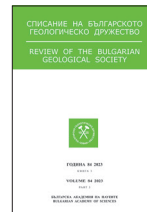




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Coexisting nickel diarsenide polymorphs in the five-element mineralization of the Bihor metallogenetic district, Apuseni Mountains, Romania

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СЪВМЕСТНО СЪЩЕСТВУВАЩИ ПОЛИМОРФНИ МОДИФИКАЦИИ НА НИКЕЛОВ ДИАРСЕНИД В ПЕТ-ЕЛЕМЕНТНАТА МИНЕРАЛИЗАЦИЯ ОТ МЕТАЛОГЕННИЯ РАЙОН БИХОР, АПУСЕНИ, РУМЪНИЯ

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Abstract. The three known polymorphs of nickel diarsenide were found to coexist in apparent equilibrium in the five-element mineralizations of the Bihor Metallogenetic District. It is the first identification of pararammelsbergite and krutovite in Romania, and the locality joins a very limited list of occurrences where all three NiAs_2 polymorphs coexist. Both phases newly identified in Romania are easily distinguishable from rammelsbergite by their optical properties and display consistent compositional differences manifested in stoichiometry and degree of isomorphic substitution. The NiAs_2 polymorphs coexist with nickeline and skutterudite and apparently predate cobaltite-gersdorffite in a mesothermal depositional sequence characterized by initial separation of Ni and Co in metal-poorer arsenides, followed by continuous decrease of arsenic activity, increase in sulfur activity, modal increase of nickeline and Co enrichment in the gersdorffite-cobaltite series.

Keywords: nickel diarsenide, rammelsbergite, pararammelsbergite, krutovite, Bihor metallogenetic district.

Background information

In spite of numerous occurrences worldwide and an extended mining history, in addition to raising interest in the strategic raw materials they contain, five-element mineralizations are still incompletely understood in terms of origin of the metals and concentration processes, as well as relevance of the mineral assemblages to the conditions of emplacement along the usually multistage depositional sequence. The complex mineralogy is illustrated by polymorphism and polytypy of key species (Vinogradova et al., 1976; Bayliss, 1982), compositional overlaps of different minerals (Spiridonov, Chvileva, 1995; Fanlo et al., 2004), along with limited relevance of high-temperature experimental data (Yund, 1962;

Hem, Makovicki, 2004) to often lower temperature assemblages from natural occurrences (Kiefer et al., 2017). These features reflect themselves in a fleeting inventory of newly recognized species (orthogersdorffite, paragersdorffite – Miyawaki et al., 2022), conflicting accounts of the properties of some of the minerals, discredited minerals (cloanthite, smaltite), discredited and afterwards revalidated species (dienerite – Bonazzi, Bindi, 2019).

The compound NiAs_2 belonging to this type of mineralization is known to assume three natural polymorphs, rammelsbergite (space group $Pn\bar{m}$, isostructural with marcasite), pararammelsbergite (space group $Pbca$, with a structure transitional between pyrite and marcasite – Fleet, 1972) and krutovite (space group $P2_13$, having a pyrite-type structure).

Rammelsbergite is the oldest identified and most widespread polymorph, included in Dana (1854). Pararammelsbergite was identified as a distinct polymorph by Peacock (1939), and Peacock and Dadsen (1940) in three co-type localities in the Cobalt-Gowganda region, Ontario, Canada. Experimental results indicate rammelsbergite as the high-temperature polymorph, the stoichiometric compound undergoing inversion to pararammelsbergite at 590 °C (Yund, 1961), yet being indefinitely stabilized towards temperatures lower than the value of 475 °C identified in the pure Ni-As-S system (Yund, 1962) by isomorphic substitution in both lattice sites. Krutovite was initially described by Kašpar and Paděra (1970) as gersdorffite with an unusually large lattice constant, supposed to originate from the Potůčky uranium deposit, but was subsequently identified as such by Vinogradova et al. (1976), who also update the locality of origin to the Geschieber Vein, Svornost Mine, Jáchymov deposit, and list a further occurrence (Khovu-Aksy) in Co-As deposits. However, the type locality is still erroneously considered to be Potůčky. Only 13 krutovite localities are known to date (excluding Potůčky), of which krutovite is mentioned to coexist with rammelsbergite in four ones, whereas proven coexistence of all three polymorphs is documented in two of them (Svornost Mine and Belorechensk, Maykop District, Russia).

