

Thiosulphates as precursors of banded sphalerite and pyrite at Bleiberg, Austria

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Abstract

Banded sphalerite from Bleiberg, Austria, contains ubiquitous relics of Fe-thiosulphates and Fe-sulphites up to 50 μm in size. Zn, Pb, Ni and As form admixtures ranging from a few to 12 wt.% in these compounds. It is suggested that banded sphalerite is formed by a replacement of banded thiosulphate and thiosulphite precursors. This suggestion is supported by a significant admixture of Fe (0.41–8.20 wt.%) and the presence of goethite inclusions in banded sphalerite. In contrast, crystalline ZnS intergrown with the banded variety is Ni-free and contains only 0.06–0.14 wt.% Fe.

Banded pyrite contains inclusions of Fe-thiosulphate up to 200 μm in size. These thiosulphates contain (wt.%): 0.09–1.92 Zn, and 2.67–4.02 Pb. Pyrite formed by replacement (breakdown) of Fe-thiosulphate precursors contains 3.69–3.83 wt.% Pb.

It is suggested that banded sulphides precipitate from solutions carrying sulphur with mixed valences, and crystalline sulphides grow from solutions where the dominant dissolved sulphur is in the form of sulphidic anions.

KEYWORDS: sphalerite, pyrite, thiosulphate, thiosulphite, banding, Bleiberg, Austria.

Introduction

SULPHUR occurs in five major valence states: 2–, 0, 2+, 4+ and 6+. It also readily forms compounds with mixed valencies such as thiosulphates and polythionates (Valensi *et al.*, 1963). Thiosulphates of the alkali earths are soluble in water; those of heavy metals are weakly soluble or insoluble (cf. Ba, Pb; Valensi *et al.*, 1963; Greenwood and Earnshaw, 1984). There are, however, remarkable exceptions from this rule—thiosulphates of Ag and Au are soluble in water (Mann, 1984). The thiosulphate anion is unstable in acid environments, where it is subject to disproportionation; but in alkaline solution it may be able to survive for thousands of years (Pryor, 1960). This means that thiosulphate anions may be stable in pore networks of carbonates, which typically keep an elevated pH.

The importance of the concept of precursors in ore genesis and metamorphism has been stressed by the pioneering work of Stanton (1989). He distinguishes three possible mechanisms, i.e. (1)

the simple ordering and coarsening of compounds formed during sedimentation and diagenesis; (2) nucleation and growth of ordered crystal structures within amorphous materials and gels; and (3) the solid–solid transformation of ‘pure’ and ‘impure’ crystal structures formed during chemical sedimentation and diagenesis (op. cit., p. 552). To these may be added the formation of sulphides from thiosulphate precursors, and it is the purpose of this note to draw attention to these processes.

The naturally occurring sulphite, scotlandite (PbSO_3) was reported from Scotland (Paar *et al.*, 1984) and lead thiosulphate from Ballinalack, Ireland, together with Fe-sulphite and thiosulphate (Kucha, 1988). Naturally occurring melnikovite is reported to be composed of banded spheres of Fe-sulphite, Fe-thiosulphate, pyrite and goethite (Kucha *et al.*, 1989). Hot springs from New Zealand contain in solution more sulphur in the form of thiosulphate than as sulphide or sulphate (Webster, 1987).

Materials and methods

Samples containing banded sphalerite from the Bleiberg Zn-Pb deposit, Austria, were used for this study. Their chemical composition was measured with an ARL SEMQ microprobe at 20 kV using the following X-ray lines and synthetic standards; $K\alpha$ lines—S and Fe (FeS_2), Mn, Ni, Co, Cu, Zn (ZnS), Se; $L\alpha$ line—As, Ag, Cd, In; $M\alpha$ line—Pb (PbS). Measurements were corrected with the MAGIC IV program.

