SHORTER COMMUNICATIONS

MÖSSBAUER SPECTRA OF SYNTHETIC IRON-BEARING SPHALERITE

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From a study of absorption spectra, Manning (1967) has postulated the occurrence of ferric iron in interstitial (octahedral) sites in sphalerite. If this is true, then although the bulk iron content of sphalerite does not constitute a useful geothermometer (Boorman 1967; Scott & Barnes, 1967, in press), the state of the iron may be an indicator of sulphur fugacity (f_{S_2}) and/or temperature during deposition. As a preliminary investigation of this possibility the valence and co-ordination of iron in four synthetic sphalerite samples covering a range of growth conditions and compositions (Table 1) were examined by Mössbauer spectroscopy.

Crystals were grown hydrothermally by transporting crushed pyrite and/or pyrrhotite and initially iron-free sphalerite over an 18°C temperature gradient in 5m NH_4I solutions at ½ kb pressure. The coexisting sulphides grew at the cooler end of the gradient as euhedral crystals which were easily separated under a binocular microscope. The sphalerite crystals were up to 2 mm in diameter and were compositionally homogeneous within the uncertainties in Table 1. Details of the growth method are given by Scott (1968) and Scott & Barnes (in press).

The Mössbauer spectra were obtained at room temperature using Co^{57} in palladium as the gamma-ray source. The absorber consisted of crushed

TABLE 1. CONDITIONS OF GROWTH AND MÖSSBAUER SPECTRA OF SPHALERITE

Sample No.	Coexisting Phases[1]	Growth Temp. °C	$-\log f_{S_2}$[2] atm	Mole % FeS in Sphal.[3]	IS mm/sec.	QS
339	po	527 ± 5	6.9	34.0 ± 1.0	0.93	0.67
349	py + po	526 ± 2	3.4	20.8 ± 0.7	0.90	0.62
352	po	427 ± 7	8.3	29.8 ± 2.3	0.91	0.64
508	po	331 ± 9	13.4	43.6 ± 0.8	0.92	0.66

[1] Po = pyrrhotite, py = pyrite.

[2] From the composition of the coexisting pyrrhotite using the data of Toulmin & Barton (1964).

[3] Microprobe analyses. Uncertainty = 1 standard deviation.

sphalerite crystals mounted on a thin glass slide. Velocities were measured relative to a sodium nitroprusside standard within probable errors of ±0.04 mm/sec.

The spectra obtained from all four sphalerite samples are nearly identical. Each shows two lines of equal intensity (Fig. 1) resulting from quadrupole splitting. The isomer shift (IS) and quadrupole splitting (QS) derived from the spectra are listed in Table 1. The values are similar to

