

# Mineralogical and S isotopic features of the supergene profile of the Zapadno-Ozernoe massive sulphide and Au-bearing gossan deposit, South Urals

E. V. BELOGUB<sup>1,\*</sup>, C. A. NOVOSELOV<sup>1</sup>, B. SPIRO<sup>2,†</sup> AND B. A. YAKOVLEVA<sup>3</sup>

<sup>1</sup> Institute of Mineralogy of Urals Branch of RAS, Miass, 456301, Russia

<sup>2</sup> NERC Isotope Geosciences Laboratory, Keyworth, Nottingham NG12 5GG, UK

<sup>3</sup> Saint-Petersburg State University, Saint-Petersburg, Universitetskaya nab. 7/9, 199034, Russia

## ABSTRACT

The profile of the supergene zone of the Zapadno-Ozernoe massive sulphide Cu-Zn deposit differs from the classic model (Emmons, 1917) in that it includes a prominent dark sooty subzone rich in secondary sulphides. This subzone is situated above residual pyrite sands, which overlie the massive sulphide body and below quartz-baryte leached sands. It contains a diverse mineral assemblage which consists of secondary sulphides such as galena, sphalerite, metacinnabar, Se-bearing pyrite–dzharkenite series, tiemannite, native Au, native S and native Se, and unidentified sulphosalts of Ag and Hg. The very light S isotope composition of the secondary sulphides (lowest values  $\delta^{34}\text{S} = -17.2\%$  VCDT) in comparison with primary pyrite  $\sim 0\%$  and baryte  $+18.4\%$  is indicative of bacterial sulphate reduction. The overlying oxidized part of the supergene column contains minerals of the jarosite–beudantite–segnitite series. The maximum concentrations of Au, up to 150 ppm, occur in the lower part of the profile. The atypical structure, mineral assemblage and S isotope composition of the secondary sulphides in the dark layer of the supergene profile are indicative of particular geochemical conditions due to the existence of a stagnant water body that gave rise to intense bacterial activity, in turn controlled by fluctuations in the redox boundary.

**KEYWORDS:** supergene zone, oxidation zone, gossan, weathering, S isotopes, Se, secondary sulphides, dzharkenite, metacinnabar, galena, tiemannite, beudantite, segnitite, jarosite.

## Introduction

THE geological and mineralogical investigations of gossans in the Urals, formed by supergene alteration of massive sulphides, began during the first part of the last century. Between 1900 and 1950 the general schemes of structure and genesis of gossans were developed by Emmons (1917) and Smirnov (1955). Their scheme was based on gossans formed *in situ* on outcrops of ore bodies. The generalized zonation of gossans according to Emmons (1917) and Smirnov (1955) is as follows

(from the base upwards): (1) secondary sulphide enrichment zone (secondary minerals usually include Cu sulphides such as bornite, chalcocite and covellite); (2) leaching zone (residual quartz and baryte sand) and jarosite zone (overlying the pyrite ore bodies); (3) ‘iron’ cap (mainly goethite with various carbonates and sulphates of metals. Some authors (e.g. Zaykov and Leyn, 1998) identified an additional residual pyrite sand zone, located between the oxidized ores with secondary Cu sulphides and the overlying leached ores, which contain layers and lenses of native S.

The present study of the detailed mineralogical and isotopic composition of the supergene zone of the Zapadno-Ozernoe deposit was prompted by the observed differences between the features of the supergene zone of this deposit and those described by Emmons (1917) and Smirnov

\* E-mail: bel@ilmeny.ac.ru

DOI: 10.1180/0026461036720105

† Present address: Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD, UK

(1955). The features of the wall-rock alteration and secondary mineral assemblages are more akin to those of polymetallic SEDEX ore bodies (Yakhontova and Grudev, 1987). Moreover, these features enable a more detailed assessment of the local and regional weathering regime. The integration of these findings with stratigraphic and geochronological information has the potential to contribute to the reconstruction of the palaeo-environment and palaeoclimate of the Southern Urals.

**Geological features of the Zapadno-Ozernoe deposit**

The Zapadno-Ozernoe deposit is situated 18 km south of the town of Uchaly on the western flank of the Uzelginskoye ore field (East-Magnitogorsk palaeo-island arc) within the edifice of a central-type volcano (Fig. 1). Massive sulphide ores are related to volcanic-sedimentary sequences of Eifelian age (D<sub>2</sub>ef), which, in the regional terminology, correspond to the Karamalytash formation. The overlying rocks belong to the Ulutau formation (D<sub>2</sub>ef-zv–D<sub>3</sub>fr). In this deposit there are 15 massive sulphide ore bodies located in two ore-bearing levels. Only the No. 5 ore body has a developed Au-bearing supergene zone. It occurs among subvolcanic andesites in a tectonic extensional zone. The ore body of

primary sulphides has an elliptic form in plan view. In cross-section it has a drop-like shape with a wide mound-like upper part and narrow lower part. This outline which delimits the orebody may be a result of tectonic rupture. The ore body is blind and its roof is 30–50 m below the surface. The host rocks consist mainly of andesitic porphyries with less common rhyolite porphyries and rhyolites, volcanoclastic rocks and amygdaloidal basalt. A major subvertical body of rhyolite-porphyry seems to have a controlling influence both on the massive sulphide ores and the supergene zone. During 1998 the Bashkirian Gold-mining Company exploited the Au-bearing oxidized ores of this deposit.

The primary ores of the Zapadno-Ozernoe deposit contain mainly pyrite, chalcopyrite and sphalerite. The colloform pyrite and massive chalcopyrite-sphalerite-pyrite ores are dominant in the No. 5 ore body with minor fahlore, galena and baryte. The ores have high Se contents (up to 516 g/t) and As and small quantities of Cu, Au and Ag (Gavrillov *et al.*, 1984).

**Geological age and palaeoclimate of supergene alteration**

Previous work (Sigov, 1969, and others) showed that the formation of the oxidation zones in the Urals began in Triassic times under tropical, and

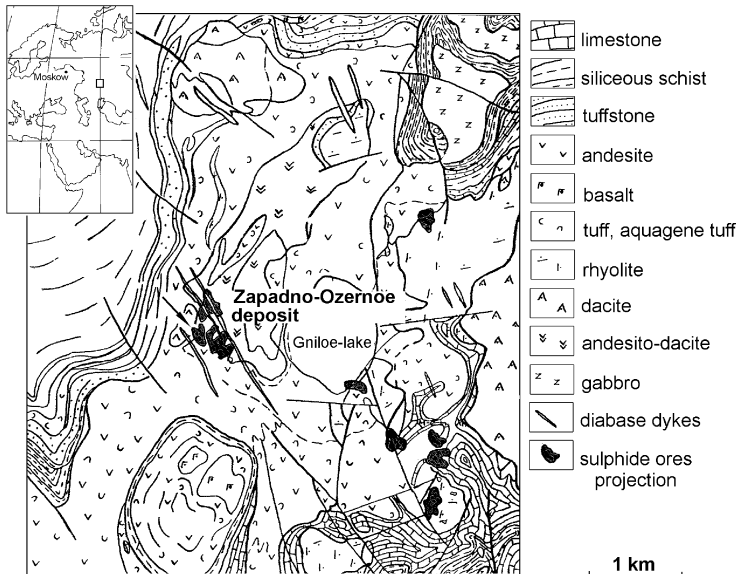


FIG. 1. Schematic geological map of the area of the Zapadno-Ozernoe deposit (after Gavrillov *et al.*, 1984). An arrow points to a projection to the surface of the No. 5 ore body.

later arid and semi-arid conditions in the South Urals whilst humid conditions prevailed in the Middle Urals. Currently the Urals represent over their length a variety of relief and a range of climatic regimes. Studies of preserved vegetation remains, spores and the mineralogical features of ancient weathering crusts in the location of the Zapadno-Ozernoe deposit showed that the climate changed from tropical in the Triassic, Jurassic and Cretaceous to arid, semi-arid and humid in the Cenozoic (Sigov, 1969).

A Palaeoclimatic and Palaeotopographic reconstruction shows that weathering was confined to the Palaeogene period in the Zapadno-Ozernoe area (Sigov, 1969). In detail, the evidence for weathering of the deposit under arid conditions is provided by the presence of specific jarosite and opal subzones in the supergene profile. During the subsequent change to a more humid climate, opal was replaced by halloysite, but its primary structure was preserved.