Sulphur valence can be determined from valence-related shifts of the S- $K\alpha$ and S- $K\beta$ lines using XRF (Faesler and Goehring, 1952; Lehr *et al.*, 1980) but it also can be quantitatively measured using EPMA (electron probe microanalysis) (Kucha *et al.*, 1989). The S- $K\alpha$ and S- $K\beta$ emission wavelength is valence dependent. The S- $K\alpha$ shift between sulphide, S^{2-} , and sulphate, S^{6+} was found by XRF to be 1.33 eV (Faesler and Goehring, 1952), 1.37 eV (Lehr *et al.*, 1980), 1.43 eV by EPMA (Kucha *et al.*, 1989), and 1.47 eV in this study (Fig. 1). The S- $K\beta$ wave-

length difference between sulphide and sulphate sulphur was measured by XRF to be 2 eV (Jenkins and de Vries, 1975). A value of 1.78 eV was obtained by EPMA (Kucha *et al.*, 1989), and of 1.83 eV in this study (Fig. 2). A fine structure of the S- $K\beta$ lines reveals valence-related satellites on both sides of the sulphite $K\beta$ peak but only one on the low-energy side of the sulphate $K\beta$ peak. Thiosulphate shows a similar S^{6+} related satellite but half as intense as in sulphate (Kucha *et al.*, 1989). Taking into account valence-related shifts of the S- $K\alpha$ and S- $K\beta$ lines as well as valence-related characteristic satellites, sulphur valence can be determined quantitatively in sulphur compounds with single as well as with mixed sulphur valencies (Kucha *et al.*, 1989).

Sulphur valence was determined from valence-related S- $K\alpha$ and S- $K\beta$ shifts and valence-related

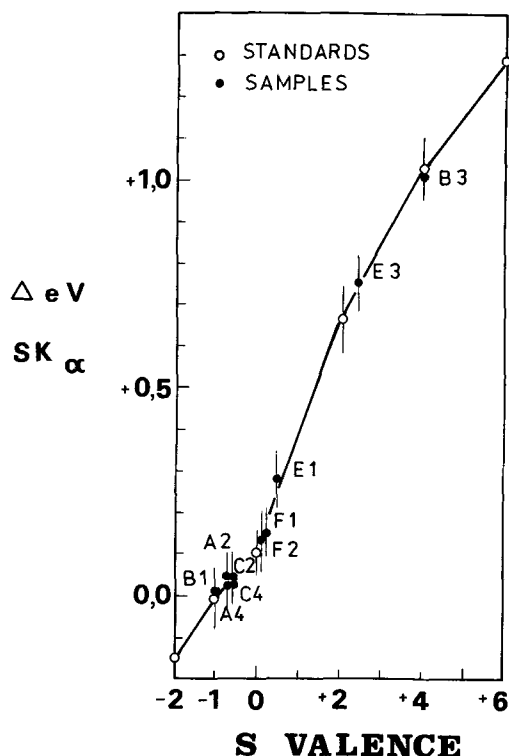


FIG. 1. S- $K\alpha$ shift plotted against sulphur valence. The vertical scale is in eV, the horizontal scale shows sulphur valence. Short, vertical lines represent accuracy bars. Sample numbers are denoted by capital letters and Arabic numerals (Tables 1-6).

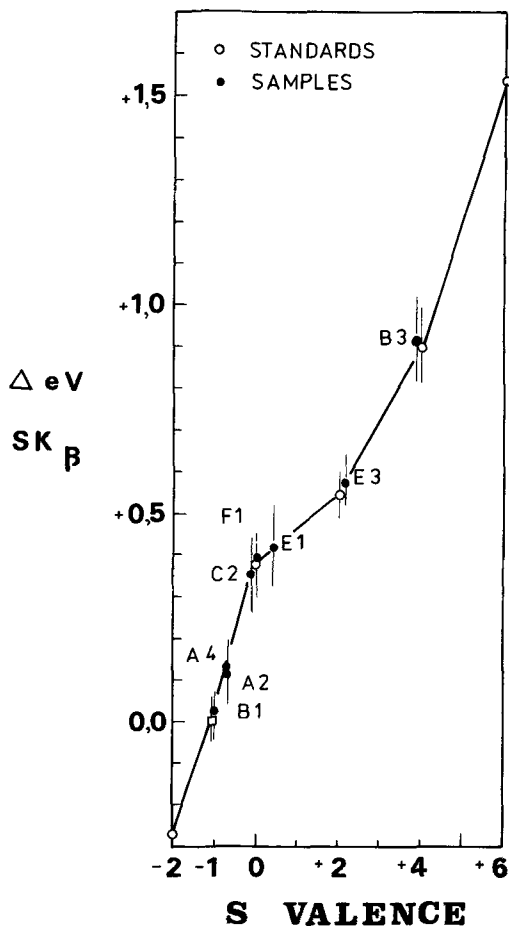


FIG. 2. S- $K\beta$ shift plotted against sulphur valence. The vertical scale is in eV.