Here we report a further such occurrence and describe the characteristics of the polymorphs identified in the five-element mineralization of South Bihor, Apuseni Mountains. The ore is concentrated in veins and metasomatic bodies hosted by the low-grade metamorphic basement (Biharia Complex) of the “mid”-Cretaceous Biharia Nappe, consisting of albite-chlorite rocks with amphibolite and marble intercalations (Bordea et al., 1988). The mainly Ni-Co arsenide and sulfoarsenide assemblage is described in Zajzon et al. (2015), who identified diarsenides as terms of the rammelsbergite-safflorite series.

During the examination of ore samples provided by LEM Resources SA from their exploration works, we identified the three NiAs₂ polymorphs in apparently stable coexistence.

Materials and methods

Two samples with abundant Ni-Co mineralization were selected from the available material for detailed optical microscopic study, backscatterd electron (BSE) imaging, energy dispersive X-ray spectroscopy (EDS) point analyses and X-Ray mapping on a Hitachi TM3030 tabletop scanning electron microscope equipped with a Bruker’s QUANTAX 70 EDS system. The conditions were: uncoated samples, acceleration voltage of 15 kV, emission

current of 25 000–40 000 nA, focused beam in scanning mode, at a working distance of 7.5–9 mm, and variable counting times averaging 120 s, adjusted to obtain a suitable noise vs. signal ratio. Calculated EDS compositional data were checked against quantitative data acquired on carbon-coated samples with a field-emission gun JEOL HyperProbe JXA-8530F at the Central Lab of the Natural History Museum in Vienna (wavelength dispersive mode, 25 kV, 20 nA, 2 µm beam diameter, counting times of 20 s on peak and 5 s on background) using troilite (Fe and S), nickeline (Ni and As) and Co metal standards, and the JEOL and Probe for EPMA software.

Results

One of the examined samples (VLM8) consist of an assemblage of skutterudite, rammelsbergite and cobaltite solid solution, containing also nickeline, pararammelsbergite and krutovite (Fig. 1). Rammelsbergite may contain micron-sized native Bi blebs. Another sample analysed (VLM13) contains dominant nickeline associated with gersdorffite, and minor pararammelsbergite sometimes displaying vermicular microchannels, tourmaline, brannerite, coffinite, uraninite in a calcite gangue.

The minerals composing the assemblage are clearly distinguishable, displaying different optical properties (Fig. 1A, B). The most reflective phase is pararammelsbergite, at variance with the data of Vinogradova et al. (1976). It is whitish, rammelsbergite appearing duller and with grey-blue hues in side-by-side comparison. It is strongly anisotropic, without being noticeably bireflective in air; the anisotropy colours lack the bluish hue of rammelsbergite, appearing brownish in comparison, and is not twinned. Skutterudite is isotropic, slightly more reflective than rammelsbergite and displays a slightly yellowish tint as compared with the latter. Rammelsbergite is conspicuously bireflective and strongly anisotropic, with bluish hues, features enhanced by its lamellar twinning. Nickeline has a characteristic yellow colour, displaying distinct bireflexion at grain boundaries, and an anisotropy with green-violet hues. Cobaltite is isotropic, having a reflectivity similar to krutovite, but a slightly pinkish overtone. In contrast krutovite, also isotropic with the lowest reflectivity (*n.b.*) among the associated phases, appears slightly yellowish, forming subhedral square outlines displaying a cleavage-like partition along (100).

Skutterudite displays scalloped and convex-inward contours towards rammelsbergite, the mutual boundary or its vicinity being marked by rows of smaller-sized equant cobaltite grains.

Compositionally (Fig. 1H, I), pararammelsbergite is the purest polymorph, while rammelsbergite