**The zonation of the supergene profile and the related distribution of Au**

The supergene oxidation zone of the sulphide ores is located within the regional surficial weathering zone of volcanic rocks of primarily dacitic and andesitic compositions. This oxidation zone has the shape of a bowl and consists of gossans, ferruginous and weathered rocks, whilst the bottom consists of residual pyrite sand, quartz with supergene sulphide sand and gossan. The filling of the bowl consists of mudstones, ochres and gossans. The morphology of the oxidation zone is dictated by the structure of the deposit. In plan view the oxidation zone extends along a subvertical rhyolite body (Fig. 2).

The supergene profile generally consists of the following subzones (from the base upwards) (Table 1): secondary Cu enrichment subzone (0); leaching subzone (residual pyrite sands), up to 10–20 m (1), covered by a quartz crust with tetrahedrite, up to 10 cm thick (2); ‘black’

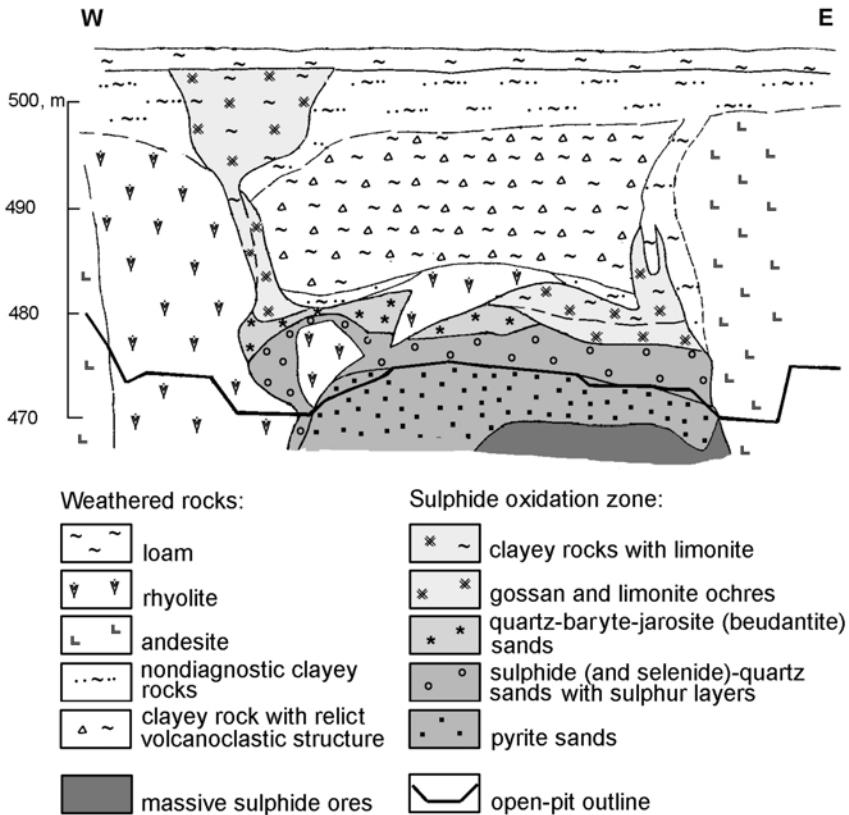
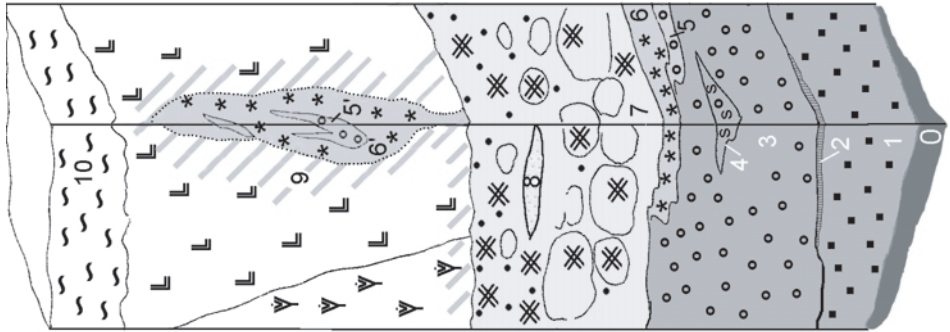


FIG. 2. Cross-section of the Zapadno-Ozernoe gossan (simplified after Kuptsov, 2000).

TABLE 1. Schematic supergene profile of the Zapadno-Ozernoe deposit.

OD, m	Description	Mineral composition
505	Soil Loams (10)	
500	Volcanic rocks weathering crust: andesites, quartz rhyolites, volcanoclastic rocks, and basalts.	Smectite, sericite, kaolinite, gypsum, goethite Feldspar (albite), pyroxene, hornblende, (relics), quartz, chlorite, opal, kaolinite, smectite, sericite, muscovite, epidote. Ore clasts: pyrite, chalcopyrite, covellite. In lower part: opal, malachite, azurite.
485	Distant infiltration zones: powder baryte sands (5), jarositized and aluminized volcanic rocks (6), gossans, bleached volcanic rocks with local jarosite veinlets (9).  'Iron cap': Gossans with massive, vuggy, powdery structure (7) with halojarositized opal lenses (8). Lower part contains red quartz-jarosite-limonite ochres, siliceous jarosites.	Distant infiltration zones: quartz, goethite, jarosite, beudantite, sodium alunite, sericite, kaolinite, baryte, pyrite.  Goethite, hematite, quartz, chalcedony, baryte, jarosite-beudantite series, alunite, native gold, relics of pyrite.
480	Quartz-sulphate subzone (6). Solid green altered volcanic rocks or clay, ochres with local jarosite veinlets.	Quartz, smectite, jarosite-beudantite-seginitite series, goethite, unidentified oxide-hydroxide of Fe and Sb, skorodite, cerussite, baryte, anglesite
480	Quartz-baryte sands (5)	Quartz, baryte, cerussite
480	Supergene sulphides subzone (3). The quartz-sulphide rocks with solid, banded, and powdery structure with native sulphur layers (4) and baryte-enriched sands locally, strong smell of sulphur gases.	$\alpha$ -sulphur, native selenium, native gold, galena, sphalerite, jordanite, tiemannite, dzharckenite-pyrite series, jodargirite-embolite, unnamed selenide-sulphide of silver and mercury, unnamed stibnide-arsenide-sulphide of lead, metacinnabar, quartz, pyrite, baryte, cerussite.
475	Residual pyrite sands (1). Mound-shaped sands covering a thin quartz crust (2). At depth, this subzone is in contact with secondary copper enrichment subzone (0) overlying primary sulphide ore	Pyrite, quartz, in crust – secondary tetrahedrite and silica oxide.  Secondary Cu-sulphides in the particularly oxidized ores: covellite, chalcocite. Primary ores: pyrite, chalcopyrite, sphalerite, tennantite



subzone: quartz + secondary sulphides sand (3) with native sulphur lenses (4); 'grey' subzone: quartz, quartz-baryte sand (5); 'green' subzone: beudantite-baryte-quartz ochres and sands with smectite and beudantite replacements of volcanic rocks (6); 'red' subzone: goethite, jarosite and alunite replacement of volcanic rocks, an "iron cap" (7); opal partially replaced by halloysite (8); and, bleached subzone (9).

The secondary Cu enrichment (0) was observed at the top of the primary ore body as an impurity of Cu sulphides, mainly chalcopyrite, in the primary ores during prospecting (Surin *et al.*, 1997). This zone is not exposed in the open pit.

Residual pyrite sands (1) form a mound-like body (Fig. 2). The concentration of Au varies from 4.4 to 100.8 g/t (average 15.1 g/t), Ag 110.3–448.6 g/t. The top of the body is enriched in Au in comparison with its sides.

The mound of pyrite sand is covered by a very thin discontinuous crust of fine to very fine chalcidony and quartz, with some tetrahedrite and other Sb-bearing sulphosalts (2). The Au concentration is ~14 g/t.

The dark (black, grey and cherry-brown) colour and strong sulphurous smell characterize the sulphide-quartz sand (3). The sand forms bodies of complex shapes, which in general follow those of the mounds of the residual pyrite sands. However, the upper boundaries of these bodies have apophyses penetrating into the host volcanic rocks. The dark quartz pyrite sands show various textures such as: spotted, streaky, banded and concentrically banded similar to Liesegang rings. The mineralogical composition of sulphide-quartz sand varies over a wide range. At the base, microcrystalline quartz with baryte is abundant. The secondary sulphides comprise from a few to a few tens of percent and are associated with colloform pyrite. Locally, galena, tetrahedrite, and Pb-bearing sulphosalts are the dominant sulphide phases. The Au concentration is high and varies from 3.5 to 161.8, with an average of 52.4 g/t. The Au is accompanied by high Ag concentrations from 245.6 to 1347.8 with average of 662.7 g/t (Kuptsov, 2000).

