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# The Occurrence of Thiosulfates and Other Unstable Sulfur Species as Natural Weathering Products of old Smelting Slags

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## Summary

Orthorhombic barium thiosulfate monohydrate, triclinic barium thiosulfate fluoride, triclinic barium sulfite and monoclinic hydrated barium aluminium trisulfide hydroxide have been isolated and identified as natural weathering products in old smelting mill slags. None of them have been found in nature before, but two of them are known as laboratory products. They represent a stepwise sequence in sulfur oxidation numbers and are potential intermediates in the familiar but little-understood oxidation of sulfides to sulfates and thus throw light on the mechanism of the natural oxidation of sulfide ores. The nature of these phases and co-existing species suggests formation between about Eh $-0.45$ v at pH 11 and Eh $-0.6$ v at pH 13.

## Zusammenfassung

*Das Vorkommen von Thiosulphaten und anderen unstabilen Schwefelverbindungen als natürliche Venwitterungsprodukte alter Schmelz-Schlacken*

Orthorhombisches Barium-Thiosulphat-Monohydrat, triklines Barium-Thiosulfat-Fluorid, triklines Barium-Sulfit und monoklines, hydriertes Barium-Aluminium-Trisulfid-Hydroxyd sind isoliert und als natürliche Verwitterungsprodukte in alten Schmelzschlacken identifiziert worden. Keine dieser Verbindungen sind bisher in der Natur nachgewiesen worden, jedoch sind zwei davon als Kunstprodukte bekannt. Sie stellen eine schrittweise Abfolge von Schwefeloxydationszahlen dar und sind potentielle Zwischenglieder in der bekannten, aber wenig verstandenen Oxydation von Sulfiden zu Sulfaten. In diesem Sinne werfen sie auch Licht auf den Mechanismus der natürlichen Oxydation von Sulfiderzen. Die Art dieser und koexistierender Verbindungen legt eine Bildung zwischen Eh −0.45 v bei pH 11 und Eh −0.6 v bei pH 13 nahe.

## Introduction

Sulfides and sulfates are of common occurrence in nature, having appreciable thermodynamic stability envelopes at near earth's surface conditions.

The transformation of sulfides to sulfates under oxidising conditions is a familiar but not well understood process (see *Williams*, 1990, and references cited therein). It is normally represented as a simple boundary line in Eh–pH diagrams—the "sulfide-sulfate fence" familiar to geochemists. Being an 8-electron process, however, it is highly unlikely to proceed in one step, but apart from native sulfur, S(0), and disulfides such as pyrite [average S(−1)] the possible intermediates, being of limited stability, were unknown in nature until the discovery of the first sulfite mineral, scotlandite, $PbSO_3$, reported as recently as 1984 (*Paar* et al.). Two other sulfites have subsequently been reported as well-characterised species, hannebachite, $CaSO_3.0.5H_2O$ (*Hentschel* et al., 1985) and gravegliaite, $MnSO_3.3H_2O$ (*Palenzona* and *Corallo*, 1991). The only isolated and well-characterised thiosulfate-containing species reported to date in nature is bazhenovite, $CaS_5.CaS_2O_3.6Ca(OH)_2.20H_2O$, formed as a result of fires in coal dumps in the Urals (*Chesnokov* et al., 1987), though known since 1816 as a laboratory product ("Büchner's Compound", *Büchner*, 1816; see *Lutz* et al., 1969). Small relics of thiosulfates and sulfites of iron and lead have been detected by the valence-related shift of the S $K\alpha$ and S $K\beta$ lines in the X-ray spectra of ore samples from carbonate-hosted deposits in Ireland, Poland and Austria (*Kucha*, 1988; *Kucha* et al., 1989; *Kucha* and *Piestrzynski*, 1991; *Kucha* and *Viane*, 1991; *Kucha* and *Stumpfl*, 1992), but none of these phases have been isolated and fully characterised as yet.

We have now discovered well-crystallised specimens of two barium thiosulfates, a barium sulfite and a barium aluminium hydroxy-trisulfide as natural weathering products in cavities in old slags derived from the smelting of sulfide ores. Two of these are known as laboratory products, the other two are previously unrecorded phases. It is intended to publish full details of these species separately. Specimens have been presented to the British Museum (Natural History) and to the Natural History Museum of Los Angeles County. A number of other co-existing phases are under investigation.