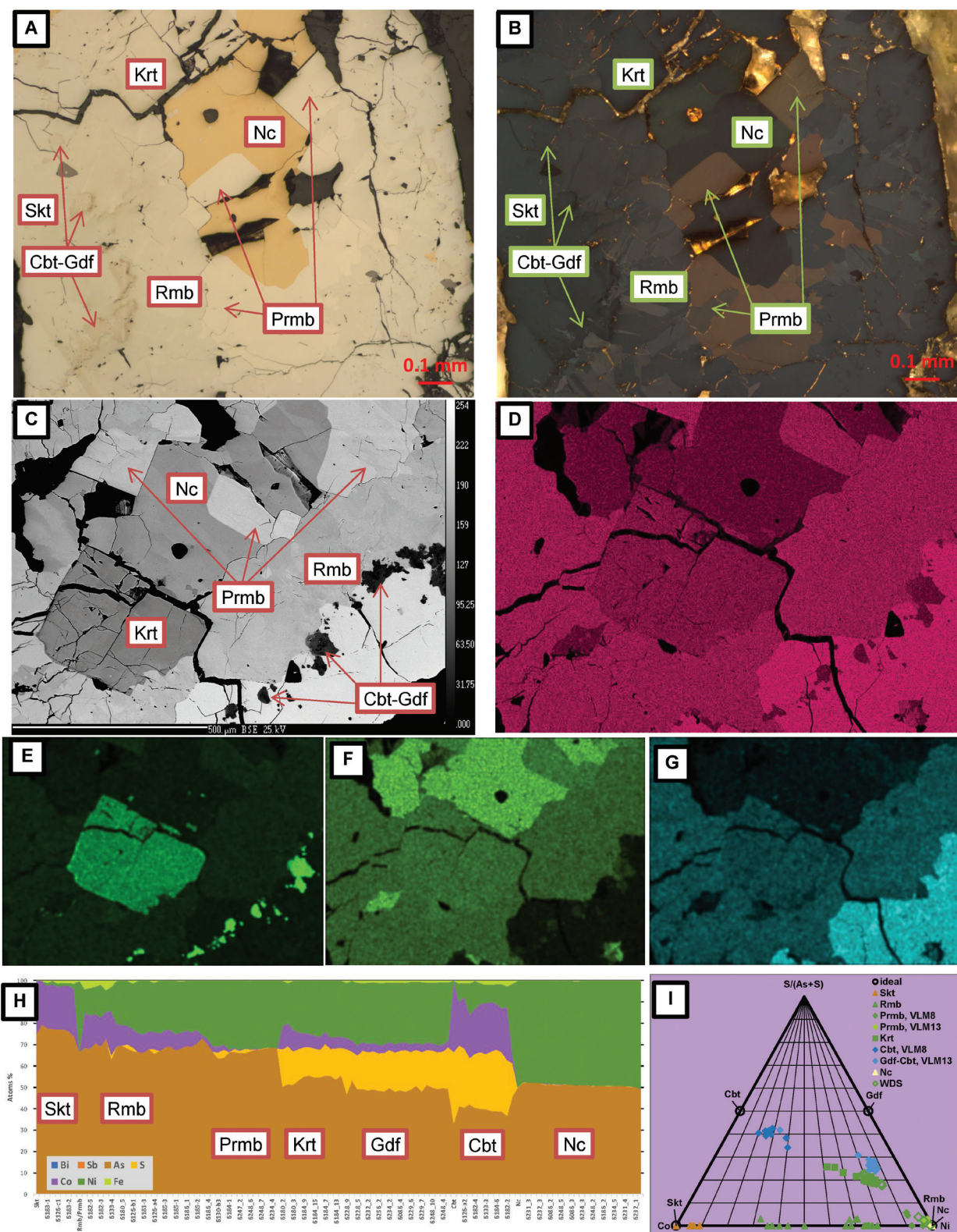


Fig. 1. *A*, reflected light microphotograph showing the relationships among the NiAs₂ polymorphs and the accompanying phases; *B*, the same image with crossed polarizers, showing the anisotropy of the phases. *C*, BSE image of the same field slightly shifted upwards and rotated by 180°. Element distribution maps showing compositional differences among phases for: *D*, As; *E*, S; *F*, Ni; *G*, Co; *H*, Stacked atomic abundances plot of the Co-Ni-As-S minerals. Each species preceded by the ideal composition, except NiAs₂ polymorphs; *I*, polar plot in the simplified Co-Ni-As-S space. Mineral abbreviations according to the standard IMA notation (Warr, 2021).

is inhomogeneous, containing two compositional clusters, one rich in Co and containing Fe, and another with rather lower and constant Co. Krutovite is non-stoichiometric, containing appreciable S and less Co than rammelsbergite. Cobaltite is conspicuously zoned, S deficient, with Ni-substitution towards gersdorffite to gersdorffite-dominant when coexisting with abundant nickeline, and contains minor Fe.

Conclusions

All three known polymorphs of NiAs₂ appear to coexist stably with nickeline and at least partly with skutterudite. Yet, the latter is slightly corroded towards rammelsbergite, the boundaries being lined by later cobaltite-gersdorffite rows. The depositional sequence started with di- and triarsenides, evolving towards less As-rich species like nickeline and cobaltite-gersdorffite, the latter being also S-enriched. Native Bi inclusions in rammelsbergite indicate conditions around its melting temperature (271 °C).

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