Within the quartz sulphide sands there are lenses and layers that contain native sulphur (4). They are up to 2.8 m thick and extend laterally up to 9 m. These have banded structures and are interbedded with the sulphide-quartz layers. Their Au concentration is from 1.1 to 4.4 with an average of 2.8 g/t.

Quartz and quartz-baryte sands (5) form sporadic lenses and discontinuous layers. Their contact with the underlying dark sulphide quartz sand is gradual. The quartz-baryte sands are grey or greenish-grey with a banded texture following that of the original volcanic rocks. Their Au concentration varies from 1.7 to 70 g/t with an average of 50 g/t in the southern part of the deposit and 30 g/t in the northern. The Au content is directly related to the baryte concentration. Within this unit, two recharge (distant infiltration) zones were identified, represented by quartz-baryte sand with 2 g/t Au (see Table 1).

Quartz-baryte-beudantite sands (6) usually lie above the residual quartz-baryte sands. They form lens-like and more complicated bodies with a thickness of 1 m or more. As a rule they have relict structures of volcanic rocks but locally they have a homogeneous sandy structure. They are mineralogically varied and are enriched in Au, especially those with high baryte content (up to >100 g/t). Minerals from the jarosite–beudantite series occur as replacements in the wall rocks.

Gossans occur as hard, ochre-coloured 'iron cap' or red, yellow or orange complex replacement bodies in the wall-rocks. There is a wide range of structures of gossans, that have the shape of a cup with hard walls. Locally the beudantite-jarosite ochre zone interfingers with the gossans. The Au concentration ranges from 0.9 to 22 g/t at the bottom of the cap with an average of 4–5 g/t.

### The mineralogical composition of the supergene subzones

The general mineralogical composition of each subzone was described above and is given in Table 1, and detailed features are described below. The most interesting secondary minerals are associated with the leached parts of the profile: quartz, quartz-baryte sands (5), secondary sulphides and quartz (3) and S-containing sands (4). Many rare minerals are present: secondary galena, tetrahedrite, jordanite, tiemannite, dzharkenite and native selenium, native gold and iodoargyrite. The formation of those minerals takes place mainly near the oxidation-reduction boundary. A list of secondary minerals is given in Table 2.

Detailed study of the mineralogical composition of the fine-grained oxidation products, the assemblage of supergene sulphides, and related phases, was carried out using the following methods: X-ray diffraction (XRD), qualitative microchemical tests, optical microscopy and

TABLE 2. Secondary minerals found in the supergene profile of Zapadno-Ozernoe deposit.

No.	Mineral	Formula	Subzone	First description in Zapadno-Ozernoe, including unpublished work and personal communication	Recent first discovery
	Sulphur native	S	4	Belogub <i>et al.</i> (2000b)	
	Selenium native	Se	3	Yakovleva (2001)	
	Gold native	Au	3, 5, 6	Surin <i>et al.</i> (1997)	
	Pyrite	FeS <sub>2</sub>	3, 4	Belogub <i>et al.</i> (2000b)	
	Dzharkenite	FeSe <sub>2</sub>	3, 4	Yakovleva (2001)	Yashunsky <i>et al.</i> (1995)
	Galena	PbS	3	Belogub <i>et al.</i> (2000b)	
	As-bearing galena	Pb(S,As)	3	Yakovleva (2001)	
	Tetrahedrite	Cu <sub>12</sub> (SbS <sub>3</sub> ) <sub>4</sub> S	2	Belogub <i>et al.</i> (2000b)	
	Tiemannite	HgSe	3, 4	Yakovleva (2001)	
	Naumannite	Ag <sub>2</sub> Se	3	Belogub (2001) (unpublished)	
	Metacinnabar	HgS	3	Yakovleva (2001)	
	Complex sulphosalts with Pb, Sb, S		3	Belogub <i>et al.</i> (2000b)	
	Complex sulphosalts with Hg, Ag, As, S		3	Yakovleva (2001)	
	Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	7	Surin (1997)	
	Beudantite	PbFe <sub>3</sub> (SO <sub>4</sub> )(AsO <sub>4</sub> )(OH) <sub>6</sub>	6	Belogub <i>et al.</i> (2000a)	
	Segnitite	PbFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> (H <sub>2</sub> O)	6	Belogub <i>et al.</i> (2000a)	Rattray <i>et al.</i> (1996)
	Na-alunite	NaAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	9	Belogub <i>et al.</i> (2000a)	
	Baryte	Ba(SO <sub>4</sub> )	3, 5, 6	Yakovleva (2001)	
	Anglesite	Pb(SO <sub>4</sub> )	5, 6	Belogub (2001) (unpublished)	
	Skorodite	Fe(AsO <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> O	6	Surin (1997)	
	Cerussite	Pb(CO <sub>3</sub> )	3, 4, 5, 6	Belogub <i>et al.</i> (2000a)	
	Tripuhite (?)	Fe <sup>2+</sup> Sb <sub>2</sub> <sup>3+</sup> O <sub>6</sub>	6	Belogub <i>et al.</i> (2000a)	
	Quartz	SiO <sub>2</sub>	2, 3, 4	Surin (1997)	
	Opal	SiO <sub>2</sub> <i>n</i> H <sub>2</sub> O	8	Belogub <i>et al.</i> (2000a)	
	Goethite	FeOOH	7, 8	Surin (1997)	
	Iodargyrite-embolite	Ag(Cl, Br, I)	4	Belogub (2001) (unpublished)	

scanning electron microscopy (SEM). The instruments used were: SEM REMMA-2M with WDX at the Institute of Mineralogy (Miass), GEOL JSM-5900LV, at the Natural History Museum (London), microprobe S-PSU, Philips SEM 501B with EDAX 9100 and WDX-2A, GEOL-JXA-8900RL at Freiberg TU-BAF.

The distribution of these minerals in the supergene zone of Zapadno-Ozernoe and their association with the major and minor minerals is given below.

#### Secondary Cu enrichment subzone (0)

Covellite and chalcocite are described in the detailed survey report of the Au-bearing gossans (Surin *et al.*, 1997) as part of the oxidized sulphide ores which were not stripped by quarrying. Covellite is an alteration product of chalcopyrite. Chalcocite develops after sphalerite

and is normally associated with fine-grained disseminated chalcopyrite.

#### Pyrite sand (I)

Pyrite sand contains only residual pyrite with some quartz and baryte. The hard and dense silica crust (2) consists of very fine residual quartz and secondary silica phases, cemented with secondary tetrahedrite and some pyrite both as relics and secondary phases. Tetrahedrite was determined by XRD, SEM and optical microscopy and is present as sparse disseminations between secondary quartz; its grain size is of the order of several  $\mu\text{m}$ . Locally Sb-sulphosalts with amorphous silica are overgrown by silica with grains of native selenium, dzharkenite, tiemannite, naumannite and Se-bearing pyrite. On the surface these aggregates also contain framboidal pyrite (Fig. 3).

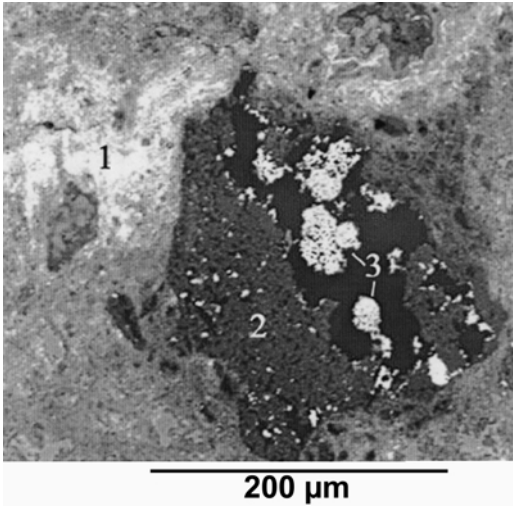


FIG. 3. Distribution of minerals in the silica crust (subzone No. 2). (1) tetrahedrite + silica, (2) silica with grains of selenides (dzharkenite, naumannite, tiemannite), (3) pyrite framboids.

