American Mineralogist, Volume 63, pages 516–519, 1978

Experimental extension of the sphalerite geobarometer to 10 kbar

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Abstract

Sphalerite coexisting with pyrrhotite and pyrite has a constant FeS content of 10.3±0.5 mole percent at a confining pressure of ~ 10 kbar and temperatures between 420° and 700°C. Experiments therefore show that the sphalerite geobarometer is applicable up to at least 10 kbar.

Introduction

Barton and Toulmin (1966) and Scott and Barnes (1971) pointed to the importance of the FeS content of sphalerite coexisting with pyrite and hexagonal pyrrhotite as a potential geobarometer. Scott (1973) subsequently calibrated the pressure-dependence of sphalerite solvii at pressures of 2.5, 5, and 7.5–8 kbar and temperatures between 325° and 710°C. For pressures of 2.5 and 5 kbar, he demonstrated a temperature-independence below 600°C, and determined FeS contents of 17.9±0.4 and 14.5±0.1 mole percent, respectively. However he interpreted his 7.5–8 kbar results as indicating both a temperature- and pressure-dependence.

Lusk *et al.* (1975) suggested that Scott's (1973) inferred 7.5 kbar solvus may be in error, primarily due to his reliance on a suspect result (*i.e.* Run 12, Table 2, p. 468). Scott (1976) has since conceded that this result is unreliable, and now prefers a 7.5 kbar isobar which is temperature-independent, at least between 500° and 700°C.

Experiments and analyses

Sulfide nutrients used in the present experiments comprised chemically-precipitated iron-free sphalerite (and galena in runs 5 and 11, Table 1), together with pyrrhotite and pyrite synthesized from moderately pure Fe and S. These products were finely ground and loaded into heavy-walled gold capsules 20 mm in length. Aqueous solutions of 4.5 *M* KCl or 5 *M* NH_4Cl were used as fluxes in the majority of recrystallization experiments (Scott, 1973). However for runs 1 and 2, and for run 9, eutectic melts of KCl–LiCl and NH_4Cl–LiCl mixtures were used as fluxes, respectively, according to the method of Boorman (1967).

Runs were made in internally-heated pressure vessels with charge temperatures controlled to better than ±3°C, although temperature gradients along the lengths of the capsules are estimated to have produced a mean total uncertainty of ±6°C. Pressures were measured daily using a calibrated manganin pressure cell. Leakage of the argon pressure medium was a constant problem of varying severity from run to run, and was aggravated by the long durations (14 to 38 days) of the runs. However precisions were better than ±0.25 kbar for most runs.

Sphalerite compositions were determined using an ETEC microprobe operated at an accelerating voltage of 15 kV and a specimen current of 0.5 microamps. Synthetic Fe-free sphalerite and pyrrhotite were used as primary standards for Zn and for Fe and S, respectively. A sphalerite standard of similar composition (12.1±0.1 mole percent FeS) to the experimental-run sphalerites was analyzed several times with each group of analyses to check for machine drift.

At least fifteen 30-second spot analyses were performed on each sample, and not more than 3 analyses made on any one grain. A single analysis was possible only on coarser grains of very fine-grained products

Table 1. Sphalerite FeS contents and conditions of 10 kbar experiments

Run No.	duration (days)	Temperature, °C (± 6°C)[1]	Pressure, kb	mole % FeS in sphalerite	Number of Analyses
1*	14	776	10.0 ± 0.15	9.9 ± 0.2	15
2*	11	776	10.0 ± 0.15	9.9 ± 0.2	27
3	19	752	9.6 ± 0.25	10.0 ± 0.2	21
4	21	703	9.9 ± 0.3	10.4 ± 0.2	27
5[2]	22	652	9.9 ± 0.15	9.9 ± 0.2	16
6	24	653	9.7 ± 0.10	10.2 ± 0.2	17
7	14	602	9.9 ± 0.15	10.5 ± 0.5	17
8	32	552	9.9 ± 0.2	10.5 ± 0.5	28
9*	32	552	9.9 ± 0.2	10.2 + 0.4	16
10	34	500	9.9 ± 0.2	10.2 ± 0.4	20
11[2]	38	420	9.7 ± 0.6	10.5 ± 1.04[3]	18

[1] estimated mean error

[2] samples contained galena

[3] reliability uncertain

*eutectic salt mixture used as flux

of lower temperature runs (*e.g.* 11). A small proportion of analyses were found to be appreciably more Fe-rich than common values for these samples, and the former were rejected on the grounds that pyrrhotite contamination was probably responsible. None of the lower Fe-containing analyses were rejected.

