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THE VALENCE OF SULFUR IN GLASS OF BASALTIC COMPOSITION FORMED UNDER CONDITIONS OF LOW OXIDATION POTENTIAL

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Abstract

The wavelength of $SK_{\alpha 1}$ radiation emitted from a synthetic basaltic glass and a sample of scapolite, where sulfur occurs as sulfate, is measured and compared. In view of this and the data on other similar measurements, it is concluded that sulfur in the basaltic glass formed at 1200°C and oxygen and sulfur fugacities of $10^{-9.08}$ and $10^{-0.91}$ atmospheres respectively, occurs as a negative ion coordinated with positively charged ions such as Fe^{2+}.

Introduction

X–ray emission spectra have been used by previous researchers to determine the nature of the environment of elements in compounds (Albee and Chodos, 1970; Day, 1963; Dodd and Glen, 1968.) In particular much work has been done on the valence state of sulfur utilizing the emission spectrograph and the electron microprobe to determine the position of $SK_{\alpha 1}$ in the spectra of compounds of interest (Chapell and White, 1968; Faessler and Goehring, 1952; Faessler and Schmid, 1954; Wilbur and Gofman, 1966).

Recent experimental studies by Haughton and Skinner (1972) have indicated that at 1200°C and sulfur and oxygen fugacities of the order of 10^{-1} and 10^{-9} atmospheres respectively, a melt of basaltic composition will contain approximately 0.1 wt. percent S. The environment of sulfur in such a basaltic glass has been determined by measurement of the $SK_{\alpha 1}$ line of sulfur in a synthetic "basaltic" glass, relative to that in a sample of scapolite, where sulfur occurs as sulfate.

Sulfur in Basaltic Melts

Studies of Al_2O_3–CaO–SiO_2 rich slags equilibrated at 1350–1650°C by Fincham and Richardson (1954) have indicated that, at oxygen partial pressures below 10^{-5} atmospheres, the incorporation of sulfur into the melt is controlled by the exchange reaction:

$$\underset{(\mathrm{slag})}{O^{2-}} + \underset{(\mathrm{gas})}{1/2\,S_2} \rightleftharpoons \underset{(\mathrm{slag})}{S^{2-}} + \underset{(\mathrm{gas})}{1/2\,O_2} \tag{1}$$

Reaction (1) suggests that at low oxygen partial pressures S occurs in melts of basaltic composition predominately as a negative ion bonded to a cation such as Fe^{2+} rather than as a positive ion coordinated to oxygen in a sulfate group.

Chapell and White (1968) have utilized the measurement of wavelength shift to determine that sulfur in scapolite occurs as sulfate; such a measurement can be used to determine the environment of sulfur in basaltic glass. A synthetic glass of basaltic composition containing 0.104 wt. percent S was prepared at 1200°C, under partial pressures of oxygen and sulfur of $10^{-9.08}$ and $10^{-0.91}$ atmospheres respectively. The measurement of $\lambda SK_{\alpha 1}$ from this glass was compared with that of $\lambda SK_{\alpha 1}$ from a gem quality scapolite containing 0.44 wt. percent sulfur as sulfate. For a complete description of this sample see Haughton (1971). Other measurements of interest to this study are presented in Table 1.

TABLE 1. $\Delta SK\alpha$ VALUES

Investigator	Mineral	$\Delta SK\alpha_1$ (A°)	ΔE (eV)	Remarks
Faessler and Goehring (1952)	MnS_2	0.00092	0.40	$\Delta SK\alpha_1$ $= \underset{FeS_2}{\lambda SK\alpha_1} - \underset{\mathrm{Sample}}{\lambda SK\alpha_1}$
	$FeS_{1.98}$	0.00035	0.15	
	CoS_2	0.00053	0.23	
	NiS_2	0.00025	0.11	
Chapell and White (1968)	CaS	0.0	0.0	$\Delta SK\alpha_1$ $= \underset{\mathrm{CaS}}{\lambda SK\alpha_1} - \underset{\mathrm{Sample}}{\lambda SK\alpha_1}$
	$CaSO_3$	0.00108	0.46	
	$CaSO_4$	0.00200	0.86	
	Laacher See Scapolite	0.00200	0.86	
	Delegate Scapolite	0.00184	0.79	
Connolly and Haughton (this study)	$CaSO_4$	0.0021	0.92	$\Delta\lambda SK\alpha_1$ $= \underset{FeS_2}{\lambda SK\alpha_1} - \underset{CaSO_4}{\lambda SK\alpha_1}$
	Sulfur Saturated Basaltic Glass	0.0021	0.92	$\Delta\lambda SK\alpha_1$ $= \underset{\mathrm{Basalt}}{\lambda SK\alpha_1} - \underset{\mathrm{Scapolite}}{\lambda SK\alpha_1}$

The operating conditions for measurements of $\lambda SK\alpha_1$ using an MS–64 microprobe are: analyzing crystal: KAP; accelerating potential: 20 kV; detector: Flow proportional counter utilizing a mylar window and P10 gas; sample current: 50×10^{-9} A., pulse height analysis was used. The spot size of the electron beam was 50 μm and the sample was continually moved.

The peak position was obtained from a measurement of the midpoint of $\lambda SK_{\alpha 1}$ at the ⅔ height position. Precision was estimated to be ± .00032A (±0.14 eV). Counting times for small amounts of sulfur were 100 seconds. Those for sulfur above 10 percent were 20 seconds.

The data presented in Table 1 indicate that $\Delta\lambda SK_{\alpha 1}$ for the pair basalt–scapolite is the same as for the pair FeS_2–$CaSO_4$ and, in general, similar to values reported for sulfide–sulfate pairs. It may, therefore, be concluded that sulfur in the basaltic melt described occurs not as a sulfate group but as a negative ion coordinated with positively charged ions in the melt; in agreement with the work of Haughton and Skinner (1972) which suggests that the sulfur is predominately coordinated with Fe^{2+}.

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