**Secondary sulphides zone (3) with native sulphur lens (4)**

Native sulphur forms colloform aggregates of microspheres 5-10 µm across (Fig. 4a). Native sulphur is a common mineral in the supergene zones of outcropping massive sulphide deposits in the South Urals such as Gai, Blyava and Sibai.

Native selenium was detected by microprobe analysis of the heavy fraction of a sample from a lens containing native sulphur. Crystals of native selenium have rhomb-like shapes within Se-bearing pyrite aggregates (Fig. 4b). Native selenium was first described in the layers containing native sulphur in the supergene profile of the Kul-Yurt-Tau deposit (South Urals) (Paley, 1957).

Native gold occurs as spherical grains 5-7 µm across associated with pyrite. Its composition, as determined by microprobe analysis, is  $Au_{94.9}Ag_{5.1}$ . Supergene native gold and electrum were described from the layers containing native sulphur at the Gai deposit (Sergeev *et al.*, 1994).

Pyrite is the most widespread secondary sulphide in the deposit. In the sulphide-quartz sands it has colloform textures with rare occurrences of relic corroded grains. Microprobe

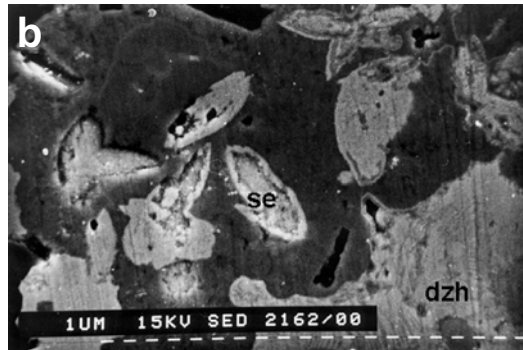
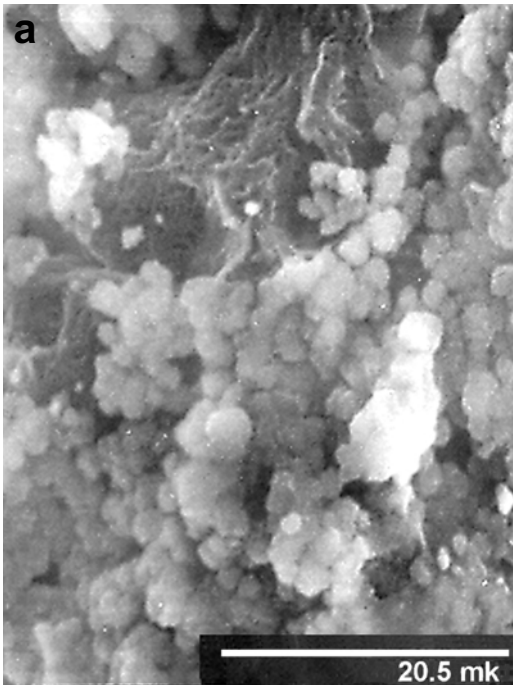


FIG. 4. SEM images of native sulphur (a) and dzharkenite and selenium (b) from the heavy fraction of native sulphur lenses. Each white line in the dashed-line scale bar of  $b = 1 \mu\text{m}$ . This also applies to some later figures.

analyses results have been used to calculate the stoichiometric formulae for the pyrite–Se-pyrite–dzharkenite series (Yakovleva *et al.*, 2001; 2003).

Numerous attempts at identification of sulphide phases in the black sulphide sands resulted in the identification of pyrite, non-stoichiometric sulphides, sulphides having a composition close to that of pyrrhotite and containing Ag, As, Se, occasionally Pb and Sb. The SEM study using EDAX analysis shows the widespread occurrence of sulphides with trace elements such as Ag, Se and Sb. These minerals form thin rims around the colloform pyrite. A microprobe analysis of one of these rims gave the formula  $\text{Fe}_{0.98}\text{Ag}_{0.02}(\text{S}_{0.86}\text{Se}_{0.07}\text{Sb}_{0.05}\text{As}_{0.02})_{\Sigma 1.00}$ . X-ray diffraction patterns show a predominance of pyrite with additional pyrrhotite, greigite or unidentified minerals.

Other As, Sb and Pb-bearing minerals show XRD patterns close to those of sulphosalts (tennantite or boulangerite group). They occur in the dark-grey predominantly siliceous rocks with relics of a dacite structure.

Galena was detected by XRD in the sooty black quartz-bearing sands having a strong sulphurous smell (Fig. 5). Microprobe EDAX analysis indicated enrichment in As. Galena forms cements in quartz microbreccia and as skeletal crystals in cavities (Fig. 6a,b). Also, prismatic-oblong crys-

tals growing on the colloform pyrite were detected. Their composition is indicative of the formula of jordanite ( $\text{PbS}_x\text{As}_y$ ) with a varying ratio between S and As. Supergene galena with an extremely light S isotope composition ( $\delta^{34}\text{S} = -40\text{‰}$  VCDT) was described before only in the supergene zone of the Broken-Hill deposit (Lawrence and Rafter, 1962) and SEDEX-type deposit (Yakhontova and Grudev, 1987). Sphalerite was identified under the optical microscope as very rare zoned spheres and angular relics. Metacinnabar was identified under the optical microscope and by microprobe. It has a pure composition and occurs as skeletal crystals and as rims around angular relics of sphalerite (Fig. 7a,b).

Dzharkenite was identified by SEM in heavy mineral concentrates of sulphide-quartz sands and confirmed by its optical emission spectra and XRD pattern (Yakovleva *et al.*, 2001; 2003). It occurs in irregular, round and oblong shapes with pyrite. Pyrite also forms coatings on the pyrite-dzharkenite spherulites of  $<5\ \mu\text{m}$  across (Fig. 8). The microprobe analyses give a maximum  $\text{Fe}(\text{Se}_{0.8}\text{S}_{0.2})_{\Sigma 2.0}$  formula. No previous report on supergene dzharkenite is known to the authors.

Tiemannite ( $\text{HgSe}$ ) was identified intergrowing with pyrite and dzharkenite in the heavy mineral concentrate of the sulphide-quartz sand. The grain

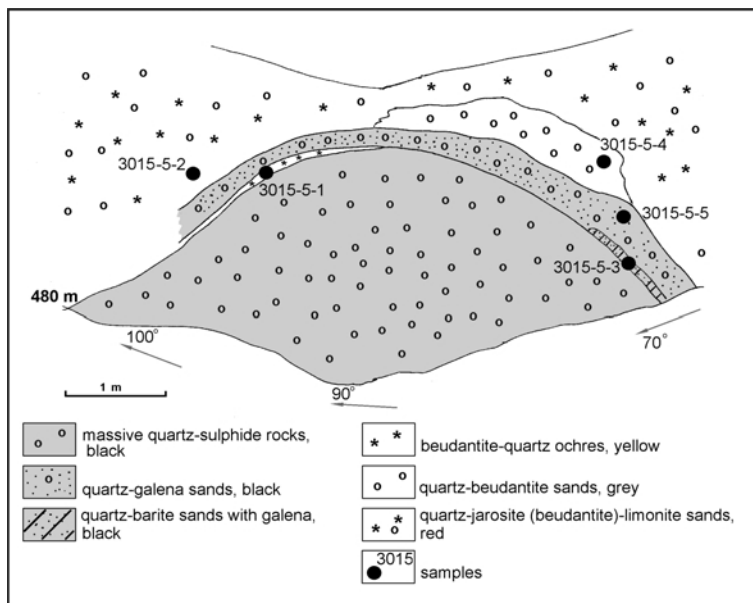


FIG. 5. Cross-section showing the contact between sooty-black quartz-sulphide sands and sands with quartz-jarosite-limonite.