satellites using the ARL SEMQ microprobe at 20 kV, with a beam spot size of 15 μm . The spectrometer with PET crystal was calibrated with the following sulphur standards: CaSO_4 , (Figs. 1, 2) $\text{Na}_2\text{S}_2\text{O}_3$, S, FeS_2 , and FeS (Figs. 1, 2). Cubic FeS_2 was used as a zero reference point determined directly before and after the given sulphur compound was tested. When drift of the zero reference point was smaller than one standard deviation (one σ) the measurement was accepted. Sulphur valence was calculated applying procedures developed for the electron probe microanalyser (Kucha *et al.*, 1989).

Sphalerite

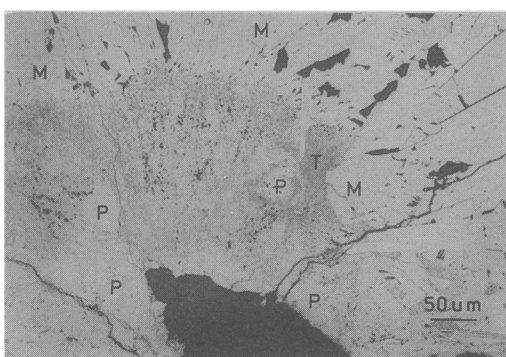
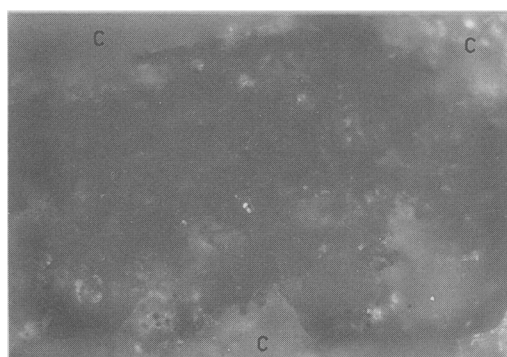
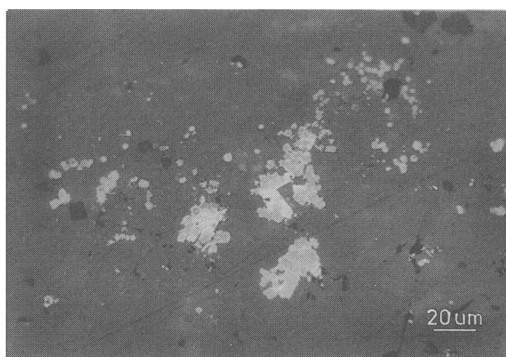
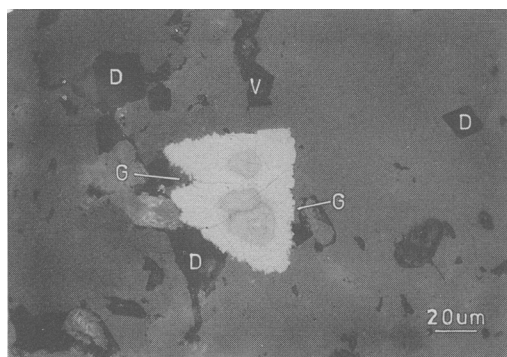
Two types of sphalerite in the samples studied can be distinguished as regards microtexture and crystal habit: (i) banded, with dark internal

reflections and ubiquitous inclusions of pyrite-thiosulphate, Fe-Zn-dolomite and goethite (Figs. 3, 4) and (ii) crystalline with bright internal reflections forming a regular or rectangular fabric discernible under crossed nicols (Figs. 4, 5).

