POLSKIE TOWARZYSTWO MINERALOGICZNE – PRACE SPECJALNE
MINERALOGICAL SOCIETY OF POLAND – SPECIAL PAPERS
Zeszyt 24, 2004; Volume 24, 2004

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IRON ARSENATES FROM THE STARA GÓRA DEPOSIT AT RADZIMOWICE IN KACZAWSKIE MOUNTAINS, POLAND − A PRELIMINARY REPORT

Abstract: The phenomena of very intensive oxidation processes of ore minerals of iron and arsenic occur within supergene zone of polymetal deposit of Stara Góra in Radzimowice (Kaczawskie Mountains, Poland). The weathering of pyrite results in strongly decrease of pH and also in release of considerable quantity of iron ions. In such conditions intensive decomposition of arsenopyrite took place, yielding scorodite, kaňkite, pitticite, zykaite and iron hydroxides as the weathering products. These phases control amounts of arsenic in ochrous sediments and mine drainage waters.

Keywords: kaňkite, scorodite, pitticite, zykaite, iron oxide, Radzimowice, Sudetes

INTRODUCTION

The polymetal deposit of Stara Góra is located about 20 km to the north of Jelenia Góra within Radzimowice village. The quartz-sericite and quartz-sericite-graphite schists (Radzimowice schists) exposed in this area are cut by rhyolites, rhyodacites and trachytes intrusions and also by polymetal ore veins. Frequently, the polymetal ore veins are found close to the contact of schists with igneous rocks. Ore veins contain pyrite, arsenopyrite, chalcopyrite, sphalerite, tetrahedrite, bournonite, boulangerite, galena and other ore minerals (Manecki 1965, Mikulski 1999). Quartz, rhodochrosite, siderite, dolomite, ankerite, and calcite are barren minerals.

Very intensive processes of alteration of ore and barren minerals took place in old adits and on waste dumps. Oxide iron hydroxides, sulphates, carbonates and arsenates are the products of these processes (Siuda 2001, 2003).

The altered vein containing pyrite, arsenopyrite and quartz were found in the abandoned Wilhelm Mine within its second exploitation level. The ore vein is characterized by west-east orientation and has steep dip (about 87^{o}).

METHODS

X-ray diffraction patterns were recorded CP 120 INEL diffractometer with Co radiation and quartz monochromator. The qualitative chemical compositions of minerals was measured with CAMECA SX-100 electron microprobe at the Inter-Institution Laboratory for Minerals and Synthetic Substances (Faculty of Geology UW) with the technical assistance of Dr Piotr Dzierżanowski and Lidia Jeżak.

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MINERALS

Scorodite $Fe^{3+}AsO_4{\cdot}2H_2O$ forms thin yellow-honey or brown colour coats and incrustations on arsenopyrite surface and ryolitic rocks. The specimens usually are characterized by conchoidal fracture and resinous luster.

Kaňkite $Fe^{3+}AsO_4{\cdot}3.5H_2O$ occurs in two types of aggregates. The first type of kaňkite, which is associated with scorodite, jarosite and zykaite, forms thin, pale green coats with botryoidal surface on the rhyolitic rocks containing ore mineralization. The second one occurs as yellow-green, powdery masses with dull luster. Moreover, the colour of kaňkite changes from bright green to green with yellow tint during natural drying of the samples. This type of kaňkite creates large aggregates with diameter up to 0.3 m and weight up to 1 kg. The biggest kaňkite specimens are found on the border between altered ore vein and wall rock.

