

Bieber – a widely unknown ancient Ore – Deposit in the Spessart Mountains (Germany)

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The Bieber locality includes at least three different types of historically mined ore-deposits:

- Kupferschiefer (blackshale) with mainly tennantite and galena (both silver-containing) and additional chalcopryrite,
- "Kohaltrücken" hydrothermal veins with Co-, As-, Ba-, Fe-mineralization,
- Eisensteinlager: oxidic iron ore deposit in upper permian limestones.

These occurrences have been described first by CANCRIN (1787) and then by BÜCKING (1892) more than hundred years ago. A new investigation of the former ore deposits has been carried out in the last ten years with a special focussing on mineral assemblages and up to now not defined minerals.

Moreover Bieber Spessart is type locality for bieberite and rösslerite.

Uranyl-selenites, unique minerals of Musonoi Mine, Katanga, DRC

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Musonoi Mine lies in the western part of the Katanga copperbelt, in the Kolwezi thrust outlier. This Cu-Co mine shows a tectonic unit called thrust-slice 2400 (*Cécille 2400*) which has a typical Cu-U-Se mineralization. This ore body has given magnificent examples of uranium-bearing minerals such as vandenbrandeite, cuprosklodowskite or torbernite but it has also provided 4 new species of uranyl-selenites which were described in the 70's.

The present study has permitted to make an inventory of the minerals occurring at Musonoi, and to better characterize their chemical compositions by using electron microprobe. The growing environment of uranyl-selenites and their sequences of crystallization together with other minerals are also discussed.

Selenian digenite $[\text{Cu}_2(\text{S}, \text{Se})_2]$, berzelianite $[\text{Cu}_2(\text{Se})_2]$ and trogtalite $[(\text{Co}, \text{Cu}, \text{Pd})\text{Se}_2]$ are the primary minerals. Their main alteration products are chalcocite $[\text{Cu}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}]$ and cobaltocite $[\text{CoSeO}_4 \cdot 2\text{H}_2\text{O}]$, which can be found in several places through the deposit. These electric-blue and red-pink crystals are common oxidation products in selenium-bearing rocks.

Four of the seven known uranyl-selenites have been first described at Musonoi Mine and do not seem to occur elsewhere in significant amounts. Guilleminite $[\text{Ba}(\text{UO}_2)_2(\text{SeO}_3)_2 \cdot 3\text{H}_2\text{O}]$, marthozite $[\text{Cu}(\text{UO}_2)_2(\text{SeO}_3)_2 \cdot 8\text{H}_2\text{O}]$, and its dehydrated equivalent with $6\text{H}_2\text{O}$, are frequent in cavities filled by their yellow and green plates. Relationships with other copper- and uranium-bearing phases indicate that these two minerals crystallize at all stages of the alteration process. Bottle-green pinacoids of demesmaekerite $[\text{Pb}_2\text{Cu}_3(\text{UO}_2)_2(\text{SeO}_3)_6(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, frequently dehydrated in brownish crystals and olive-green derriksite $[\text{Cu}_4(\text{UO}_2)_2(\text{SeO}_3)_4(\text{OH})_6]$, are far less common and generally occur as crusts on cobaltocite malachite. Genetic relationships seems to show that demesmaekerite appears quite early in the deposit, just after the crystallization of barium-bearing minerals (guilleminite, barite) and before the crystallization of vanadates (sengierite, volborthite). Derriksite is a late phase crystallizing with the last uranyl-silicates (cuprosklodowskite, α -uranophane).

During this work, at least one new uranyl-selenite has been discovered, with a $(\text{H}_3\text{O}^+)_4(\text{Cu}, \text{Mg}, \text{Ca})(\text{UO}_2)_2(\text{SeO}_3)_2(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ composition. The yellow-green platy crystals are associated with marthozite and seem to be related with the latest deposition of rutherfordine and soddyite in the ore body.

Tephrochronology of the manganese wad deposit at the Akan Yunotaki hot spring

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An outcrop of manganese oxide about one meter thick, inter-bedded with several volcanic ash layers, is found at the Yunotaki hot spring, Hokkaido, Japan. The manganese wad is precipitated from hydrothermal water. On the basis of the previously known age of the inter-bedded volcanic ash layers, linked to well-known eruptions, it has been possible to determine the chronology of the manganese oxide precipitation. The ash layers were identified by the chemical composition of the separated volcanic glasses. Since the lowermost manganese oxide layer occurs immediately above the mud flow of Mt. Ponnmachineshira without the presence of any intermediate soil layer between them, its age of formation could be near the age of the mud flow, i.e. 4500 - 5000 years BP. The manganese oxide layers in the top 50 cm of the outcrop are comparatively softer than those occurring below 50 cm and commonly have the texture of the aggregate of a filament structure. Manganese oxide layers occurring below 50 cm is hard and has a diagenetically altered texture reflecting change in the filament structure to a grain aggregate structure. These oxides have lost their structural water and the mineralogy has begun to change from 10 Å phase to 7 Å phase during the diagenetic process.

