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Maldonite (Au_2Bi) from hydrothermal U-As mineralization near Henclová (Spišsko-gemerské rudohorie Mts., Western Carpathians): the first occurrence in Slovakia

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Abstract

In Slovakia, maldonite was identified in the hydrothermal vein with U-sulphidic ore mineralization near Henclová village (Gelnica district) in the Spišsko-gemerské rudohorie Mts. (Vlachovo Formation, Gemeric Unit). It is the first occurrence of this mineral in Slovakia. Mineralization is developed in a hydrothermal quartz-chlorite (± fine grained white mica) vein with abundant arsenopyrite and minor quantities of uraninite, gersdorffite, löllingite, galenobismutite, bismuthinite, maldonite, bismuth and gold. Maldonite forms irregular grains up to 12 μm in size embedded in arsenopyrite, or extremely fine capillary veinlets in it. An intergrowth of maldonite with bismuthinite was rarely also observed. The chemical composition of maldonite is relatively monotonous, its average empirical formula can be expressed as $(Au_{1.79}Fe_{0.15})_{\Sigma 1.94}(Bi_{0.98}As_{0.02}S_{0.04})_{\Sigma 1.04}$. Microstructural relationships of ore minerals suggest that maldonite precipitated in the final stages of ore mineralization, when the temperature of the system decreased (after the crystallization of sulphoarsenides and löllingite).

Key words: *maldonite, hydrothermal vein U-sulphidic mineralization, Gemeric Unit, Western Carpathians.*

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Introduction

In general, gold frequently occurs in the Slovakia. In today's picture of the geological structure of the Slovak part of the Carpathians, it occurs in greater or lesser (even accessory) quantities in almost all Paleoalpine (Triassic - Upper Cretaceous) tectonic units, or Neoalpine (Paleogene - Recent) post- tectonic sedimentary and volcanic formations (Bakos et al. 2017).

On the other hand, occurrences of mineral phases that contain gold in their structure, sulphides, tellurides or alloys of gold with metals (other than Ag) are relatively rare. According to the Mindat database (www.mindat.org), several gold-bearing mineral phases have been detected in Slovakia (Table 1). Such minerals also include the natural alloy of Au and Bi - maldonite (Au_2Bi), which was not known here until now.

Maldonite was first described in 1870 (Ulrich 1870) at the Nuggety Reef deposit near Maldon (Australia). The Mindat database (maldonite - www.mindat.org) indicates 116 locations of this mineral in the world. Maldonite is found mainly in microscopic quantities, so despite the relatively large number of locations, it can still be considered a rare mineral. It occurs in various genetic types of ore deposits and in different geological environments. Many occurrences of mineralization with maldonite occur directly in granitoid bodies (*Butarny gold deposit, Russia* - Volkov et al. 2013), but mainly in endo- and exocontacts of granitoid intrusions, or in porphyry systems (Ulrich 1870; *Shotgun, Alaska, USA* - Rombach, Newberry 2001; *Maldon, Australia* - Ciobanu et al. 2010; *Morila, Mali*- McFarlane 2011; *Lugokan, Russia* - Redin et al. 2015; *Xiayingfang, China* - Li et al. 2022). For exocontacts of intrusions, the occurrence of maldonite is typical in skarn type of mineralization (in Fe-Mg-Al silicate rocks) or in marbles (*Lucky Draw, Australia* - Sheppard et al. 1995; *Bhukia, India* - Golani et al. 1999; *Río Narcea gold belt, Spain* - Cepedal et al. 2006). Maldonite was more rarely found in submarine-exhalation type of ore mineralization (massive sulfides; *Escanaba Trough, northeast Pacific* - Törmänen, Koski 2005) or in shear zone related vein mineralizations (*Złoty Jar, Poland* - Mikulski 1996; *Guelb Moghrein, Mauritania* - Kolb et al. 2006; *Viceroy Mine, Zimbabwe* - Oberthür, Weiser 2008). Through the weathering of primary mineralized hydrothermal structures, together with other resistant minerals, maldonite reaches the placers (*Horská Kvilda, Czech Republic* - Šrein et al. 2008).