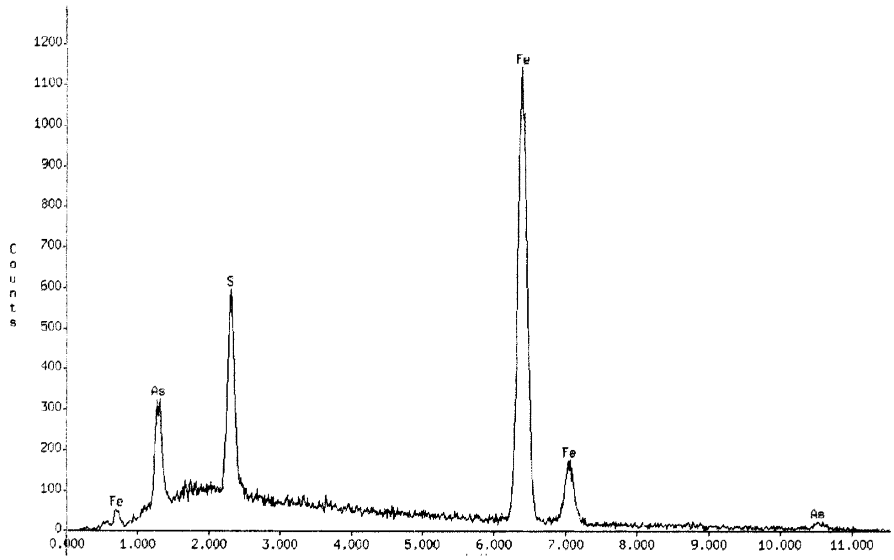

Fig. 1. EDS spectrum of pitticite

Pitticite $Fe^{3+}{}_{20}(AsO_4, SO_4)_{13}(OH)_{24}{\cdot}9H_2O$? is a general name for poorly-defined Fe arsenate sulphate hydrate mineral, which is amorphous to X-ray. Pitticite from the investigated zone builds small, dark-brown or reddish-brown with waxy luster stalagmites up to 3 cm in length. Qualitative chemical composition shows presence of Fe, S and As as major elements (Fig. 1), what is comparable with other chemical analyses of pitticite (Dunn 1982) from Germany (Schwarzenberg, Freiberg) and England (Cornwall).

Zykaite $Fe^{3+}_4(AsO_4)_3(SO_4)(OH)\cdot 15H_2O$ (Fig. 2) typically occurs as oval nodules up to 4 cm in size, rarely forms isolated globules on surface of rhyolitic rock. Zykaite nodules are very soft, greasy and plastic in ambient conditions.
After drying at the room temperature, this mineral becomes brittle.
Zykaite has grey-white colour with a weak green shade and dull luster.
Sometimes irregular aggregates of kaňkite grow on the zykaite surface.

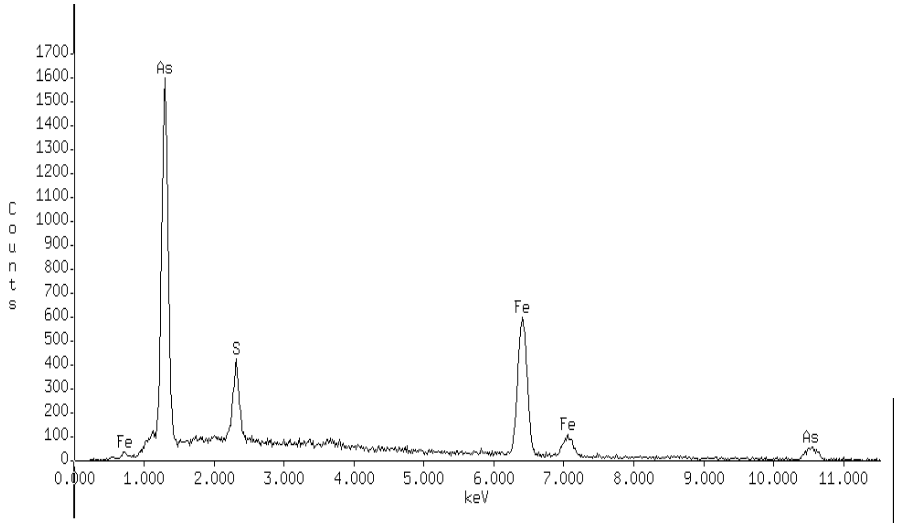

Fig. 2. EDS spectrum of zykaite

The above described arsenates occur with other secondary minerals such as gypsum, melanterite, jarosite, schwertmannite and goethite.