The two sphalerite types differ significantly in their chemical composition. Banded sphalerite contains pyrite-thiosulphate inclusions and has high Fe and significant Ni contents but a low Cd admixture (Table 1) In contrast, crystalline sphalerite is Fe-poor, contains no Ni and is significantly richer in Cd (Table 2). The observed difference in the chemical composition of the two sphalerites probably reflects their different origin.

Pyrite-thiosulphate inclusions in banded sphalerite

Banded sphalerite typically contains pyrite inclusions up to 150 μm in size (Figs. 3, 4). These



FIGS. 3–6. FIG. 3 (*top left*). Photomicrograph of sphalerite (dark grey) containing inclusions composed of pyrite (white), thiosulphite (darker areas inside pyrite). Also Fe-Zn-dolomite (D), voids (V) and goethite (G) intergrown with pyrite are visible. Reflected light, oil, sample BL1/A. FIG. 4 (*top right*). Photomicrograph of banded sphalerite (dark grey) containing ubiquitous inclusions of pyrite (white) and thiosulphates (darker, intergrown with pyrite). Reflected light, oil, sample BL1/F. FIG. 5 (*lower left*). Area of Fig. 4 shown under crossed nicols. Two sphalerite types are revealed: crystalline (C), with bright internal reflections and banded with dark internal reflections containing pyrite and thiosulphate inclusions. Reflected light, oil, crossed nicols, sample BL1/F. FIG. 6 (*lower right*). Photomicrograph of banded pyrite (P) and marcasite (M). Pyrite is intergrown with darker thiosulphate (T). Pyrite-thiosulphate assemblage is overgrown by radial marcasite. Reflected light, oil, sample BL1/E.

Table 1.

Microprobe composition of sphalerite formed by replacement of thiosulphate precursor, Bleiberg (wt.% / atomic proportion).

SAMPLE	S	Mn	Fe	Ni	Zn	Cd	In	TOTAL
BL1/F4	32,99 1,0000	≤ 0,02	6,18 0,1075	0,59 0,0097	55,52 0,8254	0,12 0,0010	≤ 0,04	95,43
BL1/F5	32,93 1,0000	≤ 0,02	0,48 0,0084	0,08 0,0014	67,43 1,0044	0,14 0,0012	0,11 0,0009	101,17
BL1/F6	32,71 1,0000	≤ 0,02	1,24 0,0217	0,08 0,0013	66,54 0,9979	0,14 0,0012	≤ 0,04	100,70
BL1/F7	32,38 1,0000	≤ 0,02	0,41 0,0072	≤ 0,03	67,24 1,0185	0,39 0,0035	0,05 0,0005	100,47
BL1/F8	33,46 1,0000	≤ 0,02	8,20 0,1407	0,09 0,0014	58,70 0,8605	≤ 0,04	≤ 0,04	100,48
BL1/F9	33,23 1,0000	≤ 0,02	2,21 0,0381	0,11 0,0017	65,31 0,9641	0,14 0,0012	≤ 0,04	100,86
BL1/F10	32,80 1,0000	≤ 0,02	4,30 0,0753	0,13 0,0022	61,82 0,9246	≤ 0,04	≤ 0,04	99,05
BL1/F11	32,82 1,0000	≤ 0,02	1,00 0,0174	0,05 0,0007	66,15 0,9886	0,20 0,0018	≤ 0,04	100,22
BL1/F17	32,99 1,0000	0,04 0,0006	1,51 0,0263	≤ 0,03	65,15 0,9687	0,14 0,0012	≤ 0,04	99,83

Sought for but not detected: Cu ≤ 0,04

Table 2.

Microprobe composition of crystalline sphalerite present inside banded ZnS, Bleiberg, Austria (wt.% / atomic proportion)

SAMPLE	S	Fe	Zn	Cd	In	TOTAL
BL1/F12	32,98 1,0000	0,14 0,0025	67,37 1,0020	0,44 0,0038	≤ 0,04	100,93
BL1/F13	33,29 1,0000	0,11 0,0020	67,29 0,9915	0,47 0,0040	≤ 0,04	101,16
BL1/F14	33,33 1,0000	0,08 0,0013	66,93 0,9850	0,22 0,0019	≤ 0,04	100,56
BL1/F15	32,99 1,0000	0,07 0,0012	67,31 1,0009	0,23 0,0020	0,05 0,0004	100,65
BL1/F16	33,13 1,0000	0,11 0,0019	66,59 0,9860	0,39 0,0034	≤ 0,04	100,22
BL1/F18	32,71 1,0000	0,06 0,0010	66,09 0,9913	0,28 0,0025	≤ 0,04	99,14