This short contribution is dedicated to the first description of maldonite in the Western Carpathians area.

Location and a current status of occurrence

The studied occurrence of hydrothermal vein U-sulphidic mineralization is located approximately 0.9 km

NW of the church in Henclová village (Gelnica district). The occurrence/prospect is located on the right, the north-oriented slope of the Henclová Brook valley, at an altitude of 809 m a. s. l., approximately 780 m to the ESE from the elevation Uherčíková (1066 m a. s. l.). Geographical (WGS) coordinates of the occurrence are 48.79005° E; 20.58122° N. Directly on the site, one can currently see a trench of an exploited quartz lens with sulphides (E - W direction, subvertical arrangement, length approx. 5 m, estimated maximum thickness about 30 - 40 cm; based on the debris fragments in the vicinity). The host rock is rhyolite metatuff (Early Palaeozoic). The vein was also explored about a 10 m beneath from the surface outcrop by a short, now collapsed exploration adit (Fig. 1a, b); however, the vein structure at the adit level was not reached.

Geological setting and mineralogy

The surroundings of the studied occurrence are built by rocks of the Vlachovo Formation (Lower - Middle Silurian) of the Gelnica Group of Gemeric Unit (Fig. 2). The Gelnica Group is a several thousand meters thick Early Palaeozoic volcanosedimentary (rhyolite-dacite volcanism) complex (Snopko, Ivanička, 1978; Ivanička et al. 1989). The Vlachovo Formation consists mainly of rhyolite metatuffs and various metasediments (mainly sericitic, quartz-sericitic and sericitic-graphitic phyllites) with interbeds of sandstones, conglomerates metawackes, carbonates and lydites. Grecula et al. (2009, 2011), divide the original Vlachovo Formation into the Betliar and Smolník formations. The authors of this work adhere to the concept of the authors Snopko, Ivanička (1978) and Ivanička et al. (1989) for the geology of the Gemeric Unit.

Table 1 *Identified gold-bearing minerals in Slovakia (as of July 2024)*

mineral	formula	Au (wt. %)	locality	references
aurostibite	$AuSb_2$	44.72	Zlatá Idka*	Pršek, Lauko (2009)
			Rochovce*	Radková et al. (2019)
petrovskaite	AuAgS	58.06	Hodruša-Hámre	Kubač et al. (2018)
			Nová Baňa	Majzlan et al. (2018)
petzite	Ag_3AuTe_2	25.39	Hodruša-Hámre	Kubač et al. (2018)
			Kremnica	Ďuďa (1993)
			Zlatá Baňa	Ďuďa, Baláž (2001)
sylvanite	$AgAuTe_4$	34.36	Smolník*	Koděra at al. (1986 - 1990)
			Zlatá Baňa	Ďuďa, Baláž (2001)
uytenbogaardtite	Ag_3AuS_2	33.69	Banská Belá	Berkh et al. (2014)
			Hodruša-Hámre	Vlasáč et al. (2021a)
			Nová Baňa	Majzlan et al. (2018)
			Rudno nad Honom	Vlasáč et al. (2021b)
			Kremnica	Števko et al. (2018)
			Vyhne	Vlasáč et al. (2021a)
auropolybasite	$Ag_{15}AuSb_2S_{11}$	8.17	Nová Baňa	Mikuš et al. (in press)

* sites outside the Neogene volcanics, in the Palaeozoic and Mesozoic rocks

Fig. 1 *Remains of the survey on U ores near Henclová. A trench after an exploited quartz vein with U mineralization (a), undermined by a collapsed exploration adit (b). Photo: R. Kopáčik (2022).*

The mineralogy of the occurrence was previously studied (without any microprobe analyses) one only by Varček (1977), who characterized it as a uranium-sulphidic type of ore mineralization. The main vein filling is represented by quartz with clusters of chlorite and muscovite (var. *sericite*), abundant arsenopyrite and uraninite, accompanied by minor amounts of brannerite and rutile. In addition, unspecified Ni, Co and Bi accessory minerals are also present here. Uraninite has high values of microhardness (H_{VHN}; without giving specific values), which, together with the present association of minerals, indicates the higher temperature nature of this mineralization.

