

Validity of sphalerite geobarometry and garnet-biotite geothermometry to estimate P-T conditions of metamorphism for the sediment-hosted base metal deposits in Besham area, northern Pakistan

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ABSTRACT: Regionally metamorphosed sediment-hosted stratiform exhalative type base metal deposits are exposed in the Lahor and Pazang properties of Besham area at the northern margin of the Indian plate. Sphalerite geobarometer and garnet-biotite geothermometer were used to calculate the P-T conditions of metamorphism. These geothermobarometers yielded most convincing results for the studied deposits. These deposits and the host metasediments were subjected to amphibolite facies metamorphism with a metamorphic temperature of $585 \pm 35^\circ\text{C}$ and a pressure of $8 \pm 2 \text{ kb}$.

INTRODUCTION

The rocks of the Indian plate have a complex tectonic-metamorphic history with polyphase deformation accompanying prograde metamorphism (Baig et al., 1988; Treloar et al., 1989). Base metal deposits in Besham area occur in this highly deformed and metamorphosed terrane. Lahor and Pazang are the two properties in Besham area where promising prospects of Zn and Pb mineralization are present. This type of mineralization is confined to the Pazang group, a supracrustal sequence of metasediments, which has been thrust over the basement gneisses of the Besham group (Fletcher et al., 1986). These deposits are considered to be the Proterozoic stratiform massive sulfide deposits of exhalative origin (Fletcher et al., 1986; Shah, 1991; Shah, et al., 1992). Sphalerite geobarometry and garnet-biotite geothermometry were applied to these deposits and host metasediments to find out the P-T conditions of metamorphism.

RESULTS AND INTERPRETATION

Garnet-biotite geothermometry

Garnet-biotite geothermometers are applied to the rocks of the Pazang group which are subjected to high grade of regional metamorphism. Two samples containing coexisting garnet (spessartine rich) and biotite were selected for geothermometry.

Biotite is either in contact with garnet or is at a small distance from it within a single thin section. Core to rim chemical analyses of garnets and biotites were determined by the electron microprobe. No compositional zoning is observed in either garnet or biotite. Still core-core and rim-rim compositions of both garnet and biotite are used to estimate the metamorphic temperatures.

Various geothermometers have been used in order to get the estimates of metamorphic temperature. The results obtained through the geothermal equations are given in Table 1. During these calculations the metamorphic pressure was assumed as 8 kb. Several geothermometers have been proposed for Fe-Mg exchange equilibria in garnet-biotite pairs, e.g. Ferry and Spear (1978), Newton and Haselton (1981), Hodges and Spear (1982), Pigage and Greenwood (1982), Ganguly and Saxena (1984), and Indares and Martignole (1985). These geothermometers will first be evaluated in context to the compositions of studied garnet and biotite, and then the appropriate metamorphic temperatures will be selected.

Ferry and Spear (1978) geothermometer is based on experiments in purely binary Mg-Fe system. Their calibration does not account for Ti and ^{vi}Al substitution in biotite and high Ca and Mn in garnet. The direct application of this calibration will then give error in temperature, if the garnet is not a simple

TABLE 1. GEOTHERMOMETRY: selected data of coexisting garnet and biotite in two samples and temperature estimates for the rocks of Pazang group, Besham.

Sample#	Pos	Xsp	Xgr	Xal	Xpy	XFe	%Ti	T1	T2	T3	T4	T5	T6	T7
BP109	Core	0.37	0.34	0.27	0.02	0.36	0.59	305	857	371	578	418	425	571
	Rim	0.37	0.34	0.26	0.02	0.37	0.59	313	868	378	590	427	429	573
BP190	Core	0.64	0.15	0.21	0.00	0.66	2.51	281	425	308	557	397	293	539
	Rim	0.64	0.15	0.21	0.00	0.66	2.45	321	489	351	615	445	335	596
GR2		0.67	0.11	0.21	0.01	0.67	2.14	328	447	350	619	453	333	610

Xsp, Xgr, Xal, Xpy = mole fractions of spessartine, grossular, almandine, and pyrope. XFe = (Fe/Fe+Mg) in biotite. T1: Ferry and Spear (1978), T2: Newton and Haselton (1981), T3: Hodges and Spear (1982), T4: Pigage and Greenwood (1982), T5: Ganguly and Saxena (1984), T6: Indares and Martignole (1985), without Mn correction, T7, Indares and Martignole (1985), with Mn correction.