Sought for but not detected: Mn ≤ 0,02, Ni ≤ 0,03, Cu ≤ 0,04

pyrite grains are optically inhomogeneous. They contain rounded (Fig. 3) or elliptical-patchy areas (Fig. 4) with a reflectance of 17–32% in air. The major elements constituting the darker inclusions in pyrite are S and Fe, but contents of Pb, As, Zn and Ni are also significant and may reach a few

wt.% (Table 3). All quoted EPMA analyses fall short of 100%. The difference is accounted for by oxygen. Sulphur valence determined by microprobe (Kucha *et al.*, 1989) indicates that the compounds investigated are either a mixture of di-sulphide (pyrite) with thiosulphate (BL1/A2,

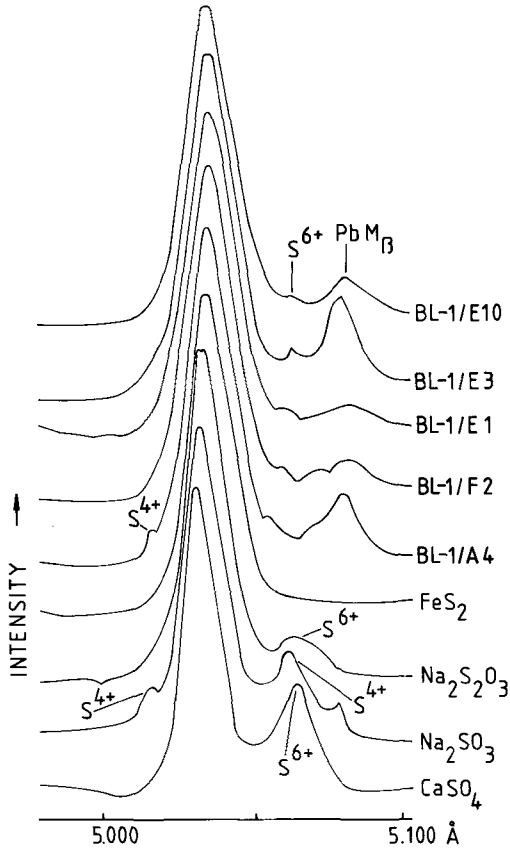


FIG. 7. Scans of the S-K β line in standards and in the tested thiosulphites and thiosulphates. The S⁴⁺ and S⁶⁺ satellites are clearly resolved.

BL1/F1, BL1/F2) or a mixture of pyrite with thiosulphite (Table 4, BL1/A2, BL1/A4) or sulphite (Table 4, BL1/B3). Valence-related satellites confirm this interpretation (Fig. 7).

Sulphur valencies determined from valence-related satellites, S-K α and S-K β shifts (Figs. 1, 2) and sulphur valence calculated to satisfy the observed chemical formula (Figs. 1, 2) are in good agreement (Table 4) underlining the value of the procedures applied for such measurements (Kucha *et al.*, 1989).

There is a general rule concerning observed sulphur valence and reflectance—the lower the reflectance the higher the sulphur valence.

Fe-thiosulphates in banded pyrite–marcasite

Banded pyrite–marcasite from Bleiberg also contains inclusions of Fe-thiosulphates (Fig. 6). The size of low-reflecting thiosulphate inclusions

reaches 200 μm . The pyrite host has unusually high Pb content (Table 5). Sulphur valence deduced from the chemical composition and calculated from the S-K α and S-K β shifts show a good compatibility. The observed dark areas in pyrite (Figs. 6, 7) show only S⁶⁺ satellites. Therefore they are either a mixture of pyrite and Fe-thiosulphate (Tables 5, 6; E1, E2, E6) or Fe₅S₅O₈ (FeSO₂) alone (Tables 5, 6; E3). The latter mineral has a grain size of 200 μm and is large enough to be studied by X-ray powder methods.

