ON THE TRACE ELEMENT GEOCHEMISTRY OF ZAWAR SULPHIDES AND ITS RELATION TO METALLOGENESIS

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ABSTRACT

Several trace elements have been determined in Zawar sulphides and their relation to ores are discussed. Following the concentration of the trace elements, an attempt has been made to answer the question of ore-genesis.

INTRODUCTION

The lead-zinc-pyrite deposits at Zawar (Lat. 24°22′ N; Long. 73°43′ E.) lie about twenty-nine miles southeast of Udaipur City, in the south of the state of Rajasthan, Central India. The mine, as yet, is the only source of lead and zinc in the country. The area lies in a wide expanse of typical Aravalli rocks, comprising an immensely thick sequence of monotonously uniform argillaceous rocks associated with quartzites and dolomites. The formations at Zawar are of Upper Aravalli (Archaean?) age and the area has suffered low grade regional metamorphism (green schist facies). The mineralization has a wide regional distribution whose constant feature is its localization in the dolomites. Galena and sphalerite are major sulphides in the area and pyrite occurs in various proportions along with them.

TRACE ELEMENT DISTRIBUTION

The different trace elements in the samples of galena, sphalerite and pyrite are given in Table 1. The samples were collected from all the four levels of the mine, which are 120 feet apart vertically. The ratios of Sb:Ag in galena and Co:Ni in pyrite have also been included in the table.

DISCUSSION

The trace elements in the sphalerite samples studied are Ag, In, Ga, Ge, Sb, Mn and Cd. Of these elements, Sb was completely absent, while Ag was present in low concentration ranging from 15 to 48 ppm. The presence of Ag may be due to the contamination by galena. In, Ga, and Ge occur in very low amounts, just above the detection limit, and it seems that In varies approximately inversely as the content of Ga or

Table 1. Trace Element Content of Sulphides

Sp. No	Mineral	Ag(ppm)	In(ppm)	Ga(ppm)	Ge(ppm)	Sb(ppm)	Mn(ppm)	Ni(ppm)	Co(ppm)	Cd(ppm)	Sb/Ag	Co/Ni
I.1	Sphalerite	40	60	10	—	—	160	—	—	100	—	—
.2	Sphalerite	20	—	—	—	—	250	—	—	150	—	—
.3	Sphalerite	15	Tr*	Tr	10	—	320	—	—	210	—	—
.4	Galena	3000	—	—	—	1200	25	—	—	—	0.4	—
.5	Galena	1500	—	—	—	750	75	—	—	—	0.5	—
.6	Pyrite	20	—	Tr	—	—	40	50	200	—	—	4.00
.7	Pyrite	100	—	—	—	—	35	62	125	—	—	2.02
II.1	Sphalerite	45	31	11	20	—	700	—	—	520	—	—
.2	Sphalerite	24	20	12	10	—	810	—	—	559	—	—
.3	Sphalerite	34	—	Tr	—	—	400	—	—	250	—	—
.4	Galena	800	—	—	—	1400	30	—	—	—	1.75	—
.5	Galena	300	—	—	—	550	15	—	—	—	1.73	—
.6	Pyrite	70	—	Tr	Tr	—	10	120	240	—	—	2.00
.7	Pyrite	10	—	—	—	—	51	80	228	—	—	2.88
III.1	Sphalerite	21	19	20	—	—	400	—	—	243	—	—
.2	Sphalerite	48	33	27	—	—	212	—	—	119	—	—
.3	Galena	1500	—	—	—	750	46	—	—	85	0.50	—
.4	Galena	500	Tr	—	—	300	30	—	—	69	0.60	—
.5	Pyrite	20	—	—	—	—	90	120	140	—	—	1.16
IV.1	Sphalerite	20	Tr	—	Tr	—	210	—	—	110	—	—
.2	Sphalerite	15	60	15	—	—	300	—	—	197	—	—
.3	Sphalerite	30	Tr	30	—	—	300	—	—	195	—	—
.4	Galena	1500	—	—	—	500	20	—	—	—	—	—
.5	Galena	1500	—	—	—	750	33	—	—	—	—	—
.6	Galena	350	—	—	—	290	11	—	—	—	—	—
.7	Pyrite	40	10	—	—	—	25	85	230	—	—	2.72
.8	Pyrite	21	—	—	—	—	12	60	120	—	—	2.00
.9	Pyrite	19	Tr	Tr	—	—	19	62	126	—	—	2.02

Note: I.1 refers to level one, sample No. 1
.2 refers to level one, sample No. 2
Similarly II.1 refers to level two, sample No. 1, etc.

*Tr. refers to trace amount.