## Sites Examined

Sites so far examined and found to contain at least one of the species described are (taken from north to south): Whashton Smelting Mill, Whashton, Yorkshire (NZ 144055); Surrender Smelting Mill, Reeth, Yorkshire (NY 990000); Marrick Low Mill, Marrick, Yorkshire (NZ 079995); Hipper Slag Mill (Harewood), Holymoorside, Derbyshire (SK 310687); Cromford Smelting Mill, Cromford, Derbyshire (SK 298571). It is, however, highly likely that these species are of much more widespread occurrence in this and analagous areas.

These sites are all smelting mills associated with lead-zinc mineralisation in the Pennine Carboniferous limestone; Whashton smelting mill dealt with ores also containing chalcopyrite. Baryte was an important gangue mineral in the material processed at all these sites, in addition to calcite and fluorite.

## Description of Species

### *Orthorhombic Barium Thiosulfate Monohydrate*

This phase forms colourless rectangular crystals and glassy crack linings with a prominent rectangular set of cleavages parallel to the crystal faces ({100}, {010} and {001}). The normal habit is in length-striated bar-like crystals, but it is occasionally found as needles, sometimes in radiating clusters, as more platy crystals, and as thin coatings filling cracks in the slag. It is associated with the other three phases described here.

The X-ray powder diffraction pattern and infrared spectrum of our material match the published data for orthorhombic $BaS_2O_3.H_2O$ (XRD: *Aka* et al., 1980; *Nardelli* and *Fava*, 1962. IR: *Silvonen*, 1923; *Miller* and *Wilkins*, 1952; *Newman* and *Powell*, 1963. Note also the neutron diffraction study by *Manojlović-Muir*, 1975).

The average of three closely similar electron microprobe analyses on a sample from the Surrender Mill slags, using a synthetic $BaS_2O_3.H_2O$ crystal for standards gave Ba, 51.7; S, 23.5%, with traces of Sr and Al. $BaS_2O_3.H_2O$ requires Ba, 51.4; S, 24.0%. Thermogravimetric analysis of another sample gave results suggesting a 9% contamination of the sample with inert material, such as $BaSO_4$.

This phase is of widespread occurrence, and has so far been positively identified on slags from Whashton, Surrender, Marrick Low, Hipper and Cromford Mills, but doubtless occurs elsewhere.

### *Triclinic Barium Thiosulfate Fluoride*

Quite a common species in the slags studied, characteristically forming colourless, transparent, near-rectangular plates, which look like simple single crystals, but are polysynthetically twinned and triclinic. These plates vary considerably in size, but are usually up to about 2 mm across, one exceptional crystal (from Cromford Mill) being 5 mm across. This large crystal is alone in a cavity, but the crystals are usually clustered closely together as cavity linings. Sometimes found as fine-grained somewhat pearly white coatings with a radiating texture, e.g. at Surrender Mill. Typically associated with all the other three phases described here.

This species is a new phase, not recorded in the literature. Energy dispersive microprobe scans indicate the presence of major Ba, S and F, and quantitative microprobe analyses for Ba and S indicate a formula of $BaS_2O_3.BaF_2$, with small amounts of Al and Sr being present, the Sr analyses being surprisingly variable, indicating impurity, whereas the Al values are constant, suggesting incorporation into the crystal lattice (surprising in view of the small ionic radius of the $Al^{3+}$ ion). The average of 15 similar (apart from Sr values) analyses give Ba, 65.9; S, 13.5; Al, 0.4; Sr 0.3%. $BaS_2O_3.BaF_2$ requires Ba, 64.7; S, 15.1%. A microchemical test with $NaN_3 + I_2$ reagent gave strong effervescence, typical of thiosulfates. The infrared spectrum of this phase is characteristic, and clearly indicates that it is an anhydrous thiosulfate with no hydroxide or any other oxyanions present. Sharp absorption maxima appear at 1132 ($\nu_4$), 1019 ($\nu_2$), 687 ($\nu_3$), 554 and 527 ($\nu_5$) $cm^{-1}$. These assignments are in accord with those published for the thiosulfate anion (*Ross*, 1972).

