

Pickeringite from the Pieprzowe Mts. (the Holy Cross Mts., Central Poland)

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The Pieprzowe Mts., which constitute the eastern part of the Holy Cross Mts. (Central Poland), are considered a large complex of mid-Cambrian strata (Alexandrowicz 1972). In a 2-km long exposure of the Pieprzowe Mts succession, along the Vistula River bank near the town of Sandomierz, shales, quartz-mica shales, quartzites, sandstones, mudstones and conglomerates are outcropping. All shaly facies are enriched in pyrite. The occurrence of secondary minerals in the weathering zone of the mid-Cambrian shale formation in the Pieprzowe Mts. is known for an extended period of time. Differences in color efflorescence observed on the weathered surface were considered as alum incrustations; hence, the term “alum shale” has been used with reference to these rocks. The phase composition of fine-crystal aggregates was determined by Kuhl (1931). Based on observations under polarizing microscope, he interpreted them as a composition of mirabilite, epsomite and alunogen, thus contradicting his earlier hypothesis about pickeringite occurrence.

Pickeringite is a sulphate mineral owing its origin to oxidation of pyrite in low pH conditions (Kruszewski 2013) and is a member of the halotrichite group with theoretical formula $MgAl_2(SO_4)_4 \cdot 22 H_2O$. However, chemically pure pickeringite is rare as most of its occurrences form transitional phases between pickeringite and halotrichite (Parafiniuk 1991). This mineral is usually observed in aggregates with other sulphates; the most common association consists of alunogen

and epsomite. Crystallization and preservation of pickeringite depend on air humidity, which results from its high solubility in water (Balcerzak et al. 1992, Parafiniuk 1991). The aim of this study is to describe conditions of pickeringite crystallization in the weathering zone of the Pieprzowe Mts. shale formation.

SEM-EDS analysis made it possible to detect three types of sulphide minerals occurring within aggregates. The most common is pickeringite forming elongated crystals with smooth surfaces, which demonstrate absence of dissolution processes. Fibers of pickeringite are associated with a mineral of tabular shape named alunogen – $Al(SO_4)_3$. Epsomite was detected in subordinate quantities. XRD analysis confirmed the polymineral character of efflorescences. The main reflex for pickeringite (ca. 4.80 Å) is fragmented into two peaks: (1) 4.8061 Å and (2) 4.7958 Å. These values are reduced as compared to ICDD data, which could result from admixtures of other sulphates, alunogene and epsomite. Another options is that this reduction means that pickeringite is forming transitional phase into halotrichite, which has its maximum reflex at 4.81 Å. This could be confirmed by chemical composition (Fe impurities).

The Pieprzowe Mts. shale formation presents specific conditions favouring evaporation of pickeringite. The elements required for pickeringite crystallization originate from the host rocks. The source of Al^{3+} could be kaolinite, which is common as a product of alteration processes as well

as an authigenic compound. Processing of micas transformation causes environmental enrichment in Mg^{2+} . The published sources indicate that the presence of pyrite is a key-factor for pickeringite crystallization. However, this mineral is also typical for shales present in the Carpathian rock units, where as a product of pyrite oxidation jarosite and gypsum are common. This suggests that some other initiator is required for the formation of pickeringite. It has been suggested that surface evaporation of groundwater causes the precipitation of sulphates (Cody & Briggs 1973 vide Parnell & Roderic 1982). The Pieprzowe Mts. shale formation contains dense network of veins so it is possible that waters from deeper layers are able to migrate into the subsurface. Some documented occurrences of pickeringite are related to arid regions. Certainly, an important role is played by humidity – southern exposure and poor plant cover of the Pieprzowe Mts. could be the reason why pickeringite may not only crystallize but also exist there. Most of the pickeringite occurrences in Poland are associated with rocks of old units (mid-Cambrian in age in the Pieprzowe Mts., Proterozoic in Wieściszowice and in Krobica quarry). Older rocks are poor in carbonates so it could mean that pH is a more important factor conditioning pickeringite crystallization than pyrite occurrence. Pickeringite was found also on burning coal-mining dumps in the Upper Silesian Coal Basin (Kruszewski 2013), what confirm that pH determines crystallization of this mineral. Correlation between pickeringite and other sulphates

is also interesting. Alunogen associated with pickeringite crystallize when the delivery of Mg^{2+} is reduced. Paragenesis consisting of alunogene, epsomite and pickeringite could be a result of different solubility of these phases or changing of Mg^{2+} and Al^{3+} ions during evaporation processes. The following sequence of crystallization is proposed: alunogene-pickeringite-epsomite.

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