Celestine from the Idrija mercury-ore deposit (Western Slovenia): Its occurrence and origin

Celestin iz živosrebrovega rudišča Idrija (zahodna Slovenija): njegove značilnosti in pogoji nastanka

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Abstract: Strontium sulphate celestine ($SrSO_4$), a member of the barite group of minerals, was found in the mineralised open veins and vuggy openings of brecciated zones of the Grübler ore body. It occurs in the form of well-developed, single tabular crystals or clusters of tiny euhedral crystals, ranging up to 20 μm in size. Paragenetically, celestine is supposed to be later than the majority of ore and associated gangue minerals, the exception being the skeletal cinnabar crystals. Its origin is most probably related to the recently percolating underground mine waters and the remobilisation of the components of ore and gangue minerals from ore beds and host rocks into the fissured and brecciated zones.

Izvleček: V odprtih žilah, žilicah in orudeni breči iz rudnega telesa Grübler v živosrebrovem rudišču Idrija smo našli lepo oblikovane, največ 20 μm velike kristale celestina ($SrSO_4$). Gre za idiomorfna zrna in njihove skupke, ki so nastali po kristalizaciji pretežnega dela cinabarita in jalovinskih mineralov. Izjemo predstavlja najmlajša generacija skeletastega cinabarita. Ta tvori na nekaterih celestinovih zrnih drobnozrnat oprh mikrometrskih dimenzij. Nastanek celestina je najverjetneje povezan z remobilizacijo komponent rudnih in jalovinskih mineralov s pronicajočo podtalnico v razpoke in zdrobljene dele rudnih teles ter prikamnine.

Keywords: Celestine, Grübler ore body, Idrija mercury mine, Slovenia.
Ključne besede: Celestine, rudno telo Grübler, živosrebrovo rudišče Idrija, Slovenia.

Introduction

The world-famous Idrija mercury-ore deposit (Western Slovenia) is hosted by Younger Palaeozoic to Middle Triassic sedimentary rocks within a complex tectonic structure between External Dinarides and the Southern Alps. The geology and the geological history of the mine area have been summarized by Mlakar and Drovenik (1971), Placer

Short scientific paper

(1973; 1976; 1982), and PLACER AND ČAR (1977). According to MLAKAR AND DROVENIK (1971) the mercury ore in Idrija originated during two Middle Triassic magmatic tectonic phases of mineralization. Considerable effort has been dedicated to determine which of the two tectonic phases originated the Grübler orebody. The results of detailed studies of the mineralized open vein, the veins and the breccia zones of the Grübler ore suggest a multiphase remobilization of the ore and gangue minerals during the Alpidic orogeny in Terciar (DROVENIK ET AL., 1991). LAVRIČ AND SPANGEMBERG (2003) reported that barite, quartz, carbonates and cinnabar from open veins and brecciated zones of the Grübler orebody most probably formed at temperature between 100 and 200 °C, which is consistent with the measured homogenization temperature (between 160 and 218 °C) of the fluid inclusions in euhedral quartz and barite and irregular cinnabar crystals from the same orebody (PALINKAŠ ET AL., 2001). Taking into account that the paragenetic relationship between the analyzed minerals and the other associated ore and gangue minerals from the same type of open veins, veinlets or breccia zones are not given we expect that the previous authors did not distinguished between the tectonic structures associated with the ore-forming processes from those originating from the Alpidic orogenesis. The latter were also filled with ore and gangue mineral, which in our opinion precipitated from percolating ground water of predominantly meteoric origin. Based on our observations these veins and fractured zones contain at least four generations of cinnabar, which is the major ore mineral in these tectonic structures, whereas other sulphides, such as metacinnabar, pyrite, marcasite, sphalerite and galena, were found only sporadically. The ore minerals in the Grübler ore body are associated with various gangue minerals, including quartz, dolomite, calcite, kaolinite, barite, gypsum, celestine, melanterite and traces of organic matter. In this paper we present the result of an SEM and EDS investigation of celestine from the Idrija mercury-ore deposit, which was until now not found in any of the Slovenia ore deposits.