X-ray diffraction measurements (powder and twinned-crystal) indicate that it is polysynthetically twinned triclinic $P\bar{1}$ with a = 22.63 (2), b = 4.624 (2), c = 4.581 (4) Å, $\alpha$ = 90.03 (4) °, $\beta$ = 95.82 (8) °, $\gamma$ = 89.97 (5) °, V = 477 (1) Å$^3$, the unit cell being measured on a polysynthetically twinned crystal using a single crystal diffractometer.

This phase is of widespread occurrence. It has been identified so far in slags from Whashton, Surrender, Hipper and Cromford Mills.

### *Triclinic (?) Barium Sulfite*

This phase is one of the rarer species in the slags. It is usually found as a pale yellow to dirty greenish yellow waxy-looking material with a granular texture, completely filling small cavities (to about 2 mm across) but occasionally forms small (to 2 mm) rounded stalactitic-looking growths of the same colour and waxy lustre projecting into cavities. It is typically associated with the barium thiosulfate fluoride and with the yellow polysulfide described below.

The X-ray powder diffraction pattern and infrared spectrum of our material matches those published for synthetic $BaSO_3$, (XRD: JCPDS Cards 31–0167, 33–0179; IR: *Silvonen*, 1923; *Miller* and *Wilkins*, 1952), and those of microcystalline material synthesised by one of us (R.S.W.B). Although the X-ray powder diffraction pattern of this phase is recorded in the literature (*v. supra*) its crystal symmetry and unit cell parameters are not recorded. No suitable single crystals were available, and the recorded powder diffraction pattern contains only 10 lines, 9 of which can be indexed on a triclinic unit cell with an excellent figure of merit, but 9 lines are not enough to define the 6 parameters required for a triclinic cell with any confidence, and the unindexed line is quite strong and should not be ignored. For this reason we are not publishing these parameters.

The slag material is slightly strontian by solid solution, the average of six similar electron microprobe spot analyses giving Ba, 62.0; Sr, 0.3; S, 11.8%. $BaSO_3$ requires Ba, 63.2; S, 14.8 %; $(Ba_{0.99}Sr_{0.01})SO_3$ requires Ba, 62.7; Sr, 0.4, S, 14.8%.

So far, this phase has only been identified from the slags at Surrender Mill.

### *Monoclinic Hydrated Barium Aluminium Trisulfide Hydroxide*

This attractively crystallised phase is uncommon in the slags. It forms orange-yellow crystals, commonly to about 1 mm but sometimes larger, usually transparent, but prone to turn cloudy through dehydration, common habits being length-striated blades and pseudohexagonal plates, the plates sometimes being very thin and micaceous and which may then reach several mm across. Normal associates are the barium thiosulfate fluoride and the barium sulfite described above.

This is another undescribed species, and has been the subject of detailed studies only briefly outlined in this paper.

Energy dispersive microprobe scans indicate the presence of major Ba, Al and S, with minor Sr and traces of Ca. The results of electron microprobe analyses, infrared spectroscopy, thermal analyses, and X-ray powder and single-crystal diffractometry indicate that it is a monoclinic $P2_1/c$ layer-lattice hydroxide structure with firmly held interlayer trisulfide ions and more loosely held interlayer water molecules, with site-selective substitution of Sr and Ca for some of those barium ions that are linked to the trisulfide ions. The trisulfide ions are responsible for the colour, and are stable to 700°C. The end-member (ideal) formula is $BaS_3.Ba(OH)_2.2Al(OH)_3.8H_2O$. Three of the water molecules are particularly loosely held and were lost in the sample preparation for the microprobe analyses, the average of 16 closely similar spot analyses giving Ba, 33.6; Sr, 5.3; Ca, 0.6; Al, 9.0; S, 15.2%. $(Ba_{0.52}Sr_{0.38}Ca_{0.10})S_3.Ba(OH)_2.2Al(OH)_3.5H_2O$ requires Ba, 33.6; Sr, 5.4; Ca, 0.6; Al, 8.7; S, 15.5%. The absence of time-dependent drift in these values indicates that no further water was being lost.

The unit cell parameters for the fully hydrated phase, from single crystal diffractometer measurements are $a = 8.786$ (8), $b = 19.208$ (9), $c = 11.105$ (6) Å, $\beta = 105.98$ (5) °, V = 1802 (2) $Å^3$.