Fe-Mg binary solution. As the studied garnets are Mn-rich, therefore, this thermometer is yielding very low temperature (Table 1). Newton and Haselton (1981) geothermometry consider Ca-mixing in the garnet, but assumes that Mn-mixing is ideal. This calibration also gives low temperature estimates for the Mn-rich garnet and can not be decisive for the studied rocks (Table 1). Hodges and Spear (1982) assume non-ideal solution behavior in garnet but assume ideal Fe-Mg mixing for biotite in their calibration. This calibration gives fairly low temperatures for the Mn-rich garnet-biotite of the Pazang group rocks (Table 1).

In the calibration of Pigage and Greenwood (1982), corrections for Ca and Mn are made which could give the appropriate estimates of temperature for the studied rocks. Indares and Martignole (1985) empirically modified the original calibration (Ferry and Spear, 1978) to account for Ti and Al^{vi} substitution in biotite and non-ideality in garnet. The calibration in which they include Ca and Mn gave fairly consistent temperature estimates (Table 1. T7) to that calculated by Pigage and Greenwood (1982) (Table 1. T4) for the studied rocks. Considering the above mentioned limitations of each geothermometer, Pigage and Green-

wood (1982) and Indares and Martignole (1985) calibrations seem to be valid for estimating the metamorphic temperature for the studied rocks. Both these thermometers give a range of temperature from 539 to 619°C with an average of 585°C. This temperature is slightly less than that of 600±50°C which is estimated by Treloar and others (1989) for the high-grade cover sediments around Besham. These estimates (539-619°C) may represent the main stage of metamorphism (amphibolite facies) in the rocks of the Pazang group. No appropriate mineral assemblages have been found for calculating the metamorphic pressure on the basis of existing geobarometric parameters. However, the amphibolite facies metamorphism and the thickening of the Indo-Pakistan plate underneath the Kohistan arc terrane suggest a pressure of approximately 9±2 kb (see Treloar et al., 1989).

Sphalerite geobarometry

Sphalerite geobarometry has been investigated by several workers by using the variation in the amount of FeS in sphalerite with increasing pressure along a solvus (see Scott & Barnes, 1971; Scott, 1973; Lusk & Ford, 1978; Hutchison & Scott, 1981). To accurately apply this system, the sphalerite

must have equilibrated with both hexagonal pyrrhotite and pyrite at the time of metamorphism. Hutchison and Scott (1981) have given the more precise empirical equation to calculate the pressure from the composition of sphalerite in equilibrium with pyrite and hexagonal pyrrhotite: $P(\text{kb}) = 42.30 - 30.10$ log mole% FeS of sphalerite.

This equation draws a straight line in the Figure 1 of Hutchison and Scott (1981) and can be used as geobarometer for the ores having pyrite and hexagonal pyrrhotite coexisting with sphalerite. Hutchison and Scott (1981) concluded from their experimental work that the composition of sphalerite is independent of temperature from 625°C to a range of temperature from 550°C to 750°C for pressure up to at least 10 kb. The trace elements (i.e. Cd, and Mn) generally have no effect on the functioning of sphalerite as geobarometer; however, an appreciable amount of Cu, dissolved in sphalerite during its equilibration with chalcopyrite and intermediate solid solution (ISS), may effect the application of sphalerite during its equilibrium with chalcopyrite. Such grains should, therefore, be avoided (Hutchison & Scott, 1981).

The application of sphalerite geobarometry

has been successful in some cases but not in several other cases. Its most successful use was reported in hydrothermal mineralization, in which the cooling rate was reasonably fast such as veins (see Hutchison & Scott, 1981) and Skarn (see Shimizu & Shimazaki, 1981). Its application to prograde greenschist facies deposits has often yielded anomalously high pressures (see Bristol, 1974; Etheir et al., 1976; Jago & Sangameshwar, 1977; Sangameshwar & Marshall, 1980).