METHODS OF INVESTIGATIONS

A total of eight representative samples of open veins and tectonic breccia mineralization from the Grübler ore body were used in the present study of mineral assemblages and the determination of mineral paragenesis. Special attention was given to the celestine and the youngest generations of cinnabar as well as to other associated gangue minerals, such as gypsum and melanterite, which are also thought, to be of a supergenic origin.

Microstructural investigations were performed using a scanning electron microscope (SEM; JSM-5800, Jeol, Japan), operated at 20 kV accelerating potential, and equipped with an energy-dispersive X-ray spectrometer (EDS; Link ISIS 300, Oxford Instrument, England).

Because of relatively small size of the crystals of the accessory minerals, including celestine, most of the work was performed using scanning electron microscopy (SEM) combined with X-ray dispesive spectroscopy (EDS). For our investigations we used a 20-kV scanning electron microscope (SEM;

JSM-5800, Jeol, Japan), equipped with an energy-dispersive X-ray spectrometer (EDS). Quantification of the acquired EDS data was performed based on the standard ZAF-correction procedure included in the Link ISIS 300 software. The relative random errors of the EDS measurements were better than 3 % for all the analysed elements.

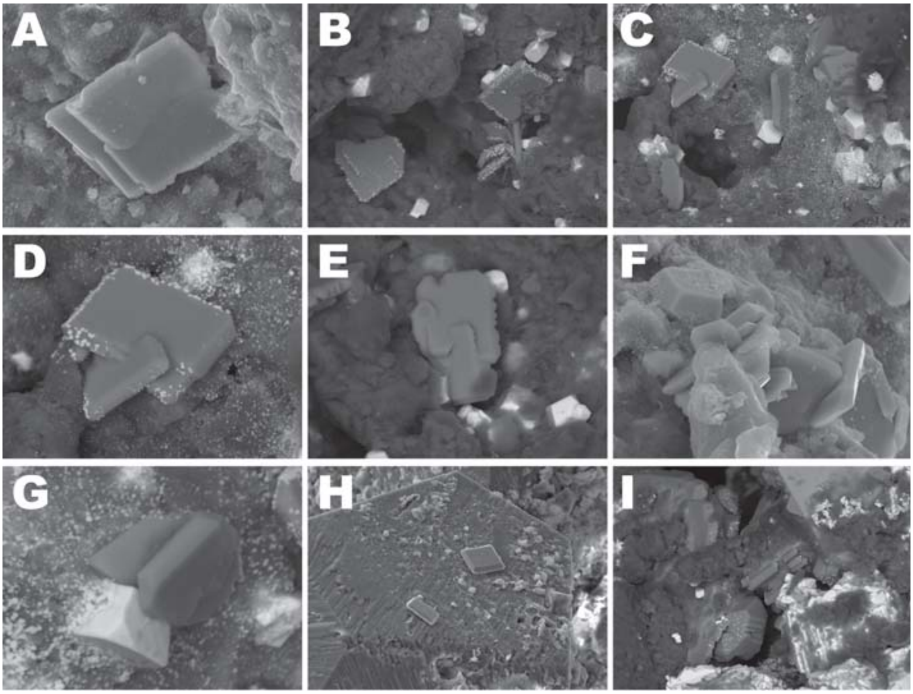

Figure 1. SEM photographs of celestine crystals from open veins and vugs from the Grübler orebody. A) Secondary-electron (SE) image of tabular celestine crystals. B) Back-scattered (BS) image of celestine clusters on cinnabar of the 3rd generation, peppered by tiny cinnabar grains of the 4th generation. C) BS image of the tabular and elongated celestine crystals on previously formed minerals. D) A detail from the image C showing tiny cinnabar grains (white) perched on the edge of celestine crystals. E) BS image of the elongated celestine crystals. F) SE image of a celestine cluster composed mostly of tabulated crystals. G) BS image of tabulated celestine crystals growing on the 3rd generation cinnabar grain. H) BS image of tabulated and elongated celestine crystal on leached prismatic calcite. I) Epitaxial growth of celestine on barite. Note the celestine crystal in the pore. Some of them are perched with tiny cinnabar. The longer edge of individual figures is: A) 44 μm, B) 88 μm, C) 88 μm, D) 38 μm, E) 53 μm, F) 38 μm, G) 26 μm, H) 176 μm, I) 120 μm.