This phase has so far been positively identified from Surrender and Hipper Mills and also in cavities in a cement-like slag fom a footpath surface at Sorn, Scotland. Small amounts of material of similar appearance, but not positively identified have been found in slag from Cromford and Bradwell Mills in Derbyshire.

### *Other Associated Weathering Products*

Other identified weathering products associated with the species described above include gypsum, sulfur (another intermediate), baryte, witherite, litharge and hydrocerussite. An off-white material cementing slag fragments at Surrender Mill proved to be an intimate mixture of baryte and witherite with minor barium sulfite.

A number of other unidentified species are present and are under study, but have not yet been fully characterised. These include a hydrated thiosulfate forming pearly, colourless, six-sided plates and pyramids with a micaceous cleavage, and a hydroxythiosulfate forming very pale yellowish spherules and sub-globular aggregates of indistinct crystals, both from the Hipper slags.

## Discussion and Conclusion

A number of intermediate phases in the aqueous oxidation of BaS to $BaSO_4$, of limited thermodynamic stability and including thiosulfates, a sulfite and a polysulfide, have been identified as natural oxidative weathering products of smelting mill slags.

It is concluded that barium sulfide, formed from the reduction of baryte impurity in the smelted ores, has been oxidising by weathering over many years back to baryte. The process has not gone to completion, however, and some intermediate phases of limited stability have crystallised out.

The isolation and identification of the species described here has filled in some of the gaps in natural occurrence in the oxidation state sequence between sulfide and sulfate, thus in proceeding from the sulfide via disulfide to the trisulfide to elemental sulfur to the thiosulfates to the sulfite and finally to the sulfate the average oxidation number of the sulfur species goes from $-2$ to $-1$ to $-2/3$ to 0 to $+2$ to $+4$ to $+6$. This does not imply that the mechanism of sulfide oxidation neccessarily follows this particular stepwise pathway, as, for example, the trisulfide could be formed by interaction of the S(0) with the starting sulfide, and the thiosulfates could be formed from reaction between sulfites and sulfides.

The nature of the associated species suggests that alkaline and mildly oxidising conditions pertain. Thus the coexistence of hydrocerussite and litharge suggests a pH in the 11 to 13 region, and as the species described are intermediates they would be expected to be formed in the region of the sulfate-sulfide fence. This suggests formation between about Eh −0.45 v at pH 11 and Eh −0.6 v at pH 13, the exact conditions being dependent on the activities of the species in solution. These are the conditions under which the species described are reasonably stable; they would be destroyed by acidic, reducing or more strongly oxidising conditions.

The geochemical similarity, particularly in ionic radius and charge, between barium and lead suggests that the weathering of these slags is acting as a model system for the oxidation of galena in the oxidation zone of orebodies.

## Instrumentation, Techniques

Microprobe analyses were performed in the Geology Department, University of Manchester, using a combination of energy and wavelength dispersive techniques, with a Cameca Camebax electron probe analyser controlled by a Link Analytical AN 10000 X-ray analysing system, the data being collected and processed using the Link Specta EDS/WDS X-ray acquisition and data reduction program. An accelerating voltage of 15 kV was used, with an incident beam current of 1 nA, a 20 micron diffused beam being employed to minimise loss of volatiles such as water. The standards used were celestine for Sr, corundum for Al and baryte for Ba and S except in the case of the analysis of the barium thiosulfate monohydrate, in which it was found that the use of a synthetic barium thiosulfate standard considerably improved the accuracy of thiosulfate sulfur determination.

Infrared spectra were run in nujol mulls between KBr plates using a Nicolet 5PC Fourier Transform infrared spectrometer, a Philips Analytical PU 3600 Fourier Transform infrared spectrometer and a Perkin-Elmer PE 783 precision grating spectrometer.

X-ray powder diffraction data were collected using a Scintag XDS 2000 powder diffractometer employing unmonochromated Cu radiation and a solid-state detector sensitive only to the $K_\alpha$ component. The samples were ground and spread thinly on a horizontal single-crystal quartz plate and scanned using a $\theta/\theta$ method. Single-crystal measurements were made on a Rigaku AFC 5R diffractometer using graphite-monochromated $MoK_\alpha$ radiation.

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