Preliminary results of electron diffraction study indicate that the mineral has an orthorhombic lattice with cell parameters (nm): $a_0 = 0.860 \pm 0.008$, $b_0 = 1.004 \pm 0.011$ and $c_0 = 0.555 \pm 0.004$.

Origin of banded sphalerite and banded pyrite

Banded ZnS from Bleiberg is intergrown with a crystalline variety (Figs. 4, 5). The former contains common inclusions of thiosulphates, thiosulphites and pyrite, while the latter has no visible inclusions. Both sphalerites are dramatically different in chemical composition (Tables 1, 2). The banded variety is rich in elements which are major constituents of inclusions of minerals with mixed sulphur valencies (Tables 3, 4). The observed difference in fabric and chemistry of the ZnS studied probably reflects a different origin of the two varieties. It is suggested that crystalline sphalerite has been precipitated from solutions carrying S²⁻ as the dominant dissolved sulphur species. Banded sphalerite was probably precipitated from solutions with thiosulphate and/or sulphate (thiosulphite) as dominant forms of dissolved sulphur in the mineralizing fluids. A gradual sulphur reduction or a gradual change in the S²⁻/S⁶⁺ and S²⁻/S⁴⁺ proportion in the solution would induce banded microtexture of sphalerite. It seems that some admixture of Pb and minor Ni and As may decrease the solubility of thio-complexes (Kucha, 1988; Kucha *et al.*, 1989) and may cause precipitation of banded thiosulphates, thiosulphites and sulphites on Zn and/or Fe. This may be supported by a high admixture of Pb, Ni and As in banded sphalerite (Table 1). Intimate intergrowths of pyrite–Fe-thiosulphate with goethite found in banded sphalerite may suggest that Fe²⁺ served partly as a reducer of S⁶⁺ or ⁴⁺ to S²⁻ necessary for the precipitation of sphalerite. A similar approach may be adopted to explain the origin of banded pyrite from Bleiberg (Fig. 6).

Two modes of formation may be envisaged for the banded sphalerite and pyrite studied:

Table 3

Microprobe composition of compounds with mixed sulfur valences present in banded sphalerite, Bleiberg, Austria (wt. % / atomic proportions).

SAMPLE	S	Fe	Ni	Cu	Zn	As	Ag	Pb	TOTAL	O (DIFF.)
BL1/A2	47,86 6,0000	40,59 2,9215	1,11 0,0760	0,04 0,0025	2,49 0,1529	0,96 0,0516	0,07 0,0027	3,21 0,0622	96,33	3,67 0,9220
BL1/A4	45,96 6,0000	39,66 2,9730	1,04 0,0743	0,08 0,0052	2,57 0,1646	1,03 0,0576	≤ 0,03	3,94 0,0795	94,28	5,72 1,1330
BL1/B1	49,93 6,0000	45,39 3,1316	≤ 0,03	≤ 0,03	1,34 0,0790	0,14 0,0072	0,06 0,0021	0,72 0,0134	97,59	2,41 0,5804
BL1/B3	19,77 1,0000	45,58 0,9996	0,04 0,0011	≤ 0,03	2,61 0,0632	0,46 0,0099	0,04 0,0006	1,05 0,0082	69,55	30,45 3,0863
BL1/C2	46,51 6,0000	39,43 2,9202	1,57 0,1105	0,09 0,0058	3,04 0,1925	1,14 0,0629	≤ 0,03	3,19 0,0636	94,97	5,03 1,3005
BL1/C4	45,99 6,0000	36,08 2,7283	3,42 0,2457	0,09 0,0061	2,63 0,1697	1,37 0,0771	≤ 0,03	3,40 0,0692	92,98	7,02 1,8533
BL1/F1	42,80 6,0000	28,59 2,3013	3,66 0,2805	≤ 0,03	12,25 0,8422	1,02 0,0609	≤ 0,03	2,78 0,0603	91,11	8,89 2,4976
BL1/F2	45,26 4,0000	37,13 1,9941	3,97 0,1918	≤ 0,03	4,78 0,2074	0,80 0,0303	≤ 0,03	2,31 0,0315	94,29	5,71 0,9770

Sought for but not detected: Mn ≤ 0,03, Co ≤ 0,03, Se ≤ 0,04

Table 4

Sulfur valence determined in compounds with mixed sulfur valences (Table 3) by the SK α and SK β shifts, by valence related satellites and compared to the valence deduced from chemical composition (Table 3).