Slika 1. SEM posnetki celestinovih kristalov iz odprtih razpok in votlinic rudnega telesa Grübler. A) Ploščati kristal celestina posnet s sekundarnimi elektroni (SE). B) Skupina kristalov celestina na cinabaritu 3. generacije, z oprhom cinabaritovih zrnc 4. generacije, posnetek je narejen z odbitimi elektroni (BS). C) BS slika ploščatega in podolgovatega kristala celestina na starejših mineralih parageneze. D) Detajl s slike C kaže drobna zrnca cinabarita (bela) na prizemskih ploskvah celestina. F) SE posnetek agregata ploščatih celestinovih kristalov. G) BS posnetek ploščatih kristalov celestina na kristalu cinabarita 3. generacije. H) BS posnetek ploščatih in razpotegnjenih kristalov celestina na šibko korodiranem kristalu kalcita. I) Epitaksialna rast celestina na baritu, kar je najlepše opazno pri celestinovem kristalu v pori. Nekateri kristali so prekriti z oprhi cinabaritnih zrnc. Daljši rob posnetkov na slikah meri: A) 44 μm, B) 88 μm, C) 88 μm, D) 38 μm, E) 53 μm, F) 38 μm, G) 26 μm, H) 176 μm, I) 120 μm.

RESULTS AND DISCUSSION

Occurrence and morphology of celestine crystals

Celestine found in open veins and in the vuggy openings of ore breccia of the Grübler orebody occur as single euhedral, mostly tabulated, well-developed crystals ranging from 5-20 μm in size. Occasionally, clusters composed of several overgrown tabulated crystals with sizes up to a few tenths of a micrometer were also found (Fig. 1).

The scanning electron microscope examination showed that the morphology of celestine crystals is dominated by basal-pinacoidal {001} faces and modified by prisms {011}, {101}, {210} and pinacoid {010}. The crystals are sometimes elongated in the [010] direction and twisted around the [001] axis, which is reflected in a jigsaw appearance of the (100) edges and the formation of rosette-like crystal clusters (typical celestine crystals from the Grübler ore body are shown in Fig. 2). Less commonly, celestine grows epitaxialy on barite crystals.

Although the present mineralogical and textural study suggests that the sequence of mineral deposition in the investigated samples is often ambiguous, because of the lack of situations where we can find the relation of the celestine with every paragenetic member, the main textural features between celestine and other minerals demonstrated that this mineral precipitated from the solutions filling the cavities and deposited on the existing minerals, such as cinnabarite, pyrite, quartz, barite and calcite. Due to the lack of coincidences between the celestine and the younger sulphates, such as gypsum and melanterite, we were not able to determine its relation with these younger paragenetic members. However, we suppose that they are

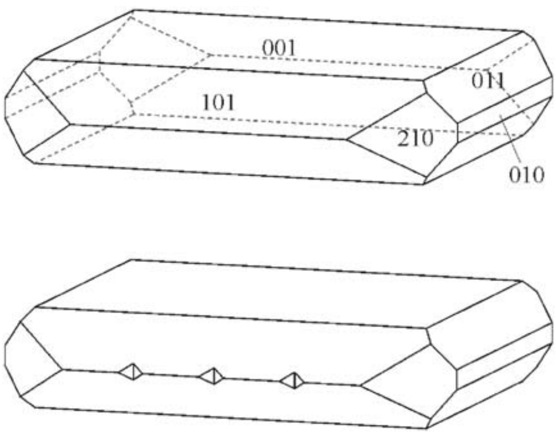

Figure 2. Morphology of the celestine crystals found in the mineralised cavities and vugs in the Grübler ore body. The crystals are dominated by large {001} faces and modified by the three prisms {011}, {101}, {210} and pedion {010}.