Results and discussion

Sphalerite compositions together with details of respective experimental run conditions are presented in Table 1 and are plotted in Figure 1. These results show that the mean mole percent FeS contents of sphalerites from all runs agree within the precision limits ($\pm 1\sigma$) of the analyses. However, a slight lowering of FeS content with increasing temperature is implied for the two highest temperature runs (*i.e.* runs 1 and 2 [776°C] and run 3 [725°C]), suggesting that the solvus composition is constant from at least 420° to 700°C. The weighted mean sphalerite composition over this temperature interval is 10.3±0.5 mole percent FeS, corresponding to a mean pressure of 9.9 kbar.

Runs 5 and 11 were unusual in that they contained galena in addition to sphalerite, pyrrhotite, and pyrite. The results show, as expected, that galena has not noticeably affected Zn–Fe–S equilibria. Nevertheless, the reliability of Run 11 is regarded as uncertain because of development of serious vessel leakage when the pressure fell as low as 7 kbar during the first 10 days of a 38-day run. This was corrected, and minimal leakage occurred during the 28 days following.

No reversal runs were attempted in this study, because all of the experiments were run for durations similar to Scott's (1973) 5 kbar experiments, which demonstrated the attainment of equilibrium down to 400°C. The present results are therefore inferred to be equilibrium results, or close approximations.

The pressure-dependence of the temperature-independent portions of sphalerite solvii corresponding to pressures of 0–1, ~ 2.5, 5, 7.5–8, and 10 kbar is shown in Figures 1 and 2. These experimental data include those of Boorman (1967), Scott and Barnes (1971), and Scott (1973) for pressures of 0, 0.25–1.0, 2.5–8.0 kbar, respectively, in addition to the present ~ 10 kbar plots. Some of these data have been omitted from consideration in computing a least-squares regression equation which takes mole percent FeS ($\pm 1\sigma$) errors[1] into account. Only sphalerite composi-

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[1] Pressure errors were not considered because of their small contribution to the total uncertainty in the regression analysis.

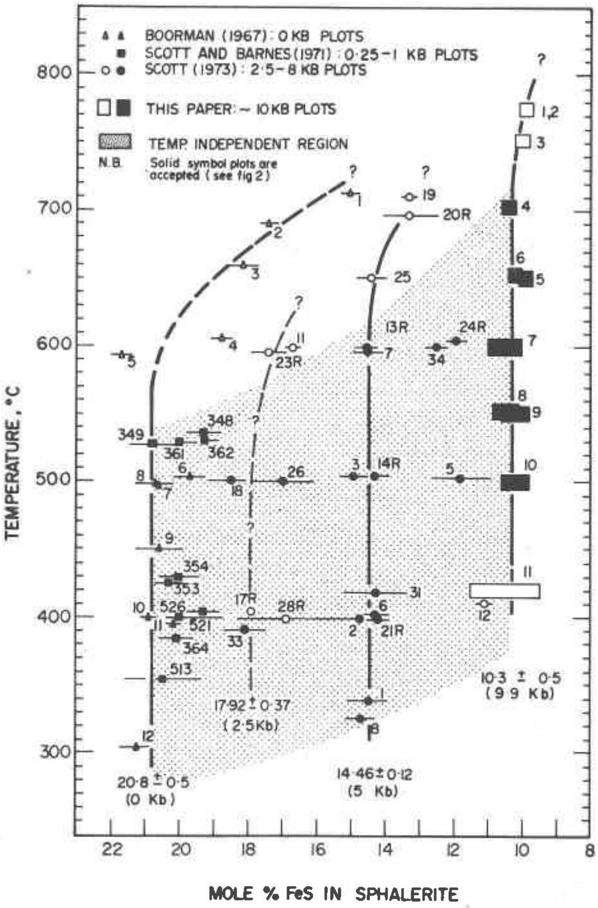

Fig. 1. Mole percent FeS in sphalerites coexisting with pyrite and hexagonal pyrrhotite as a function of temperature and confining pressure. Sample numbers correspond with those in the respective sources referred to.

tions from experiments run at temperatures between 300°–500°C at 0 kbar, 390°–500°C at 2.5 kbar, 325°–600°C at 5 kbar, 411°–605°C at 7.5 to 8 kbar, and 420°–703°C at ~10 kbar were accepted, because they fall well within the temperature-independent portions of respective sphalerite solvii. A small number of other data points were excluded also because of too few analyses (*e.g.* 17R [1 grain]; 28R [2 grains]), apparent uncertainty (*e.g.* 11), or acknowledged unreliability (*e.g.* 12).