DISCUSSION

Arsenates and other secondary minerals are the weathering products of pyrite and arsenopyrite. Oxidation of arsenopyrite is relatively slow in alkali or neutral environment. The weathering of pyrite, which is present in polymetal ores, is the reason for a very strong acidification of supergene zone (Moses et al. 1987) and release great amounts of Fe ions:

$$FeS_2 + 3{,}5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$Fe^{2+} + 0{,}25O_2 + H^+ \rightarrow Fe^{3+} + 0{,}5H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Forming as results of pyrite oxidation ferric ion is very strong oxidation agent. The chemical decomposition of arsenopyrite is faster and more intensive in low pH. The released arsenic migrates into the mine water which circulates in the supergene zone. From this solution arsenates crystallize:

$$FeAsS + 14Fe^{3+} + 10H_2O \rightarrow$$

$$14Fe^{2+} + SO_4^{2-} + FeAsO_4\cdot 2H_2O\downarrow + 16\,H^+$$

Scorodite, which is the most common secondary mineral of arsenic in Radzimowice, plays a meaningful role in the circulation of As. Stability of this mineral (and of other arsenates) strongly depends on the environment conditions. The scorodite is metastable under most groundwater conditions and tends to dissolve incongruently, forming Fe oxides and releasing As in to solution (Dove, Rimstidt 1985):

$$FeAsO_4 \cdot 2H_2O + H_2O \rightarrow H_2AsO_4^- + Fe(OH)_3\downarrow + H^+$$

This process may be controlled by changes of pH caused by intensive inflow of meteoritic waters in humid seasons (Gieré et al. 2003). That situation causes generate a periodicity of arsenic content in mine waters.

The mobility of As within the supergenic zone of Stara Góra deposit is not only controlled by precipitation of this element as secondary phases and their solubility. The oxyhydroxides of iron, which are formed by weathering of ore minerals, reveal a very strong sorption (Fukushi et al. 2003). Amorphous FeOOH, poorly ordered goethite, ferrihydrite and schwertmannite may accumulate a significant amounts of As (Schlösser et al. 1999). This process prevents removal of the As ions from the deposit and counteracts to the great scale pollution of the ground and surface water.

Research was supported by the KBN grant 3 PO4D 060 22

REFERENCES

DOVE P.M., RIMSTIDT J.D., 1985: The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. Am. Mineral., 70: 838–844.

DUNN P.J., 1982:New data for pitticite and second occurrence of yukonite at Sterling Hill, New Jersey. Miner. Mag., 46: 261-264.

FUKUSHI K., SASAKI M., SATO T., YANASE N. AMADO H., IKEDA H., 2003: A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. Appl. Geochem., 18: 1267–1278.

GIERE R., SIDENKO N.V., LAZAREVA E.V., 2003: The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). Appl. Geochem., 18: 1347–1359.

MANECKI A., 1965: Studium mineralogiczno-petrograficzne polimetalicznych żył okolic Wojcieszowa (Dolny Śląsk). Pr. Miner. Kom. Nauk. Miner. PAN Oddz. w Krakowie, 47 (2).

MOSES C.O., NORDSTROM D.K., HERMAN J.S., MILLS L., 1987: Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim. Cosmochim. Acta, 51: 1561–1571.

SCHLÖSSER D., BAACKE D., BEUGE P., KRATZ K.L., 1999: Elementary composition of sediments from a former silver mine in Freiberg/East Germany. Appl. Radiation and Isotopes, 50: 609–614.

SIUDA R., 2001: New sulphate minerals from the Stara Góra oxidized zone, Radzimowice, Kaczawa Mts. Prace Spec. Pol. Tow. Miner. 18: 186-188.

SIUDA R., 2003: Nonconsolidated, hypergenic oxyhydroxides of iron from Stara Góra – mineralogy and geochemistry. Prace Spec. Pol. Tow. Miner., 22: 197-199.