Methods

Samples with maldonite were taken in the field with a SGR scintillation radiometer, at a measurement range of 400 - 3000 KeV and a measurement frequency of 0.2 s. Microscopic properties of individual mineral phases and their mutual relations, were observed in both the transmitted and a reflected light using a Nikon ECLIPSE LV 100 POL polarizing microscope and a Nikon DS-Fil digital

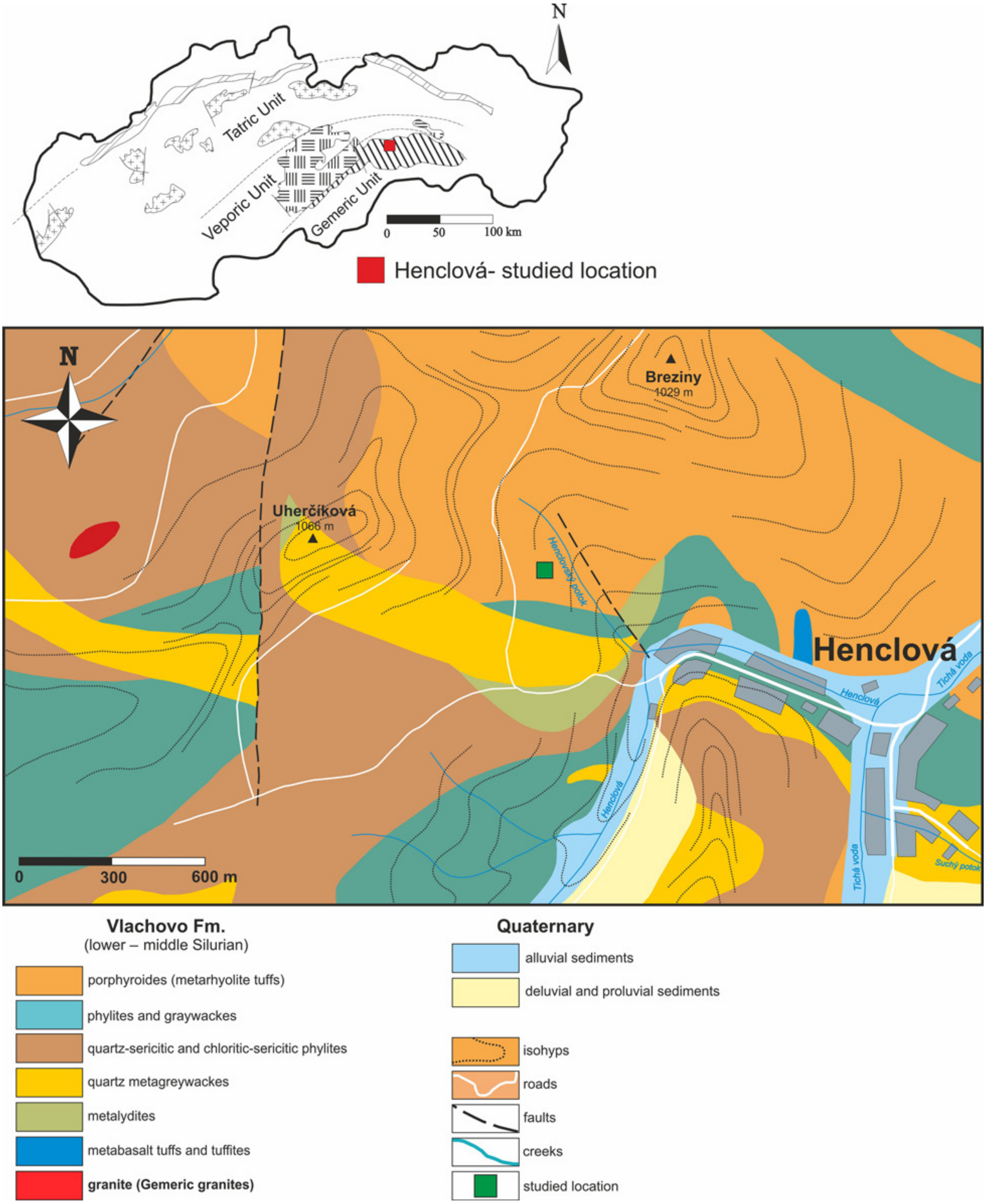

Fig. 2 *Geological map of the studied occurrence surroundings (adapted from Bajaník et al. 1984).*

camera (Matej Bel University, Banská Bystrica).

The chemical composition of maldonite was quantitatively studied using a JEOL JXA-8530 electron microprobe (Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica). In addition to point wave dispersion microanalyses (WDS), the microanalyzer was also used for photodocumentation in backscattered electrons (BSE). Microanalyses were obtained under the following conditions: accelerating voltage 20 kV, measuring current 20 nA. The diameter of the electron beam was in the range of 1 - 2 μm, ZAF correction was used. The following natural/synthetic standards and their spectral lines were used: S (*K*α) - baryte, Se (*L*β) - Bi_2Se_3, As (*L*α) - GaAs, Cu (*K*α) - cuprite, Fe (*K*α) - olivine, Sb (*L*α) - stibnite, Bi (*M*α) - Bi_2Se_3, Ag (*L*α) - Ag and Au (*M*α) - Au. The detection limit for individual elements ranged from 0.01 to 0.08 wt. %. Elements whose content values are below the detection limit are not included in the following text or in the table.

Results

Mineralogical characteristic of vein material