Several types of curve were fitted to the accepted data, but variance analysis showed a quadratic model to yield an excellent fit. The equation of the computed curve is:

$$\text{mole percent FeS} = 20.53 - 1.313\,P(\text{kbar}) + 0.0271\,P(\text{kbar})^2 \qquad (1)$$

which yields a correlation coefficient of 0.997. A more useful equation for readily computing pressure employs P(kbar) as the dependent variable. The equation

$$P(\text{kbar}) = 26.18 - 1.903\,(\text{mole percent FeS}) + 0.0309\,(\text{mole percent FeS})^2 \qquad (2)$$

allows this, but it is less reliable because errors in mole percent FeS measurement were not considered.

The geobarometric curve plotted in Figure 2 is for equation (1), which has an uncertainty (1σ) of mole percent FeS prediction of $\leq \pm 0.18$. Pressures estimated from equation (2) deviate by ≤ 0.06 kbar from pressures predicted from equation (1). Extrapolation of the calibration curve to 10.0 kbar suggests a temperature-independent sphalerite composition of 10.11 ± 0.18 mole percent FeS. It is noteworthy that the 2.5 kbar intercept equates with a predicted mole percent FeS value of 17.31 ± 0.18, which is appreciably lower than Scott's (1973) estimate of 17.92 ± 0.37. This corresponds to a pressure difference of 0.61 ± 0.41 kbar. A pressure difference of approximately 0.3 kbar is also indicated when Scott's (1976) tentative extrapolation to 10 kbar is compared with the 10.0 kbar intercept for the calibration curve presented here.

A serious discrepancy exists between experiment and theoretical analyses for the sphalerite geobarometer. Scott's (1973) demonstration of attainment

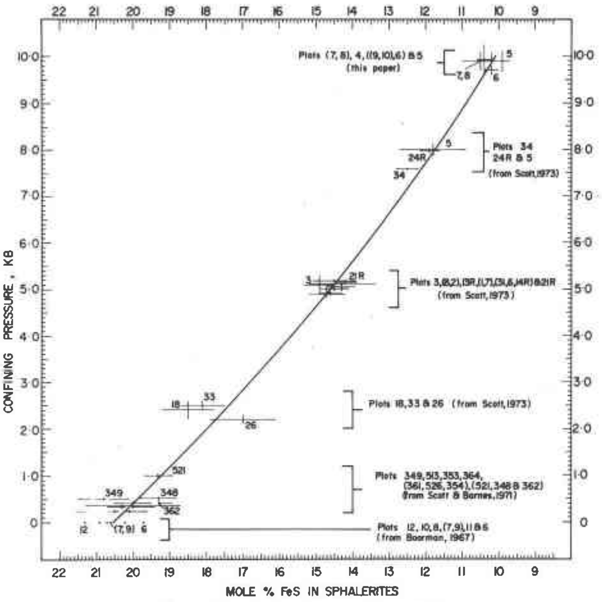

Fig. 2. Pressure dependence of mole percent FeS contents of sphalerite from temperature-independent portions of sphalerite solvii.

of equilibrium for temperature-independent portions of sphalerite solvii to 5 kbar, together with the present extension of temperature-independent relations to 10 kbar, strongly imply that the experimental data are reliable. On the other hand, theoretical treatments by Scott and Barnes (1971) and Scott (1973) predicted that sphalerite solvii are both pressure- and temperature-dependent over the same *P–T* range. It is therefore apparent that the discrepancy stems from usage of unreliable values for at least some of the parameters in the relevant thermochemical calculations (see Scott, 1973, p. 471).

Acknowledgments

We thank C. Begg of the Grant Institute of Geology, University of Edinburgh, and G. D. Pooley of the School of Earth Sciences, Macquarie University, for their willing help in surmounting experimental and analytical problems. Drs. H. M. Hudson and E. A. Eyland of the School of Economic and Financial Studies, Macquarie University, are thanked for their assistance in treating the experimental data. Drs. R. G. Arnold of the Saskatchewan Research Council, Saskatoon, and S.R.R. Sangameshwar of the N.S.W. Institute of Technology, Sydney, kindly supplied sulfide samples which were used as probe standards.

Finally, J. L. extends sincere thanks to the Grant Institute of Geology and N.E.R.C. for providing experimental facilities, and Macquarie University for a study leave grant which made the present work possible.

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Manuscript received, August 9, 1977; accepted for publication, December 12, 1977.