SAMPLE	SK α SHIFT VALENCE (eV)		SK β SHIFT VALENCE (eV)		SATELLITES	AVERAGE VALENCE FROM CHEM.COMPOSITION	CALCULATED PARTITION OF S BETWEEN DIFFERENT VALENCES			
	S6+	S4+	S2-	S2-			S6+	S4+	S2-	S2-
BL1/A2	+ 0,03	- 0,7	+ 0,11	- 0,7	+ 4	- 0,69		0,46	0,46	2,54
BL1/A4	+ 0,04	- 0,7	+ 0,12	- 0,7	+ 4	- 0,52		0,67	0,67	2,33
BL1/B1	0,00	- 1,0	0,00	- 1,0	None	- 1,00				3,00
BL1/B3	+ 1,01	+ 4,0	+ 0,90	+ 4,0	+ 4	+ 4,17	0,09	0,91		
BL1/C2	+ 0,04	- 0,6	+ 0,35	- 0,1	+ 6	- 0,57	0,43		0,43	2,57
BL1/C4	+ 0,04	- 0,6			+ 6	- 0,37	0,62		0,62	2,38
BL1/F1	+ 0,15	+ 0,2	+ 0,37	0,0	+ 6	- 0,17	0,83		0,83	2,17
BL1/F2	+ 0,13	+ 0,1	?	?	+ 6	- 0,51	0,33		0,33	1,67

(i) initially, a banded thiosulphate–thiosulphite–sulphite precursor stabilized by a Pb admixture may be precipitated. Reduction to banded sulphide takes place later. Part of the Fe²⁺ is consumed for sulphate reduction, as suggested by the presence of goethite inclusions (Fig. 3). The process of reduction is connected with a reduction in volume, and this has resulted in the formation of contraction cracks (Kucha, 1988) or voids in banded sphalerite (Fig. 3).

(ii) a drop in pH may cause disproportionation of thiosulphate anions in the solution (Kneen *et al.*, 1972). Due to different solubilities of Fe and Zn thiosulphates, thiosulphates and sulphites, iron and zinc may be separated between the liquid and

solid states producing either banded pyrite with Zn and Pb admixture or banded sphalerite with high Fe, Pb, Ni, and As content.

In the samples studied thiosulphates appear in massive, unfractured sphalerite or marcasite host. They are present as ubiquitous relics and inclusions only in some of the bands constituting large, massive, continuous banded sulphides. The chemical composition of a particular band hosting thiosulphates is dramatically different from the sphalerite band free of such inclusions (Tables 1, 2). Therefore, inclusions with mixed sulphur valencies are regarded as primary inclusions.

It is evident from the above that not only

Table 5

Microprobe composition of thiosulphate relics present in banded pyrite formed after thiosulphate precursor, Bleiberg, Austria (wt. %/ atomic proportions).

SAMPLE	S	Fe	Ni	Zn	As	Ag	Pb	TOTAL	O (DIFF.)
BL1/E1	38,21 6,0000	45,25 4,0801	≤ 0,03	1,21 0,1242	0,13 0,0089	0,50 0,0233	2,71 0,0658	88,08	11,92 3,7515
BL1/E2	44,01 7,0000	46,60 4,1642	≤ 0,03	0,88 0,0867	0,06 0,0043	0,07 0,0031	2,91 0,0716	93,57	6,43 2,0496
BL1/E3	27,14 5,0000	45,72 4,8353	0,04 0,0037	1,92 0,1738	0,08 0,0061	≤ 0,03	2,67 0,0761	77,62	22,38 8,2629
BL1/E6	46,11 4,0000	43,73 2,1779	≤ 0,03	0,09 0,0036	0,10 0,0037	0,09 0,0022	4,02 0,0540	94,17	5,83 1,0135
BL1/E10	50,11	44,20	0,06	≤ 0,03	0,05	0,08	3,83	98,37	PYRITE
BL1/E11	49,96	44,37	≤ 0,03	0,04	0,05	≤ 0,03	3,69	98,09	PYRITE

Sought for but not detected: Co ≤ 0,03, Cu ≤ 0,04

Table 6

Sulfur valence determined in thiosulphate inclusions (Table 5) in banded pyrite by the SK α and SK β shifts, by valence related satellites and compared to the valence deduced from chemical composition (Table 5).