Geobarometric studies have been carried out in the light of the results obtained from sphalerite of both Pazang and Lahor deposits of the Besham area. Seven grains of sphalerite were selected from samples having pyrrhotite (hexagonal) and pyrite as coexisting phases with sphalerite. The distribution and concentration of iron in sphalerite in the form of mole% FeS along with estimated pressure are presented in Table 2. The individual sphalerite grains show minimum and maximum standard deviation of ± 0.007 and ± 1.11 , respectively, which is indicative of more or less homogeneous nature of the sphalerite. Such homogeneous sphalerite coexisting with pyrite and pyrrhotite (hexagonal) suggests that these are equilibrium assemblages.

TABLE 2. IRON CONTENT OF SPALERITE, EQUILIBRATED WITH PYRITE AND PYRROHOTITE, FROM VARIOUS ROCK UNITS OF THE PAZANG GROUP IN BESHAM AREA, PAKISTAN

Sample No	Rock type	Grains	Mole % FeS, (S.D)	N	P
BL-2	Massiv sulfide ores	2	11.99, ± 1.11	4	7.7
BP-232		1	12.97, ± 0.84	2	6.6
BL-19		1	12.11, ± 0.007	2	7.5
BL-4	Sulfide-bearing clinopyroxenite	2	11.29, ± 0.46	4	8.5
BP-190	Sulfide rich quartzofeldspathic rock	1	11.24, ± 0.19	2	8.6
BL-43		1	10.32, ± 0.30	2	9.8
BP-149	sulfide rich calc-silicate rock	1	12.11, ± 0.23	2	7.5
AVERAGE			11.71, ± 0.45		8.0

S.D = Standard deviation of the analysis; N = Number of analysis in each grain; P = Pressure in kilobars

Special precautions were taken in the selection of sphalerite for the geobarometric studies as: (1) The hexagonal pyrrhotite has been recognized by the etching technique using saturated solution of chromic acid (Arnold, 1966) and also confirmed by x-ray diffraction technique, (2) chalcopyrite free sphalerite grains were selected, (3) those polished sections in which the sphalerite coexist with pyrite and pyrrhotite were selected for the mole % FeS determination.

The mole % FeS contents of the sphalerites from the sphalerite-hexagonal pyrrhotite-pyrite assemblage has been used to calculate the pressure according to the equation ($P = 42.30 - 30.10 \log \text{mole \% FeS}$) of Hutchison and Scott (1981). The mole % FeS compositions yield a pressure range of 6.6-9.8 kb with an average pressure of 8 kb. The pressure estimates obtained from the sphalerite geobarometry are reasonable for the base metal deposits within the Pazang group, where the grade of regional metamorphism is of amphibolite facies. The typical assemblage normally includes quartz, albite, manganese-rich clinopyroxene, manganese-rich garnet (spessartine), muscovite, epidote and amphibole.

It is already mentioned in the previous section that the rocks of the Pazang group have attained a metamorphic temperature of $585 \pm 35^\circ\text{C}$ with approximate 9 ± 2 kb metamorphic pressure. An average 8 kb pressure estimate from the sphalerite geobarometry for the base metal deposits of Besham area, is in agreement with the assumed pressure for the rocks of Pazang group. This suggests that sphalerite geobarometry can be a useful pressure indicator in the high grade regionally metamorphosed rocks as also reported by various workers.

CONCLUSIONS

The base metal deposits and the host metasediments in Besham area are subjected to amphibolite facies metamorphism. The application of sphalerite geobarometry and the garnet-biotite geothermometry is successful in delineating the P-T conditions of metamorphism for the Besham base metal deposits. These parameters, especially sphalerite geobarometry, can usefully be

applied to estimate P-T conditions of metamorphism for massive sulfide deposits occurring in regionally metamorphosed terrane.