Slika 2. Morfologija celestinovih kristalov iz mineraliziranih votlinic iz rudnega telesa Grübler. Na kristalih prevladujejo ploskve baznega pinakoida {001}, ki so po robovih modificirane s tremi prizmami {011}, {101}, {210} in pedionom {010}.

more or less contemporaneous. We found that some of the celestine crystals are covered by tiny cinnabar grains and botryoidal aggregates composed of the youngest skeletal and rod-like cinnabar crystals measuring up to 5 μm in diameter. These grains represent the youngest generation of cinnabar most probably originating from the percolating underground water.

Chemical composition

Two selected celestine crystals (one tabular and another elongated - Fig. 1) were analysed using EDS. Quantitative analyses carried out with the SEM-EDS system revealed the following elemental contents in wt %: 52.8 to 54.1 % S, 38.6 to 42.5 % Sr, 3.9 to 4.7 % Ca and 0 to 3.4 % Fe. It is interesting to note that no Ba was detected in the celestine (Fig. 3), while barites from the same orebody contain only up to 2.5 % of Sr (Dolenec et al., unpublished).

A genetic model of celestine and cinnabar formation

The exact mechanisms of celestine formation in the open veins vuggs of brecciated zones in the Grübler orebody are still unknown. Since the celestine crystals and the clusters of celestine crystals were found on the surfaces of the most previously formed ore and gangue minerals, we believe that they are essentially of recent origin and most probably precipitated like gypsum and melanterite from the acidic solutions produced by the weathering of sulphides such as pyrite. The oxidation of pyrite and the sulphate ions from pyrite trigger the formation of protons, which interact with the surrounding carbonates. The acidity is buffered by the carbonates that are present in the host rock. The process results in a typical secondary formation of sulphates (Fe, Ca) and iron hydroxides. The Sr content in the host carbonate rocks is sufficient (200 to

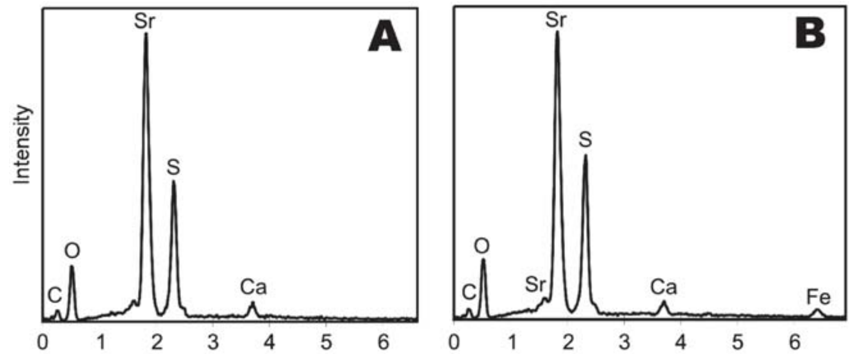

Figure 3. Energy Dispersive Spectroscopy (EDS) of tabular (A) and elongated celestine crystal (B) showing differences in Fe content, while no Ba could be detected in any of the samples.
Slika 3. EDS spekter ploščatega (A) in podolgovatega (B) celestinovega kristala z jasno izraženo razliko v vsebnosti Fe. Kristala ne vsebujeta Ba. Ba ni bil najden tudi v drugih celestinovih kristalih.

500 ppm) for the formation of celestine (CHARPENTIER ET AL., 2001), and the mineral assemblage gypsum ± celestine ± jarosite and iron hydroxide. Such mineral paragenesis closely resembles the associations described in pyrite-rich tailings or mine galleries (BLOWES AND JAMBOR, 1990; CATHELINEAU ET AL., 1995; ROUSSEL ET AL., 1999).

Percolating oxidative ground waters in the upper part of the Idrija mercury mine also oxidised the cinnabar. Under these conditions cinnabar is soluble and forms highly mobile aqueous complexes in the presence of a high (7mM) sulphide concentration at pH > 6 (MAHAHIGAM ET AL., 1998, and references therein). The presence of Fe^{3+} in acidic mine