SAMPLE	SK α SHIFT (eV)	VALENCE	SK β SHIFT (eV)	VALENCE	SATELLITES	AVERAGE VALENCE FROM CHEM. COM- POSITION	CALCULATED PARTITION OF S BETWEEN DIFFERENT VALENCES		
							S6+	S2-	S2-2
BL1/E1	+ 0,28	+ 0,5	+ 0,42	+ 0,5	+ 6	+ 0,25	1,25	1,25	1,75
BL1/E2	?	?	?	?	+ 6	- 0,42	0,68	0,68	2,82
BL1/E3	+ 0,75	+ 2,5	+ 0,57	+ 2,2	+ 6	+ 2,20	2,75	2,75	0,00

regionally metamorphosed ores, but even 'simple' low-temperature base-metal ores are products of polyphase processes. Many pertinent features can only be explained by reference to the precursor concept as outlined by Stanton (1989), which needs to be extended to include transformations such as thiosulphate → sulphide which are much more widespread than hitherto assumed.

Observations similar to those reported have also been made in:

(i) carbonate-hosted Zn-Pb deposits of Ireland, where compounds with mixed and intermediate sulphur valencies are present as relict bands in banded sphalerite and pyrite (melnikovite). In the Ballinalack Zn-Pb deposit, the presence of lead thiosulphate was suggested based on EPMA and XRD data (Kucha, 1988).

(ii) ubiquitous banded melnikovite from carbonate-hosted Zn-Pb deposits of Belgium is composed of darker bands of thiosulphate, thio-sulphite and goethite, recurrently intergrown

with bright bands of marcasite and pyrite (Kucha *et al.*, 1989).

(iii) thiosulphates of Fe, Co, Cu and Ag commonly forming the cement of framboidal pyrite and bands in pyrite-melnikovite in Kupferschiefer, Poland. The involvement of thiosulphates in the distribution of silver in Kupferschiefer has been suggested (Kucha, 1990).

(iv) in MVT deposits of Upper Silesia, Poland, zinc, lead and iron sulphides form recurrent bands intertwined with bands containing mixed and intermediate sulphur valencies. Microtextures of these bands suggest that they were formed in one continuous process. This will cast new light on the mode of formation of many low-temperature ores and on the composition of ore-forming fluids.

For two reasons it is not surprising that compounds with mixed and intermediate sulphur valencies have gone unnoticed:

(i) to obtain the higher quality of polish necessary

to identify small inclusions, an appropriate technique of sample cutting and polishing has to be used

(ii) many of these compounds have optical properties close to goethite or sphalerite. They usually form small inclusions and may be easily overlooked due to optical similarity to the host sphalerite.

However, such compounds have been noticed by some ore petrologists (Ramdohr, 1980) but have gone undiscussed, since the method of sulphur valence determination by microprobe was not used until later (Kucha, 1988; Kucha *et al.*, 1989).

Examples of natural compounds with mixed and intermediate sulphur valencies known from the literature (Paar *et al.*, 1984; Webster, 1987; Kucha, 1988, 1990; Kucha *et al.*, 1989) and presented in this paper may suggest that such compounds may be the natural precursor for banded sulphides formed below 250–300 °C.

Very little is known of the physical and chemical properties of Zn, Fe, Ni, As and Pb compounds with mixed sulphur valencies and only limited data are available for some of them (Kneen *et al.*, 1972). Therefore experimental work is urgently required. Such experiments may prove useful and possibly may answer two fundamental questions: (1) why some sulphides occur in binary mode—as banded or as larger euhedral crystals; (2) the mode of deposition of metals and sulphur in sulphide orebodies.

The involvement of compounds with mixed and intermediate sulphur valencies in the formation of ores has so far been overlooked by students of ore genesis.

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