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REFERENCES

- Arnold, R.G., 1966. Mixture of hexagonal and monoclinic pyrrhotite and the measurement of the metal content of pyrrhotite by X-ray diffraction. *Amer. Mineral.*, 51, 1221-1227.
- Baig, M.S., Lawrence, R.D. & Snee, L.W., 1988. Evidence for late Precambrian to early Cambrian orogeny in northwest Himalaya, Pakistan. *Geol. Mag.*, 125, 83-86.
- Bristol, C.C. 1974. Sphalerite geobarometry of some metamorphosed ore bodies in the Flin Flon and Snow Lake district, Manitoba. *Canad. Mineral.* 12, 308-315.
- Ethier, V.G., Campbell, F.A., Both, R.A. & Krous, H.R., 1976. Geological setting of Sullivan orebody and estimates of temperature and pressure of metamorphism. *Econ. Geol.*, 71, 1570-1588.
- Ferry, J.M. & Spear, F.S., 1978. Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.*, 66, 113-117.
- Fletcher, C.J.N., Leake, R.C. & Haslam, H.W., 1986. Tectonic setting, mineralogy, and chemistry of a metamorphosed stratiform base metal deposit within the Himalayas of Pakistan. *J. Geol. Soc. Lond.*, 143, 521-536.
- Ganguly, J. & Saxena, S.K., 1984. Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and implications to geothermobarometry. *Amer. Mineral.*, 69, 88-97.
- Hodges, K.V. & Spear, F.S., 1982. Geothermometry, geobarometry and the Al_2SiO_5 triple point at Mt Moosilauke, New Hampshire. *Amer. Mineral.*, 67, 1118-1134.
- Hutchison, M.N. & Scott, S.D., 1981. Sphalerite geobarometry in the Cu-Fe-Zn-S system. *Econ. Geol.*, 76, 143-153.
- Indares, A. & Martignole, J., 1985a. Biotite-garnet geothermometry in the granulite facies. The influence of Ti and Al in biotite. *Amer. Mineral.*, 70, 272-278.
- Jago, P.A. & Sanameshwar, S.R., 1977. Geochemistry of sphalerite from the May Day

- prospect, New South Wales (abstr.). In: Abstract of the second Australian geological convention (L.J. Wylde, ed.). Monash Univ. Victoria, 39.
- Lusk, J. & Ford, C.E., 1978. Experimental extension of the sphalerite geobarometer to 10kb. *Amer. Mineral.*, 63, 516-519.
- Newton, R.C & Haselton, H.T., 1981. Thermodynamics of the garnet-plagioclase- Al_2SiO_5 -quartz geothermometer. In: *Thermodynamics of Minerals and Melt* (R.C. Newton, A. Navrotsky, and B.J. Wood, eds.), Springer-Verlag, New York, 129-145.
- Pigage, L.C. & Greenwood, H.J., 1982. Internally consistent estimates of pressure and temperature: The staurolite problem: *Amer. J. Sci.*, 282, 943-969.
- Shah, M.T., 1991. Geochemistry, mineralogy, and petrology of the sulfide mineralization and associated rocks in the area around Besham and Dir, Northern Pakistan. Unpub. Ph.D. thesis. Univ. South. Carol. Columbia.
- Shah, M.T., Ralph, T.I. & Siddique, S.A., 1992. Lead isotope signature of the Proterozoic sediment-hosted base metal deposits at the margin of the Indian plate in Besham area, northern Pakistan. *Geol. Bull. Univ. Peshawar*, 25, 59-65.
- Scott, S.D., 1973. Experimental calibration of the sphalerite geobarometer. *Econ. Geol.*, 68, 466-476.
- Scott, S.D. & Barnes, H.L., 1971. Sphalerite geothermometry and geobarometry. *Econ. Geol.*, 66, 653-669.
- Sangameshwar, S.R. & Marshall, B., 1980. Sphalerite geobarometry of deformed sulfide ores from the C.S.A. Mine, Cobar, Australia. *Mineral. Depos.*, 15, 305-314.
- Shimizu, M. & Shimazaki, H., 1981. Application of the sphalerite geobarometer to some skarn-type ore deposits: *Mineral. Depos.*, 16, 45-50.
- Treloar, P.J., Coward, M.P., Williams, M.P. & Khan, M.A., 1989. Basement-cover imbrication south of the Main Mantle Thrust, north Pakistan. *Geol. Soc. Amer. Spec. pap.*, 232, 137-152.