

## Kaolinite-barite intergrowths associated with As-sulphides mineralization near Baligród (Polish Flysch Carpathians)

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*Abstract.* Barite-kaolinite intergrowths have been noticed in association with quartz, realgar, and orpiment mineralization in the Carpathian flysch sandstones in the Rabański stream valley near Baligród. Form of occurrence of these minerals indicates that emplacement of mineralization took part after tectonic events.

Crystallization temperatures of minerals from joints and faults from the Rabański stream valley have not been determined. The relation between quartz and realgar in joints indicates that the crystallization of realgar post-dates the crystallization of quartz. Textural relations suggest that barite and kaolinite formed contemporaneously. The temperature of barite-kaolinite intergrowths crystallization is also unknown.

Association of sulphides and barite-kaolinite can indicate the variation of chemical composition of mineralizing solutions. The origin of solutions is, however, unknown. It is possible to consider the migration of solutions from depth and their relations to magmatic phenomena, but also more local circulation and leaching of components from the flysch rocks can be accepted. Kaolinite-barite association can be formed during sandstones diagenesis. Detailed study of minerals filling joints as well as surrounding sandstones is needed for the determination of origin of solutions and conditions of mineral precipitation.

*Key words:* Flysch Carpathians, barite, kaolinite, hydrothermal mineralization, diagenesis

### Introduction

Traces of the hydrothermal mineralization are scarce in the Polish Outer Carpathians. The area near Baligród (the Bieszczady Mts.), where realgar, orpiment and other minerals of hydrothermal origin have been found (Kamieński, 1937), was studied extensively (Ślęczka, 1958, Ostrowicki, 1958, Kita-Badak, 1971). Ostrowicki (1958) based on a detailed microscopic study, determined that also sphalerite, galena, tennantite(?), enargite(?), and malachite are in the hydrothermal minerals assemblage. Gawel (1970) mentioned historical reports on mercury and cinnabar occurrences in this area. However, preliminary results of the research recently undertaken indicate, that the list of minerals is far from being complete and that the interpretation of mineralization origin should be re-interpreted.

### Material and methods

Samples have been collected in the quarry situated in the Rabański (Rabski) stream valley near Baligród (Bieszczady Mts.). Quartz, realgar, and orpiment mineralization can be macroscopically seen in joints crosscutting sandstones of the Istebna beds.

Samples were studied using optical microscopes and scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS).

### Results

Surfaces of joints and small faults planes are covered by small quartz crystals. Their size varies from several millimeters to a few microns. Realgar tightly covers surfaces of quartz crystals and fills depressions between quartz crystals. Some realgar crystals are porous and exhibit striation. Chemical composition of realgar is usually close to stoichiometric.

Organic matter aggregates were found on surfaces of quartz crystals. Aggregates are rounded and exhibit smooth surfaces. Their size is within the range from few mm up to dozens of mm. Some of aggregates are bubble-like with empty space inside.

Fine crystalline (<few mm) aggregates of K-mica-like minerals were noticed on quartz crystals walls. Barite is present in spaces between quartz crystals. The size of barite accumulations is usually not larger than dozens of mm. Kaolinite dispersed in some of barite accumulations can be seen. Kaolinite crystals, 3-5 mm in size, are pseudo-hexagonal. Kaolinite is loosely dispersed in barite. Kaolinite chemical composition is close to stoichiometric. Kaolinite seeded directly on quartz surfaces can be noticed also.

### Discussion of results and conclusions

The presence of euhedral quartz, realgar, and barite crystals in joints and small faults indicates that emplace-

ment of mineralization took part after tectonic events. It is in agreement with conclusion presented by Ślaczka (1958).

The temperature of hydrothermal minerals formation can not be determined precisely. Świerczewska et al. (1999) determined that drusy and blocky quartz in filling joints and small-scale faults within flysch rocks crystallized within temperature range of 160–220 °C and at fluid pressure 0.7–3.7 kbar (200–220 °C and 2.1–3.7 kbar in the Dukla nappe and 160–210 °C and 0.75–2 kbar in the Magura nappe). Realgar and orpiment can crystallize at temperatures less than or equal to 150–200 °C (Pokrovski et al., 1996) but significantly lower temperature (e.g. 75–85 °C) is also probable (Migdisov & Bychkov, 1998). Crystallization temperatures of minerals from joints and faults from the Rabiński stream valley have not been determined. The relation between quartz and realgar in joints indicates that the crystallization of realgar post-dates the crystallization of quartz.

Textural relations suggest that barite and kaolinite formed contemporaneously. The temperature of barite-kaolinite intergrowths crystallization is unknown. Because of difficulties in separation of minerals filling joints, the polytype variety of kaolinite has not been determined.

Association of sulphides and barite-kaolinite can indicate the variation of chemical composition of mineralizing solutions. The origin of solutions is, however, unknown. It is possible to consider the migration of solutions from depth and their relations to magmatic phenomena, but also more local circulation and leaching of components from the flysch rocks can be accepted. Leśniak et al. (1999) determined that barite concretions of the Sub-Silesian unit in flysch

Carpathians can no longer be considered as of hydrothermal origin. Kaolinite-barite association can be formed during sandstones diagenesis. Detailed study of minerals filling joints as well as surrounding sandstones is needed for the determination of origin of solutions and conditions of mineral precipitation.

## References

- Gawel, A. 1970: Origin of realgar in the flysch deposits of the environs of Baligród (Middle Carpathians). *Mineralogia Polonica*, 1, 7–16.
- Kamiński, M. 1937: O minerałach arsenowych z fliszu karpackiego okolicy Leska. *Arch. Mineral.*, 13, 1–7.
- Kita-Badak, M. 1971: On arsenic mineralization in the vicinity of Baligród. [in Polish, English summary]. *Kwartalnik Geologiczny*, 15, 155–160.
- Leśniak, P.M., Łacka, B., Hladikova, J. & Zieliński, G. 1999: Origin of barite concretions in the West Carpathian flysch, Poland. *Chemical Geol.*, 158, 155–163.
- Migdisov, A.A. & Bychkov, A.Y. 1998: The behaviour of metals and sulphur during the formation of hydrothermal mercury-antimony-arsenic mineralization, Uzon caldera, Russia. *J. Volcanol. Geothermal Research*, 84, 153–171.
- Ostrowicki, B. 1958: Novel ore-bearing minerals in the region of Baligród (Middle Carpathians). [in Polish, English Summary]. *Kwartalnik Geologiczny*, 2, 644–651.
- Pokrovski, G., Gout, R., Schott, J., Zotov, A. & Harrichoury, J.C. 1996: Thermodynamic properties and stoichiometry of As(III) hydroxide complexes at hydrothermal conditions. *Geochim. Cosmochim. Acta*, 60, 737–749.
- Ślaczka, A. 1958: Notes on the geological position of mineral ores in the region of Baligród (Middle Carpathians). [in Polish, English summary], *Kwartalnik Geologiczny*, 2, 637–643.
- Świerczewska, A., Hurai, V., Tokarski, A. & Kopciowski, R. 1999: Quartz mineralization in the Magura nappe (Poland): A combined microstructural and microthermometry approach. *Geologica Carpathica*, 50, Spec. Issue, 174–177.