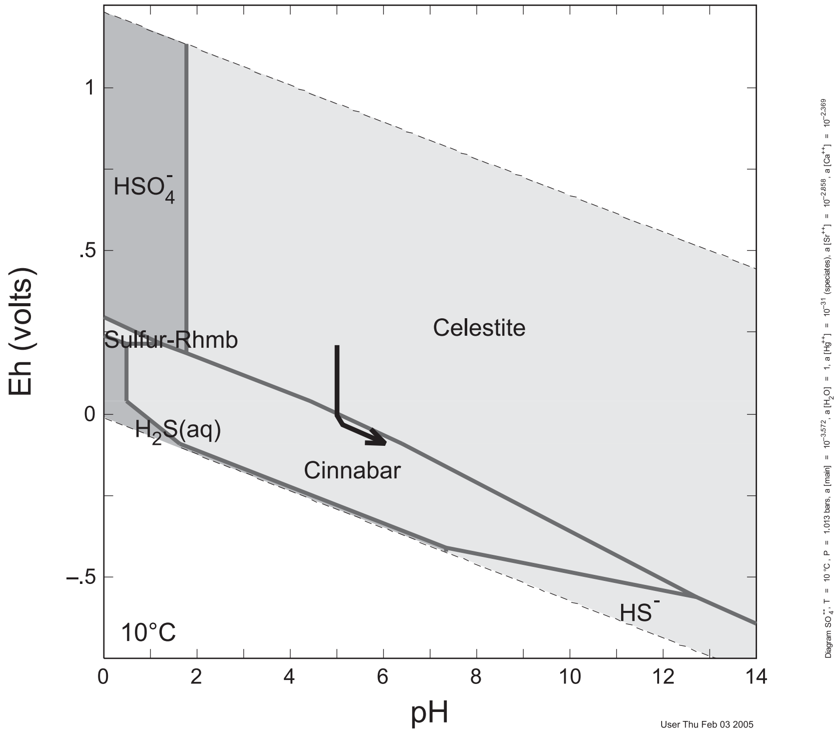

Figure 4. A simplified progressive Eh-pH diagram for celestine and the youngest generations of cinnabar formation showing the stability field of celestine and cinnabar and the approximately Eh-pH conditions of their precipitation in the open veins and breccia zones of the Grübler ore body. The diagram was calculated using the Geochemist´s Workbench Release 4.0 Software. The calculation assumed a temperature of 10 °C for the percolating mine water and a pressure of approximately 1 bar. The total concentration of components was chosen to be consistent with the elemental composition data for the Idrija mine underground water (DOLENEC, unpublished).

Slika 4. Poenostavljen Eh-pH diagram za pogoje kristalizacije celestina in najmlajše generacije skeletnega cinabarita v odprtih razpokah in zdrobljenih conah rudnega telesa Grübler. Diagram je bil napravljen s pomočjo računalniškega programa Geochemist´s Workbench Release 4.0. Temperatura rudniške vode je 10 °C pri tlaku 1 bar. Podatki o njeni kemični sestavi so privzeti po DOLENCU (neobjavljeno).

waters (pH < 2) has also been shown to release mercury through the oxidation of cinnabar (Burkstaller and McCarty, 1975). In a deeper part of the mine the percolating mine water became, due to the further oxidation of sulphides, more reducing and the cinnabar started to precipitate from the solutions. Reducing conditions governing the excretion of minute cinnabar grains that precipitated on the celestine crystals may also have occurred as a result of changes to the hydro-geochemical conditions due to the mine works. A possible model simulating the precipitation of celestine and cinnabar in open veins and vugs from the Grübler orebody is shown in Fig. 4.

Conclusion

This study demonstrated that celestine, which was up to now not known in Slovenian ore deposits, most probably precipitated recently from percolating, sulphidic, underground mine water. The association with younger sulphates such as gypsum and melanterite is supposed to be the result of several processes that led to the oxidation of sulphides, especially pyrite, the interaction between the produced acid water on the microlocations and the nearby minerals (dissolution, buffer effect - carbonates) and supersaturations of new minerals (sulphates). The precipitation of cinnabar over the celestine crystals indicates the changes in the chemical characteristics of the mine water (a more reducing character). Such a chemical evolution and an unusual textural relationship (Drovenik et al., 1991) undoubtedly suggest that the above mentioned minerals could be formed under the influence of gravity from the percolating underground water rather than from the primary ascendant hydrothermal fluids.

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