New phase relations of the system Fe—Ni—S at temperatures from 875 to 450°C as the pentlandite ore-genesis

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High-form pentlandite ($\text{Fe}_{4.91}\text{Ni}_{1.06}\text{S}_{8.00}$) first crystallizes as a product of a pseudoperitectic reaction between monosulfide solid-solution and liquid at 870°C and forms a limited solid-solution from $\text{Fe}_{5.0}\text{Ni}_{1.41}\text{S}_{7.85}$ to $\text{Fe}_{3.71}\text{Ni}_{2.28}\text{S}_{7.85}$ at 850°C. This solid-solution grows rapidly toward the Ni-rich side with decreasing temperature and joins β_1 ($\text{Ni}_{1.77}\text{S}_{1.00}$) on the Ni—S boundary at 806°C. β_1 ($\text{Ni}_{1.65}\text{S}_{2.00}$) first appears on the Ni—S boundary at 800°C and forms independently a limited solid-solution ($\text{Fe}_{0.36}\text{Ni}_{2.65}\text{S}_{2.00}$ to $\text{Ni}_{2.85}\text{S}_{2.00}$) jutting from the Ni-S boundary into a ternary field at 600°C. Crystallization of the Fe- and metal-rich extreme high-form pentlandite from liquid finishes at 762 and 739°C, respectively, because of tie-line changes. Consequently, crystallization of high-form pentlandite from liquid finishes at 739°C. Liquid occupies a wide field in the metal-rich portion of the system above 850°C. However, its field reduces and retreats to the Ni-rich side with decreasing temperature, and finally disappears at its eutectic of 637°C and $\text{Ni}_{0.67}\text{S}_{0.33}$. Pentlandite ($\text{Fe}_{5.30}\text{Ni}_{1.41}\text{S}_{7.85}$) first appears due to a phase-transition of Fe-rich extreme high-form pentlandite at 625°C, grows as limited solid-solutions from $\text{Fe}_{5.65}\text{Ni}_{1.38}\text{S}_{7.85}$ to $\text{Fe}_{3.44}\text{Ni}_{2.76}\text{S}_{7.85}$ at 600°C and from $\text{Fe}_{5.65}\text{Ni}_{1.35}\text{S}_{7.92}$ to $\text{Fe}_{2.42}\text{Ni}_{3.58}\text{S}_{9.02}$ at 500°C due to a continuing phase-transition (625 to ~550°C), exsolution (625 to 503°C) and breakdowns (pseudo-eutectoids at 625 to 579°C and 579 to 503°C) of high-form pentlandite and exsolution (below 579°C) and breakdown (pseudo-eutectoid at 579 to 484°C) of β_1 . Pentlandite solid-solution also grows slightly fat in S-composition due to exsolution (below 625°C) of monosulfide solid-solution. Pentlandite coexists with high-form pentlandite (625 to 503°C), monosulfide solid-solution (below 625°C), γ (below 617°C) and/or β_1 (579 to 484°C). A metal-rich portion of the high-form pentlandite solid-solution still remains stably below 600°C, but retreats to the Ni-rich side with decreasing temperature and finally disappears by breakdown to pentlandite, high-form godlevskite and β_1 at 503°C and $\text{Fe}_{1.03}\text{Ni}_{0.9}\text{S}_{0.44}$ (eutectoid). β_1 also breaks down to pentlandite, heazlewoodite and γ at 484°C and $\text{Fe}_{0.26}\text{Ni}_{2.47}\text{S}_{2.00}$ (another eutectoid). The assemblages with pentlandite and high-form godlevskite or heazlewoodite first appear at 568 or 498°C, respectively. This study shows that pentlandite in the Ni-Cu ores can form at temperatures from 625 to 500°C or less due to phase-transition, eutectoid and exsolution of high-form pentlandite, monosulfide solid-solution and β_1 which are the primary phases that would crystallize from sulfide magma (liquid in the system Fe—Ni—S) at around 1000°C.