structure of the K_{β} line are very marked (Faessler and Schmid, 1954). It was found that line positions could be located with a precision of $0.0025^{\circ}2\theta$ (0.00015 Å, 0.064eV), provided that the radiation being measured

TABLE 1. SHIFT IN SULFUR K_{α} LINE

	$\Delta 2\theta$	$\Delta\lambda$ (Å)	ΔE (eV)
Calcium sulfide	0	0	0
Calcium sulfite	0.0175°	0.00108	0.46
Calcium sulfate (gypsum)	0.0325°	0.00200	0.86
Laacher See scapolite	0.0325°	0.00200	0.86
Delegate scapolite	0.0300°	0.00184	0.79

was sufficiently intense. This precision compares favorably with that obtained using a focussing geometry on a microprobe (White *et al.*, 1962; White and Gibbs, 1967).

The 2θ positions of the sulfur K_{α} line of calcium sulfide, calcium sulfite, calcium sulfate and the Laacher See and Delegate scapolites were measured and these results are reported in Table 1. The measurements are given as shifts in the 2θ position relative to calcium sulfide, where the shift ($\Delta 2\theta$) is given by

$$\Delta 2\theta = 2\theta(\text{CaS}) - 2\theta(\text{sample})$$

The wavelength ($\Delta\lambda$) and energy (ΔE) differences corresponding to the 2θ shift of the K_{α} line, are also given in Table 1.

The sulfur K_{β} line has not been examined in detail because of its complex structure, the fact that the wavelength shift is comparable to the K_{α} line ($\Delta 2\theta$ between calcium sulfide and calcium sulfate was measured as 0.0375°) and since the intensity of the K_{β} radiation emitted by the scapolite samples was very low.

DISCUSSION

The historical aspects of the effect of chemical state on X-ray emission spectra have recently been summarized by White and Gibbs (1967). Specific studies on sulfur have been made by Faessler and Goehring (1952), Faessler and Schmid (1954), Faessler (1963) and Wilbur and Gofman (1966). Faessler and Goehring (1952) investigated the wavelengths of sulfur K_{α} lines from a number of compounds and found that

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the oxidation number of the emitting atom exercised primary control over the wavelengths of the K_{α} lines, so that higher oxidation numbers resulted in shorter wavelengths. The following wavelength ranges were recorded for the K_{α_1} line

Sulfate	5.36872 Å—5.36900 Å	(5 samples)
Sulfite	5.36910 Å—5.36967 Å	(6 samples)
Sulfide	average 5.37198 Å	(18 samples)

No overlapping of wavelengths was found between the three groups. The values reported for calcium sulfate and calcium sulfite were 5.36872 Å and 5.36967 Å respectively, a difference of 0.00095 Å (0.41eV), compared with a difference of 0.00092 Å (0.40eV) for the corresponding K_{α} doublets in Table 1. This indicates that the method used here is capable of some precision in measuring wavelength differences. There is an apparent discrepancy between the present data and that of Faessler and Goehring (1952) in the case of calcium sulfide, since the difference in wavelengths between both the sulfite and sulfate, and the sulfide are much greater than that recorded by Faessler and Goehring. These authors did not, however, present results for calcium sulfide and they pointed out that the sulfur K_{α} radiation of the alkali earth elements is of considerably longer wavelength than that of other elements. Results from the alkali earth sulfides were not included in their average sulfide figure.

It is clearly possible to distinguish between sulfur present in compounds as sulfate, sulfide and sulfite, by measuring wavelength shift, and it is apparent that the method adopted here is sufficiently precise to make such a distinction. Reference to the data presented in Table 1 shows that the sulfur in the two scapolite samples emits K_{α} radiation with a wavelength corresponding to that emitted by calcium sulfate, within the limits of experimental error. This radiation is of significantly shorter wavelength than that emitted by calcium sulfite and calcium sulfide, and it is concluded that the sulfur in both scapolites is present in the hexavalent state.

This is in agreement with the original suggestion of Brauns (1914). The recent structure determination of calcium-rich scapolite by Papike and Stephenson (1966) has shown that there is room for the SO_4^{2-} radicle in the cavity in the scapolite structure.

The presence of the SO_4^{2-} radicles further restricts the conditions under which sulfur-rich scapolite may occur in nature; it not only requires a high temperature and pressure (Lovering and White, 1964) but also a high oxygen fugacity for its formation.

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INEXPENSIVE CRYSTAL STRUCTURE MODELS OF FRAMEWORK TETRAHEDRA.

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INTRODUCTION

Tetrahedral framework models are particularly useful in the study, description, and visualization of the crystal structures of framework minerals such as tectosilicates. Techniques for building such models have been described by a number of authors, among them Tilton (1957), Meier (1960), Smith (1960), and Fieser (1963). V. Schomaker, cited by Breck (1964), developed a method for making models built of welded stainless steel tetrahedra joined by plastic sleeves. Here, we describe a method for producing large numbers of wire tetrahedra without expensive apparatus or materials.