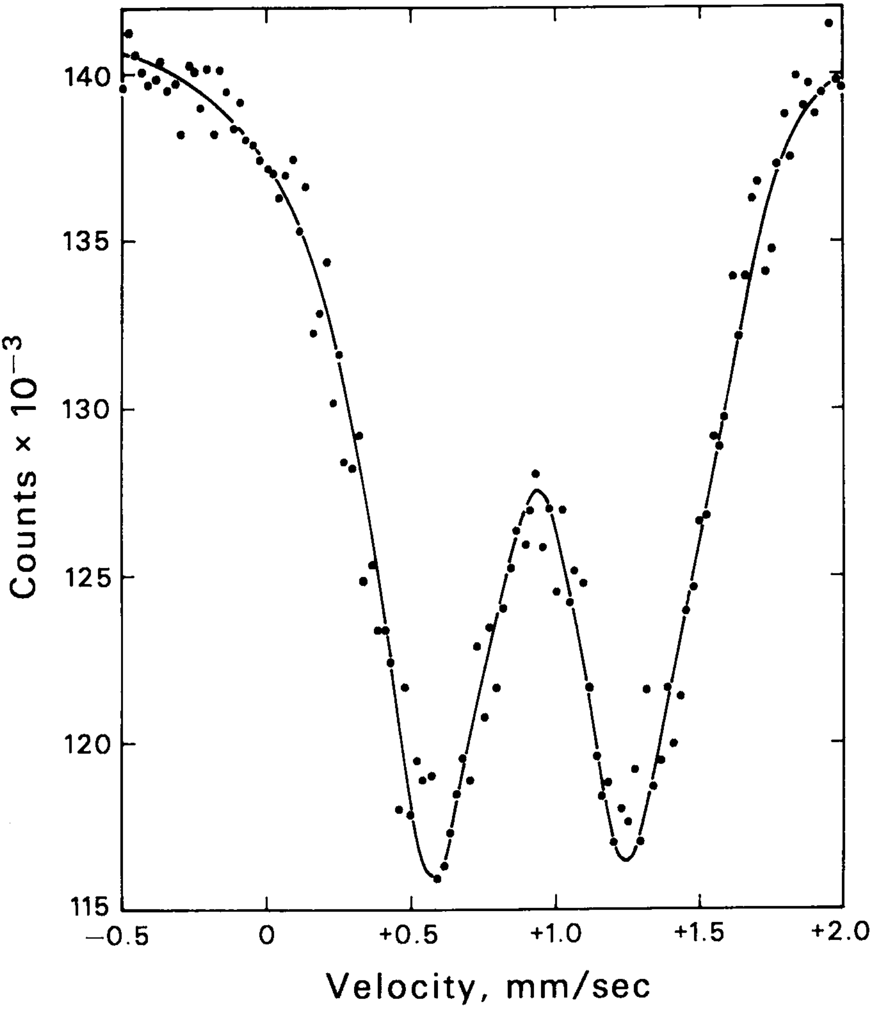

FIG. 1. Mössbauer spectrum at room temperature of sphalerite from sample 339.

those obtained by Borshagovskii *et al.* (1967) for sphalerite (IS = 0.93, QS = 0.60 mm/sec) and wurtzite (IS = 0.87, QS = 0.8 mm/sec.). The isomer shifts in Table 1 fall within the range of values for Fe^{2+} in tetrahedral co-ordination in sulphide compounds (Greenwood & Whitfield 1968). Lack of additional spectral lines demonstrates that, within the limit of detection (approximately 5 per cent of the total iron), there is no Fe^{3+} and no iron in octahedral (interstitial) sites in the samples studied. Cabri (1969) arrived at the same conclusion from accurate density measurements of synthetic iron-bearing sphalerite.

The quadrupole splitting in the Mössbauer spectra indicates that the electric field gradient about the iron is anisotropic ; *i.e.* — the point symmetry of the environment about the iron departs significantly from cubic (Wertheim 1964). Ideally, the FeS_4 tetrahedra in sphalerite have $\bar{4}3m$ symmetry. Quadrupole splitting could arise from a distortion of the ideal tetrahedral symmetry or from second-nearest neighbour effects such as stacking faults or the distribution of Fe and Zn. Precession *x*-ray photographs of a single crystal from sample 349 do not show any evidence of stacking faults or other crystallographic distortion or of Zn/Fe ordering. This problem is being pursued further by detailed structural analysis of the sphalerite crystals.

In summary, at least 95 per cent of the iron in each of the sphalerite samples is in the +2 valence state and is randomly distributed over tetrahedral (substitutional) sites. Unfortunately, the study shows that the state of the iron does not change with the conditions of growth of sphalerite and provides no useful information for geothermometry.

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AN OCCURRENCE OF VALLERIITE FROM NEW IMPERIAL MINE, YUKON

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During the course of mineralogical investigations of ores in connection with beneficiation tests being conducted in the Mineral Processing Division, Mines Branch, an ore sample was received from New Imperial Mines, Yukon. This sample had been submitted to the Mines Branch by Dr. A.C. Skerl, consulting mining geologist, Vancouver, B.C. in April, 1964. Dr. Skerl stated that the late Dr. R.M. Thompson, University of British Columbia had identified valleriite in a specimen of this ore. A thorough study of the ore failed to reveal the presence of valleriite, and therefore Dr. Skerl kindly submitted part of the specimen that had been studied by Dr. Thompson. This specimen, about ¾ inches of quartered drill core, contained a valleriite with such a distinct *x*-ray diffraction powder pattern that it was used as a standard in the Mines Branch *x*-ray diffraction laboratory. In 1969, D.C. Harris analysed the valleriite in this specimen with an electron microprobe, using synthetic $CuFeS_2$, MgO and Al_2O_3 as standards, and processing the data with a computer program that included corrections for absorption, fluorescence and atomic number. *X*-ray powder diffraction data and unit-cell dimensions were obtained by the film method

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