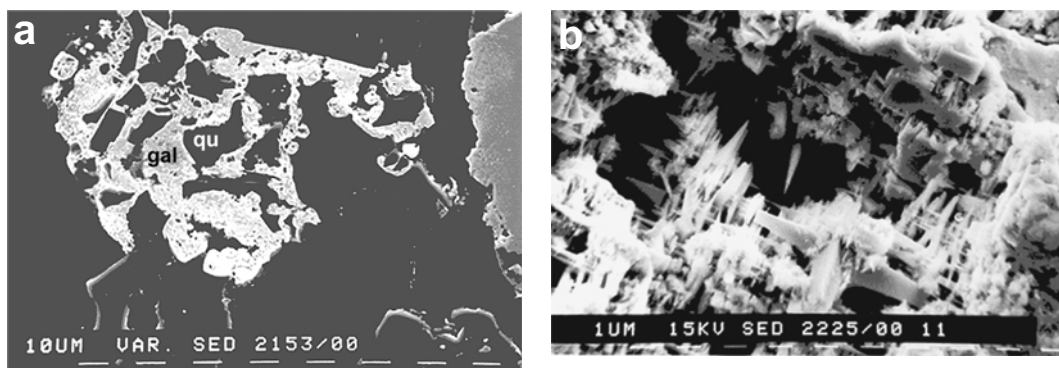


FIG. 6. SEM images of secondary galena as cement for a quartz breccia (a) and as skeletal crystals on the walls of cavities in quartz grains (b).

size is  $<0.5 \mu\text{m}$ . Microprobe analysis gave a formula for the sum of the cations of  $(\text{Hg}_{0.9}\text{Fe}_{0.1})\text{Se}$ . This mineral was first described by Sergeev *et al.* (1994) from S sands from the Gai massive sulphide deposit.

Quartz and baryte were found both as relics from primary ores and as newly-formed crystals. In the first case these minerals were covered by pits formed by leaching of sulphides and rarely contain the skeletal forms typical of secondary sulphides (galena, metacinnabar) (see Figs 6, 7). Locally, Se-bearing pyrite, galena or tetrahedrite cement the quartz breccia. Secondary quartz and baryte form crystals with well-developed morphologies and habits, which differ from primary quartz and baryte (Fig. 9).

#### Light grey quartz and quartz-baryte sands (5)

These are evidence of leaching of sulphides and precipitation of quartz, baryte and cerussite,

which have low solubility. Quartz is mainly residual. Baryte occurs in two habits: (1) platy crystals with corroded faces. Some of the corrosion pits seem to be the result of leaching of sulphides, but some, in our view, represent dissolution of baryte proven by crystallographic control. Only the faces of rhombic prisms are dissolved while the pinacoid faces are intact. (2) Clear crystals with prismatic habit and smooth faces. The source of Ba may be dissolved rock-forming feldspars from the wall rock and also primary baryte. Cerussite shows prismatic crystals up to 1.5 mm across.

#### Green beudantite-bearing sands (6)

The green beudantite-bearing sands which lie above the baryte-quartz sands usually consist of quartz and baryte together with cerussite and minerals belonging to the jarosite–beudantite–segnite series. The identification of these

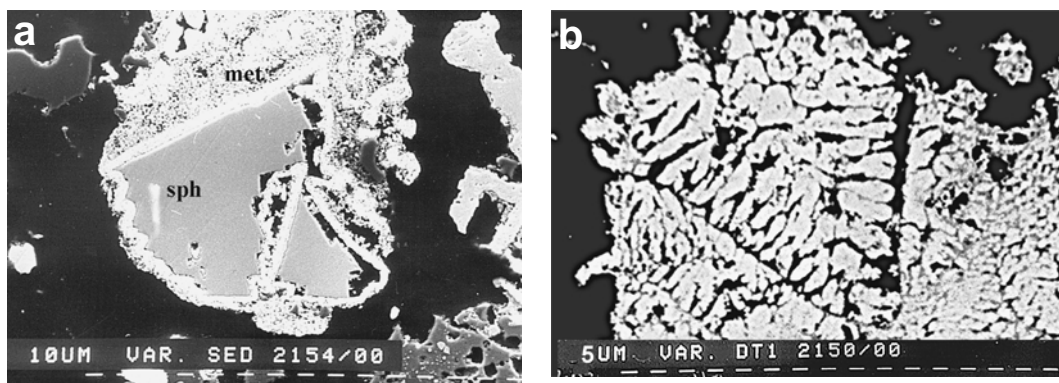


FIG. 7. SEM images of metacinnabar (met) as rims around relics of sphalerite (sph) (a), and as skeletal crystals (b).

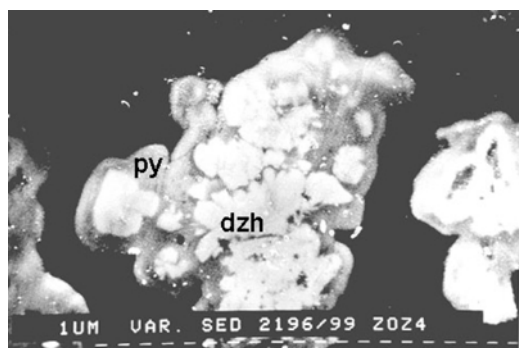


FIG. 8. SEM images of dzharkenite-pyrite aggregates.

minerals was first carried out by XRD and confirmed by microprobe (Belogub *et al.*, 2000).

The composition of beudantite nearest to the stoichiometric formula was obtained from a sample taken from a lens above the top of the residual pyrite mound. Its formula, calculated as

an average of 30 points is  $\text{Pb}_{1.04}(\text{Fe}_{3.06}\text{Al}_{0.04}\text{Cu}_{0.02})_{\Sigma 3.12}(\text{As}_{0.67}\text{S}_{0.19}\text{P}_{0.05})_{\Sigma 0.91}\text{O}_4)_2(\text{OH})_6$ . The ratio between S and As varies from 1:1 to 1:4. This is the basis for distinguishing segnitite as a mineral species in the deposit. This end-member was first discovered in the supergene zone of the Broken-Hill deposit (Rattray *et al.*, 1994). In Zapadno-Ozernoe, these minerals have locally high contents of Sb (up to 0.12 wt.%) and Se (up to 1.43 wt.%) (Fig. 10a). Two other samples from a similar mineral association and geological position, but from a different part of the ore body, are characterized by non-stoichiometric formulae with deficits in the alkaline site:  $(\text{Pb}_{0.43}\text{K}_{0.34}\text{Ba}_{0.10}\text{Ag}_{0.01})_{\Sigma 0.89}(\text{Fe}_{2.78}\text{Sb}_{0.09})_{\Sigma 2.88}((\text{S}_{0.86}\text{As}_{0.24})_{\Sigma 1.10}\text{O}_4)_2(\text{OH})_6$  (average for 8 points) (a); and  $(\text{Pb}_{0.20}\text{K}_{0.40})_{\Sigma 0.60}(\text{Fe}_{2.95}\text{Cu}_{0.19}\text{Al}_{0.19})_{\Sigma 3.33}(\text{S}_{1.02}\text{As}_{0.01})_{\Sigma 1.03}\text{O}_4)_2(\text{OH})_6$  (average for 7 points) (b). The statistical calculations show a positive correlation between Pb and As and negative correlation between S and As, Pb

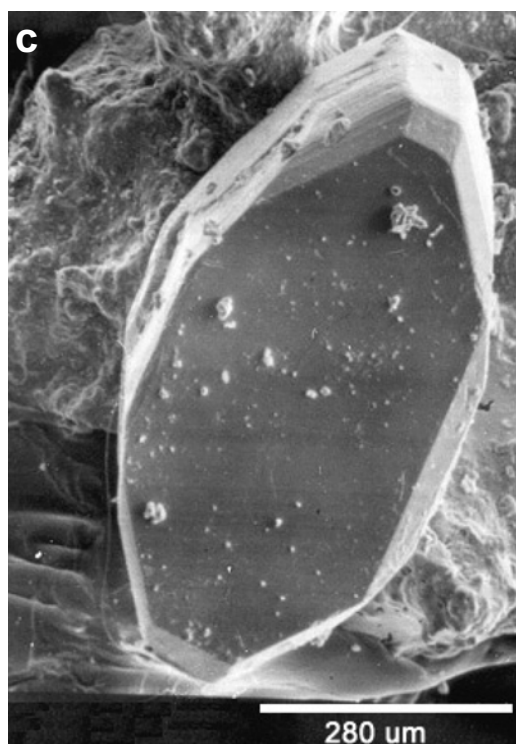
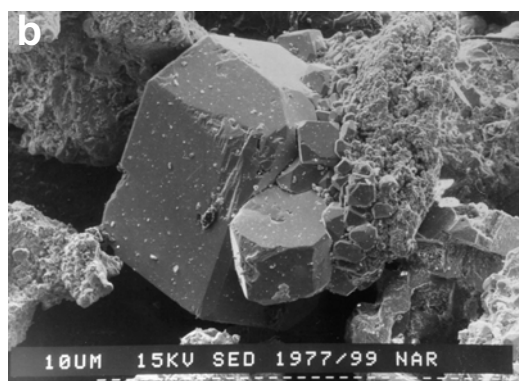
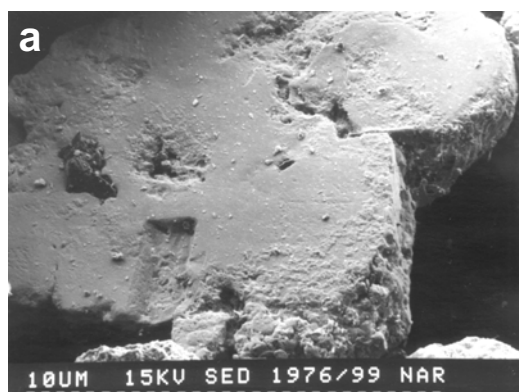


