17. Dark blue **covellite** replacing green **malachite** spherulites in cavities in quartz. FOV: 1.2 cm. **Zone 1**, level +248 m. Specimen: Anatoly V. Kasatkin. Photo: Maria D. Milshina.

with dark-blue covellite crusts (6 x 5 cm in size) in areas replacing bright blue azurite crystals and green malachite spherulites in association with brick-red supergene hematite (*Figs.* 15–17), are the most interesting with regard to collection specimens. These copper sulfides are most likely the latest supergene minerals in the vein.

Pyrite, FeS_2, is one of the major ore minerals of the Murzinskoe deposit in general, however, it is extremely rare in the oxidized ores of the Phosphatno-Arsenatnaya vein. It occurs as sporadic micrometer-size inclusions in chalcopyrite and quartz in **Zone 2**. Brown cubes up to 3 mm in size, which are limonite pseudomorphs after pyrite, were observed in **Zones 2** and **3**.

Sphalerite, ZnS was identified only at the lower levels of the vein (+235 to 230 m), where it forms iron-black massive segregations up to 5 cm in size. Sphalerite is highly oxidized at the surface and is replaced by black sooty copper sulfides and thin white crusts of smithsonite.

Chalcopyrite, $CuFeS_2$ is the major primary ore mineral of the Phosphatno-Arsenatnaya vein. It is common throughout all three zones, where it occurs as brass-yellow clusters (up to 5 cm in size) in quartz. Both fresh and altered grains are observed where it is replaced by supergene copper minerals at grain margins, most frequently sulfides, azurite, and malachite.

Uytenbogaardtite, Ag_3AuS_2 was observed during EMPA of samples from level +248 m (**Zone 1**). This sulfide of precious metals forms rare intergrowths with imiterite (up to 20 µm in size) in quartz and is associated with acanthite, iodargyrite, covellite, malachite, naumannite, pseudomalachite, chalcocite, and stromeyerite. The chemical composition of uytenbogaardtite is Ag 55.42, Au 33.55, S 10.78, total 99.75 (wt.%). The empirical formula (calculated on the basis of 6 atoms) is $Ag_{3.02}Au_{1.00}S_{1.98}$.

Sulfosalts

Sulfosalts, except for tetrahedrite group minerals, are observed occasionally as very fine grains. All sulfosalt minerals were identified by their chemical compositions (Table 3) and optical properties. These minerals belong to primary hydrothermal ores.

Aikinite, $CuPbBiS_3$ has been identified in samples from **Zone 1** (level +248 m). It occurs as veinlets (up to 0.2 x 0.05 mm in size) in chalcopyrite with anglesite, bismoclite, galena, tetradymite, and chalcocite.

Tetrahedrite group minerals are **tennantite-(Fe) – $Cu_6[Cu_4Fe_2]As_4S_{12}S$, tennantite-(Zn) – $Cu_6[Cu_4Zn_2]As_4S_{12}S$** and **tetrahedrite-(Zn) – $Cu_6[Cu_4Zn_2]Sb_4S_{12}S$**. Arsenic-dominant members of this group are common throughout all three zones and are the most abundant in **Zone 2** where they occur as massive segregations 0.5–1 cm in size, and less frequently up to 3 cm in size in quartz and chalcopyrite associated with various arsenates, malachite, azurite, and goethite. Tetrahedrite-(Zn) is rare and occurs as inclusions (up to

Cosalite – $Pb_2Bi_2S_5$, gustavite – $AgPbBi_3S_6$ (presumably) and **wittichenite – Cu_3BiS_3** have been identified in one polished section prepared from a sample from level +245 m. These sulfosalts occur at the contact of chalcopyrite and quartz as individual grains up to 0.8 mm (cosalite), 0.1 mm (gustavite), and 0.05 mm (wittichenite) in size, and also occur as aggregates up to 0.1 mm in size. We identified the member of lillianite homologous series as gustavite on the basis of its homologue number N_{chem} = 4.17, the mole fraction of the Ag–Bi end-member (L = 54.46%) and substitution parameter x = 0.59 (Makovicky and Topa, 2014; Makovicky, 2019)) calculated from its chemical composition (*Table 3, anal. 7*). Identification of cosalite is supported by single crystal X-ray diffraction (SCXRD) data. Its orthorhombic unit cell parameters are: a = 19.112(3), b = 23.794(4), c = 4.0577(9) Å, V = 1845.3(6) Å^3. In **Zone 3** (level +235 m), cosalite occurs as inclusions (up to 0.3 mm in size) in sphalerite and at the contact of sphalerite and quartz and is associated with galena, gold, smithsonite, chalcocite, and cerussite.

Halides

Minerals of this class occur as micrometer-size crystals and grains and were identified by EMPA

Bismoclite, BiOCl occurs as elongated lamellar crystals (up to 0.1 mm in size) enclosed in chalcopyrite with chalcocite and is associated with aikinite, anglesite, galena, and tetradymite. Only one sample with this mineral has been collected in **Zone 1** at level +248 m. The chemical composition of bismoclite is (wt.%, the H_2O content was calculated by stoichiometry): Bi_2O_3 90.84, Cl 9.26, H_2O 1.15, Cl=O – 2.09, total 99.16. The empirical formula calculated on the basis of two anions is $Bi_{1.00}O_{1.00}Cl_{0.67}(OH)_{0.33}$.

Iodargyrite, AgI is abundant in **Zone 1** (level +248 m) but is fine grained. Iodargyrite is observed as anhedral grains, up to 0.1 mm in size (average 10–20 µm) that are localized in the gossan where they fill fractures in quartz and limonite; also it is enclosed in malachite. In **Zone 2** (level +245 m), iodargyrite occurs as inclusions (up to 15 µm in size) in gray crusts of mimetite associated with segnitite and phosphohedyphane, and in **Zone 3** (level +235 m), it is rare but forms individual grains (up to 10 µm in size) in quartz and malachite. The chemical composition of this iodide has the ideal formula, AgI. Although the anisotropy of the mineral is masked by the pale-yellow internal reflections, it is still distinguishable allowing confirmation that this mineral is indeed iodargyrite rather than its cubic dimorph, miersite. Iodargyrite is one of the latest minerals in the oxidized ores from the vein.

Very fine (<5 µm) inclusions in beudantite, from level +245 m, have a composition that corresponds to the rare mercury bromide, **kuzminite – HgBr**. The chemical composition of this mineral normalized to 100 wt.% (after subtraction of components from the host beudantite) is Hg 72.83, Cl 2.54, Br 23.28, I 1.35. The empirical formula (calculated on the sum of all atoms equal to 2) is $Hg_{0.99}Br_{0.79}Cl_{0.19}I_{0.03}$. Various arsenates and