Ge. Mn values range from 160 to 810 ppm. Both Mn and Cd seem to be highly enriched in the sphalerite and they are directly variable with each other. Spectrographic work has proved that the sphalerite samples, rich in Mn and Cd, are also rich in Fe. These are probably all related due to similarity in ionic radii. These occurrences of Fe, Mn and Cd, may be termed as 'diadochy' replacements in sphalerite lattice. According to Kullerud (1953) the maximum solubility of Fe in sphalerite is 42% and the close association of Cd may be explained by the relative ratios of lattice parameters: Zn 1.86; Cd 1.89. The apparent preference of Ga for sphalerite rather than other sulphides can be explained after Goldschmidt (1954), that the element occurs as GaAs, which has same structural arrangement and similar lattice dimensions:

$$\left.\begin{array}{l}\mathrm{ZnS} = 5.413\,\text{Å}\\ \mathrm{GaAs} = 5.635\,\text{Å}\end{array}\right\}\text{Graton \& Harcourt (1935)}$$

Ag, Sb, and Mn were present as trace elements in the galena samples. Only in two cases (Sp. No. III.3 and III.4) Cd has been found, which is probably due to sphalerite contamination. The Mn content varies from 11 to 75 ppm. The constant association of Mn with galena, although in low amounts, suggests that the element is present as a solid solution and not merely as sphalerite contamination. Although these relations are not close enough to account for the universal presence of silver in galena; this association could be explained by Goldschmidt's "process of capture" (Goldschmidt, *op. cit.*). However, it is assumed here that the Ag-values in galena are due to solid solution in the lead sulphide lattice. The close connection of Ag and Sb values in galena have been discussed by Fleischer (1955) and the present study also shows their sympathetic relationship. The ratio Sb:Ag varies from 0.4 to 1.75, the highest value being recorded in the second level where low Ag content is noted. Marshall & Joensuu (1961), suggest that the large concentration of Ag is found in octahedral crystals of galena, although no casual relationship between the crystal habit and the concentration of trace element has been observed. It is believed that the variation in antimony content is probably an effect of comparative solubility of this mineral and the relative concentration of Sb varies with the galena crystal habit, the lowest concentrations within the mineralized area occurring in octahedral crystals.

Mn values in pyrite are rather randomly distributed, whereas the Co and Ni contents show sympathetic variation. The Co:Ni ratio varies from 1.16 to 4.00, but does not appear to show any systematic variation with depth. There is also no other regular variation of trace element content of sulphides with increasing depth.

Ore-genesis

It is necessary to admit here, that to postulate the origin of an ore deposit from its trace element concentration is rather difficult. The main purpose of this paper is to contribute data on some of the trace elements in lead-zinc deposits in Precambrian dolomites.

However, if it is assumed that the sulphides at Zawar are of epigenetic hydrothermal origin, then the high concentrations of Ag and Sb in galena and Mn in sphalerite, fall within the ranges quoted in previous data by Fleischer (1955) and El Shazly *et al.* (1957). In fact, data quoted by El Shazly *et al.*, for simple sedimentary sulphides suggests that the values for Zawar ore are, in part, too high to be considered as purely sedimentary in origin. But, at the same time, the complete lack of wall rock alteration, pre-metamorphic origin of ore minerals and strata-bound nature of the deposits, make it necessary to concede that they might have been formed during sedimentation or early diagenesis.

The Co:Ni ratio (2.35 average; range 1.16–4.00) and the higher Co-content (176 ppm; range 120–240 ppm) than that of Ni (80 ppm; range 50–120 ppm) is more consistent with hydrothermal pyrite, since Davidson (1962) points out that for sedimentary pyrite the Co:Ni ratio must be less than 1 and the Ni content should be higher than that of Co. Again, in view of the great age of the deposit (2300 m. years), a theory of biogenic origin of the pyrite cannot be entertained. However, it is believed that the Co and Ni contents are probably governed by the availability of these elements during crystallization and the crystal habit of the host pyrite, and hence, the genesis of pyrite is rather difficult to deduce from its Co:Ni ratio.

It is suggested here that a conformable sulphide deposit, such as Zawar, which might show some characteristic trace element concentration of igneous hydrothermal (epigenetic) origin, may be a result of discharge of metals from hydrothermal solutions of deep-seated origin into a strongly reducing environment, during sedimentation. Similar hypothesis has also been postulated by Dunham (1964) for Kuperschiefer, W. Germany. Probably here too at Zawar, the geological coincidences were (1) stagnant bottom condition (2) very slow sedimentation and (3) hydrothermal mineralization in progress.

SUMMARY

Galena, sphalerite and pyrite at Zawar mine are essentially localized in Aravalli (Archaean?) dolomites and the deposit is a typical two-dimensional, strata-bound type. Wide range of trace elements in sulphides are probably more consistent with the igneous hydrothermal (epigenetic) origin for the ores, particularly in view of high concentrations of Ag and Sb in galena, Mn in sphalerite and high Co:Ni ratio and abundance of Co to Ni in pyrite.

To find a compromise between pure epigenetic and syngenetic hypotheses, a theory of submarine-hydrothermal (exhalative-sedimentary) origin for galena, blende and pyrite has been postulated.

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