FIG. 9. SEM images of baryte: eroded residual crystals (a); secondary prismatic crystals (b); and from pyrite-quartz sands and prismatic crystals from vugs in gossans (c).

and Ba, Pb and K. These provide the basis for considering a continuous series from jarosite to beudantite and segnitite. It is noteworthy that this group of minerals has a high Sb content. Jarosite–beudantite (Fig. 10a) was associated with unidentified oxides or hydroxides of Sb and Fe similar to tripuhyite,  $\text{Fe}^{2+}\text{Sb}_2^+\text{O}_6$ . Also, the minerals scorodite and anglesite were found in this association (Fig. 10b). Yellow jarosite was detected in vugs within gossans. It occurs as very small platy zoned crystals in which the Pb- and As-bearing zones alternate with clearer jarosite (Fig. 10c). The size of the zones is too small for quantitative analysis.

Practically all sulphate-bearing ochres from the Zapadno-Ozernoe deposit are enriched with Pb and As, which take part in the composition of beudantite and jarosite-like minerals. This feature is more characteristic of the supergene zone of polymetallic ores than that of massive sulphides.

*Gossans (7)*

Gossans have goethite and hydrogoethite aggregations as the main components. Several facies can be identified in the gossans: massive, collo-morphic, breccia-like and ochre-like (limonite). There are some relics of quartz and baryte veins in the lower part of the gossans but at Zapadno-Ozernoe we did not observe gossans with relics of primary ore structures. Baryte crystals with prismatic habit and pure composition were found on the surfaces of small vugs in the gossans (Fig. 9c). During prospecting work, thin films of Au were identified on gossans.

Sulphate-bearing assemblages, in particular Pb-bearing jarosite and alunite, together with smectite and kaolinite occur as replacement of weathered pyroxenes and amphiboles. Opal, which is typical of weathering under arid conditions, was identified in the lower part of the gossan profile. However, its replacement by

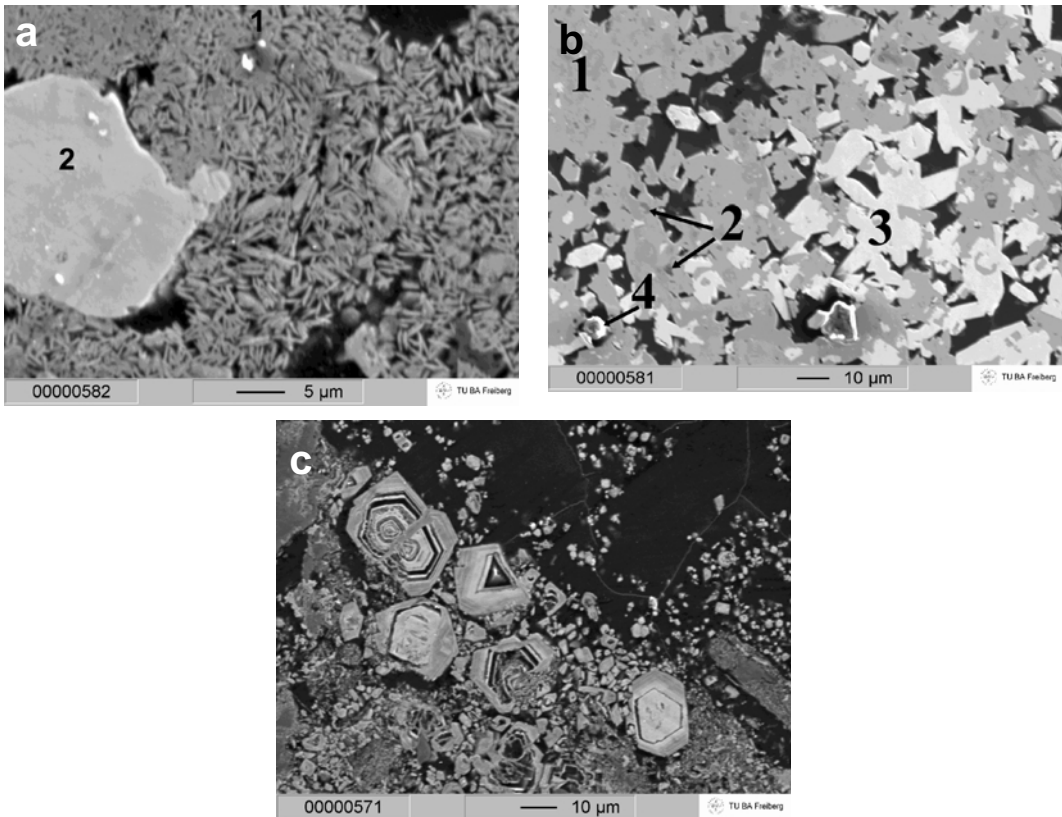


FIG. 10. (a) Sb-enriched beudantite plate-like crystals (1) with relics of baryte (2). (b) Beudantite–segnitite (1) with scorodite (2), anglesite (3) and baryte (4). (c) Zoned crystals of jarosite–beudantite (1) from segregations in gossans (quartz-goethite mixtures), anglesite (3) and baryte (4).

halloysite is evidence of a subsequent change to a more humid climate during the formation of the supergene profile.

### S isotope composition

Sulphur isotope analyses were carried out at the NERC Isotope Geoscience laboratory. Sample preparation followed the method of Robinson and Kusakabe (1975) for sulphides and of Coleman and Moore (1978) for sulphates. Analyses were carried out in a VG ISOGAS SIRA 10 mass spectrometer. The results are reported relative to VCDT with an overall analytical reproducibility of  $\pm 0.1\%$ . The IAEA-S-1 reference material gave  $-0.3\%$  and NBS 122 gave  $+0.15\%$ .

Primary sulphides and sulphates from the Zapadno-Ozernoe deposit were not investigated systematically. However, the  $\delta^{34}\text{S}$  value for sulphide ores of similar deposits in the Verchneural'sk ore district, also near Uchaly town, is  $+2.0\%$ , for the Uzel'ga deposit,  $+3.2\%$ , for the Ozernoe deposit,  $+3.2\%$ , for the Molodejnoe and the Talgan deposits,  $+2.5\%$  (Procin *et al.*, 1992), and between  $-2.5$  and  $2.9\%$  for pyrite in Yaman Kasy (Herrington *et al.*, 1998). Pyrite from a xenolith of sulphide ores at the Zapadno-Ozernoe deposit gave  $\delta^{34}\text{S}$  of  $+0.8\%$  (Table 3), while pyrite sands from the leaching zone show  $\delta^{34}\text{S}$  of  $+2.8\%$ . A coarse baryte from a vein is probably primary with  $\delta^{34}\text{S}$  value of  $+18.4\%$ , normal for massive sulphide deposits in the Urals (Procin *et al.*, 1992). Baryte sands have lower ratios ( $\delta^{34}\text{S} = +13.1\%$ ).

The upper part of the leaching zone is very interesting due to the presence of supergene

sulphides as discussed above. Sulphur in sulphides here is very light ( $\delta^{34}\text{S}$  of  $-15.1$  to  $-17.2\%$ , see Table 3). Native sulphur from strata within the 'black zone' has larger values ( $\delta^{34}\text{S} = +3.5\%$ ) than the pyrite sand and probably even from the primary ores. At the Gai deposit, the S isotope composition of elemental S, as determined by Zaykov and Lein (1998), is smaller ( $\delta^{34}\text{S} = -5.5\%$ ).

Beudantite from the vugs in the gossans with  $\delta^{34}\text{S}$  of  $0.8\%$  seems to inherit the composition of primary sulphides. The sample of tetrahedrite ( $-1.6\%$ ) reflects the mixture of S from primary sulphides and secondary reprecipitated S. The compact quartz-pyrite sand has  $\delta^{34}\text{S}$  values of  $-8.1\%$  and  $-15\%$  reflecting varying proportions of primary and secondary sulphides which have different morphological features as observed in the SEM.

### Discussion: the mineralogical and isotopic features of the alteration zones and the environmental factors controlling their formation

#### Geological, mineralogical and isotopic features

The Zapadno-Ozernoe deposit presents geological and mineralogical features that are of great interest for the study of supergene alteration. These are dictated by the geology of the ore body, the host rocks, and the climatic conditions and geohydrology during the formation of this zone. The main features are summarized below: (a) The Zapadno-Ozernoe deposit is blind and there were no visible outcrops of ores or ore-related features. Primary ores were located not far from the present

TABLE 3. S isotope composition of secondary minerals from the Zapadno-Ozernoe deposit.

No	Specimen number	Occurrence in subzone*	Description	$\delta^{34}\text{S}\%$
1	3018-3	1	Pyrite	+2.8
2	3018-3-1	2	Qz + Tetrahedrite (?)	-1.6
3	3015-3	3	Qz + galena (supergene) + baryte	-12.2
4	3015-5-5	3	Qz + galena (supergene)	-17.2
5	3015-1	3	Compact qz-pyrite sand	-8.1
6	18+17/379 3	3	Compact qz-pyrite sand	-15.1
7	3015-10	4	Native sulphur	+3.5
8	3015-5-2	7	Qz + beudantite	+0.8
9	3016-6	Xenolith of sulphide ores in (3)	Pyrite	+0.8
10	3015-9	Baryte veinlet in (3)	Baryte	+18.4
11	9038-38-2	5	Baryte	+13.1

\* numbers of subzones correspond to those in the text

land surface. The composition of the primary ores is similar to many of the massive sulphides of the Urals, which belong to the 'Urals' type. There is a large Se concentration in the ores, mainly as impurity in pyrite. (b) A 'black' subzone rich in secondary sulphides (3) is developed between the typical leaching subzones: residual pyrite sands and quartz-baryte sands. (c) These secondary sulphides and selenides include many mineral species which are in part typical of oxidation zones of SEDEX (galena, sphalerite) or epithermal style (selenides, metacinnabar, complex sulphosalts) deposits. (d) The S isotope composition of the secondary sulphides is very light, and that of native sulphur is intermediate between the light sulphides and the heavy sulphates. (e) The jarosite-beudantite subzone (6) is characterized by Pb- and As-bearing minerals and contains Sb oxyhydroxides uncommon for massive sulphide-related supergene zones. (e) The main Au concentrations occur with the secondary sulphides and baryte-bearing sands from the leaching subzone.

#### *Environmental and biological controls on the mineralogical and isotopic features*

The mineralogical composition of the supergene profile reflects largely the composition of primary ores, the gradients of Eh and pH, the activity of elements and the timing of the formation of this profile in relation to the geological and environmental history of the region. The main controlling factor on the mineralogical processes seems to be the position and movement of the redox boundary which corresponds to the groundwater table.

The sequence of subzones in the developed supergene profiles of outcropping deposits such as at Sibay and Blyava can be compared with that of Zapadno-Ozernoe. At Sibay and Blyava only common secondary sulphides such as covellite, chalcocite and pyrite were detected. However, secondary sulphides of Pb or Zn which occur at Zapadno-Ozernoe had not previously been detected in any supergene profile of massive sulphide ores in the Urals. Usually, Zn is transported in solution and Pb is precipitated as sulphate or carbonate not far from the primary ores. Also, the S isotope composition of the supergene minerals at Zapadno-Ozernoe is different from those of Gai studied previously by Zaykov and Lein (1998).

Three mineral associations were identified in the supergene zone that result from: (1) the direct

alteration of the primary ores; (2) the redeposition of ore-derived elements in the altered wall rock and ores; and (3) the interaction of rock-forming minerals with solutions within the supergene zone.

The first association is related to the primary Cu-sulphides, which are transformed mainly into covellite and chalcocite. The second association reflects the chemical activity of wall rocks and ores, the hydrogeological regime of the deposit and microbiological activity. The most important feature of this association is the assemblage of secondary sulphides (sphalerite, galena, jordanite, metacinnabar, tetrahedrite, Fe-selenides etc.), some of which have very low  $\delta^{34}\text{S}$  values, Cu- and Pb-bearing sulphates of the alunite group (beudantite, segnitite), native gold, selenium and sulphur. The third group includes Fe oxides and hydroxides, carbonates, Pb-bearing Al sulphates of the alunite group and jarosite.

The accumulation of non-ferrous metals such as Pb, Hg, Se, etc. in sulphide or other reduced forms seems to reflect local reducing conditions confined to blind ore bodies which are not exposed to the pervasive supergene oxidation. The redeposition of sulphides due to microbial activity takes place under stagnant anaerobic conditions. The subsequent increase in oxygen activity leads to the oxidation of pyrite and the generation of sulphuric acid and ferrous iron sulphate. These changes result in the transformation of the geochemical profile which may be preserved in the subsurface.

The S isotope composition of minerals in the supergene zone of VMS deposits sometimes shows values indicative of bacterial sulphate reduction (Yakhontova and Grudev, 1987). This was also considered in the discussion of porphyry-copper deposits by Sillitoe *et al.* (1996). Sulphides are a necessary substrate for sulphide-oxidizing bacteria. These in turn produce a nutrient medium for sulphide-reduction bacteria. Oxidation of sulphides, biologically mediated or not, is not associated with a significant S isotope fractionation (Mehtieva, 1964; Vinogradov and Stepanov, 1964). On the other hand sulphate reduction in nature at low temperatures is possible only as a biologically mediated process. Sulphate-reducing bacteria produce  $\text{H}_2\text{S}$  with S having  $\delta^{34}\text{S}$  values lower by ~40‰ than the source sulphate (Kaplan and Rittenberg, 1964). For geological systems, two cases should be considered: (1) reduction in a system open to sulphate. There is a constant supply of sulphate of the same  $\delta^{34}\text{S}$  and the resulting  $\text{H}_2\text{S}$  maintains the

low  $\delta^{34}\text{S}$  values. This  $\text{H}_2\text{S}$  may form secondary sulphides such as the secondary galena reported from Broken Hill (Lawrence and Rafter, 1962). As a result there is a contrast between isotopically light secondary sulphides and heavy sulphate. (2) Reduction in a system closed to sulphate. With the progression of the sulphate reduction process, the residual sulphate becomes heavier and so the  $\text{H}_2\text{S}$  produced becomes heavier and the secondary sulphides also. The results from Zapadno-Ozernoe demonstrate that this is not the case and that sulphide reduction occurred under essentially open conditions. Elemental S can be produced by reaction between reduced and oxidized S (Dinur *et al.*, 1980) and, therefore, has in this case an intermediate isotopic composition, or by oxidation of sulphides from which the elemental S inherits its isotopic composition.

Baryte can also show low  $\delta^{34}\text{S}$  values. This is likely to occur in a secondary sulphate. Baryte is a very stable mineral under supergene conditions but its solution and reprecipitation in redox fronts was demonstrated by Honor (2000). As shown above, there are residual and redeposited baryte in the supergene profile of Zapadno-Ozernoe deposit. In the first case baryte sands occur in the lower part of the supergene profile and inherit the S isotope composition from the primary baryte. In the second case baryte can form in different positions together with supergene minerals. In the latter case the S isotope composition can be determined by the composition of the surrounding oxidizing sulphide phases or the soluble sulphates.

Native sulphur in the supergene profile can form by oxidation of sulphide minerals and also by reaction of residual sulphate from microbiological sulphate-reduction with  $\text{H}_2\text{S}$ . When sulphur is formed by sulphide oxidation it inherits the isotope composition of sulphide. This is the interpretation of Zaykov and Lein (1998) for the Gai deposit where S layers overlap pyrite sands, and the  $\delta^{34}\text{S}$  value of native S is  $-5.5\%$  (Zaykov and Lein, 1998). The situation in the Zapadno-Ozernoe deposit is different, here S lenses occur inside the 'black' subzone. Sulphur is very heavy ( $+3.5\%$ ) in comparison with sulphide S of the 'black' subzone (down to  $-17.2\%$ ) and is probably the product of reaction between the dissolved sulphate and the bacterially produced  $\text{H}_2\text{S}$ . The formation of secondary sulphides, in particular pyrite, pyrrhotite and galena, requires specific reducing conditions. These could be

established when the water table rose and anaerobic conditions led to bacterial sulphate reduction.

We can see from the example of Zapadno-Ozernoe that the S isotope compositions of the secondary phases differ considerably from those of the primary ones. This fact reflects the dynamic nature of the supergene system as a dynamic one, controlled by low-temperature biological and non-biological processes under conditions of closed or open systems. Detailed investigations are needed to characterize precisely the prevailing conditions during the formation of the individual S-containing phases. However, the results presented here clearly indicate the diversity of the environmental conditions and the related processes that control the formation of the S-containing phases in various subzones of the supergene profile.

## Conclusions

The mineralogical and S isotope composition of the supergene profile of the Zapadno-Ozernoe massive sulphide Cu deposit differs from those of other VMS deposits described previously. They result from specific petrologic and tectonic features related to the location of the ore body and in relation to the surficial environment and the hydrological regime. The critical environmental factor is the formation of a body of stagnant interstitial water. This favoured bacterial activity and limited the migration of soluble Se, As, Hg, Pb and other elements from primary ores and resulted in the precipitation of sulphides, sulphosalts and selenides at the redox boundary. Also, Pb and As are concentrated in the mixing zone and formed minerals of the beudantite–jarosite series. The enrichment of Au in the supergene profile took place in both the reducing and oxidizing zones. The highest Au concentrations are found with the secondary sulphides within the dark quartz-baryte sands. This facies, to our knowledge, has not previously been described from any VMS deposit.

## Acknowledgements

We thank the Bashkirian Gold-Exploiting Company for access to the open pit and some geological documentation. We gratefully acknowledge Igor Kuptsov for his co-operation during fieldwork, and the microprobe analysts Alexander Nesterov (Saint-Petersburg State

University), Klaus Bekker (TU-BAF, Freiberg), Terry Greenwood (Natural History Museum, London) and Vasily Kotlyarov. These studies were partly supported by the Program "Universities of Russia" and by the EU Framework V Contract ICA2-CT-2000-1011 MinUrals.

## References

- Belogub, E., Novoselov, K. and Bekker, K. (2000a) Lead minerals in the supergene zones of the blind ore bodies Alexandrinskoe and Zapadno-Ozernoe deposit. *Ore Formation in Ancient and Modern Oceans—2000*. Institute of Mineralogy UBRAS, Miass, Russia (in Russian).
- Belogub, E., Novoselov, K., Yakovleva, B. and Spiro, B. (2000b) The supergene sulphides from the Zapadno-Ozernoe copper massive sulphide deposit. *Transactions of the Institute of Mineralogy Miass, Russia*, **10**, 27–34 (in Russian).
- Coleman, M.L. and Moore, M.P. (1978) Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Analytical Chemistry*, **50**, 1594–1595.
- Dinur, D., Spiro, B. and Aizenshtat, Z. (1980) The distribution and isotopic composition of sulfur in organic rich sedimentary rocks. *Chemical Geology*, **31**, 37–51.
- Emmons, W.H. (1917) The enrichment of ore deposits. *Bulletin of the US Geological Survey*, **625**, 530 pp.
- Gavrilov, V., Scuratov, V. and Ismagilov, M. (1984) The structure and conditions of localization of Zapadno-Ozernoe sulphide deposit. *Doklady Akademii Nauk SSSR, Geology*, **1**, 161–164 (in Russian).
- Hanor, J. (2000) Barite-celestine geochemistry and environments of formation. Pp. 193–276 in: *Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, **40**. Mineralogical Society of America, Washington, D.C.
- Herrington, R.J., Maslenikov, V.V., Spiro, B., Zaykov, V.V. and Little, C.T.S. (1998) Ancient vent chimney structures in the Silurian massive sulphides of the Urals. Pp. 241–257 in: *Modern Ocean Floor Processes and the Geological Record* (R.A. Mills and K. Harrison, editors). Special Publication, **148**. Geological Society, London.
- Kaplan, I.R. and Rittenberg, S.C. (1964) Microbiological fractionation of sulfur isotopes. *Journal of General Microbiology*, **34**, 195–212.
- Kuptsov, I. (2000) Geological structure of ore body V Zapadno-Ozernoe deposit oxidation zone and its genesis. *Geological Survey and Mining in Baschkortostan*. Ufa, "Tau", Russia (in Russian).
- Lawrence, L.J. and Rafter, T.A. (1962) Sulfur isotope distribution in sulfides and sulfates from Broken Hill South, New South Wales. *Economic Geology*, **57**, 217–225.
- Mehtieva, V. (1964) Sulphur isotope fractionation during its bacterial oxidation by *Thiobacillus denitrificans* culture. *Geochimia*, **1**, 61–64 (in Russian).
- Paley, I. (1957) Native selenium concentration in the oxidation zone in a sulphide deposit. *Geochimia*, **7**, 640–641 (in Russian).
- Procin, V., Seravkin, I., Buslaev, F. et al. (1992) *Urals Copper Sulphide Deposits: Genesis*. Ekaterinbourgh, UB RAS, Russia (in Russian).
- Rattray, K.J., Taylor, M.R. and Bevan, D.J. (1996) Compositional segregation and solid solution in lead-dominant alunite-type minerals from Broken Hill, N.S.W. *Mineralogical Magazine*, **60**, 779–785.
- Robinson, B.W. and Kusakabe, M. (1975) Quantitative preparation for sulfur dioxide for 34S/32S from sulfides by combustion with cuprous oxide. *Analytical Chemistry*, **47**, 1179–1181.
- Sergeev, N., Zaykov, V., Laputina, I. and Trofimov, O. (1994) Gold and silver in the supergene zone of Gayskoe sulphide deposit (S. Urals). *Geology of Ore Deposits*, **36**, 169–183 (in Russian).
- Sigov, A. (1969) *Mezozoic and Cenozoic Ore Formation in the Urals*. Nedra, Moscow (in Russian).
- Sillitoe, R.H., Hannington, M.D. and Thompson, J.F.H. (1998) Bacteria as mediators of copper sulfide enrichment during weathering. *Science*, **272**, 1153–1155.
- Smirnov, S. (1955) *The Supergene Zone of Sulphide Deposits*. Academy of Science of the USSR, Leningrad (in Russian).
- Surin, S., Krylatov, V. and Kuchkildin, K. (1997) *Report about prospecting in Zapadno-Ozernoe copper-sulphide gossan deposits, Uchaly*. Prospecting report (in Russian).
- Vinogradov, V. and Stepanov, V. (1964) About sulphur isotope fractionation in the oxidation zone. *Geochimia*, **1**, 65–69 (in Russian).
- Yakhontova, L. and Grudev, A. (1987) *The Mineralogy of Oxidised Ores*. Nedra, Moscow (in Russian).
- Yakovleva, V.A. (2001) *Secondary Sulphides and their Analogues from the Supergene Zone of Zapadno-Ozernoe Deposit*. Magister dissertation, Saint-Petersburg State University (in Russian).
- Yakovleva, V.A., Nesterov, A.R. and Belogub, E.V. (2001) Supergene sulphide and iron sulphoselenides of West-Ozernoe deposit (the South Urals): a new isomorphic series pyrite-dzharkenite. *The Metallogeny of Ancient and Modern Oceans—2001*. Institute of Mineralogy, UB RAS, Miass, Russia (in Russian).
- Yakovleva, V.A., Belogub, E.V. and Novoselov, K.A. (2003) Supergene iron sulphoselenides from the

- Zapadno-Ozernoe copper-zinc massive sulphide deposit, South Urals, Russia: A new solid solution series between pyrite  $\text{FeS}_2$  and dzharkenite  $\text{FeSe}_2$ . *Mineralogical Magazine*, **67**, 355–361.
- Yashunsky, Yu.V., Ryabeva, E.G., Abramov, M.V. and Rasulova, S.D. (1995) Dzharkenite,  $\text{FeS}_2$  – a new mineral. *Proceedings of the Russian Mineralogical Society*, **1**, 85–90 (in Russian).
- Zaykov, V. and Leyn, A. (1998) Sulphur isotope composition in minerals from Gayskoe copper sulphide deposit supergene zone (S. Urals). *Transactions of the Institute of Mineralogy, Miass, Russia*, **8**, 177–184 (in Russian).

[Manuscript received 20 January 2002:  
revised 13 March 2003]