Ore mineralization near Henclová is developed in a quartz-chlorite vein with abundant arsenopyrite (Fig. 3). The main gangue mineral is compact, coarse-grained, gray (weakly limonitized), mostly anhedral quartz I, with occasionally observed hexagonal cross-sections of euhedral crystals. Quartz I is distinctly undulose, with frequent pressure lamellae. More rarely, veinlets of younger, fibrous quartz II were observed. Fine-grained white mica (*sericite*) and clusters of tabular chlorites (up to 1 - 2 cm in size) are wide spread in the quartz.

The most abundant macroscopic ore mineral in the gangue is arsenopyrite, which forms massive fain-grained aggregates (up to 10 cm in size) of euhedral to anhedral grains. Macroscopically visible uraninite globules has only rarely been found (it is relatively abundant in microscopic amounts; it occurs in both quartz and arsenopyrite). Mineralization is irregularly distributed in the vein. Zones of quartz alternate with zones of sulphides, or chlorites. Microscopic quantities of gersdorffite, löllingite, galenobismutite, bismuthinite, maldonite, bismuth and gold were also detected.

Maldonite

Maldonite belongs to the very rare, even unique mineral phases in the studied site. It occurs most often in the form of irregular grains up to 12 μm in size embedded in arsenopyrite, or it forms extremely fine capillary veins in it (Fig. 4a). Intergrowth of maldonite with bismuthinite was also rarely observed (Fig. 4b).

The chemical composition of maldonite is relatively monotonous (Table 2). Of the impurities, Fe is the most important (mean 0.15 *apfu*). However, its increased content is apparently not caused by contamination from the underlying arsenopyrite. This is evidenced by the low contents of As (on average 0.02 *apfu*) and S (on average 0.04 *apfu*). The average empirical formula of maldonite from Henclová (4 WDS analyses) can be expressed as $(Au_{1.79}Fe_{0.15})_{\Sigma1.94}(Bi_{0.98}As_{0.02}S_{0.04})_{\Sigma1.04}$.

Fig. 3 Mineralized quartz-chlorite vein with abundant grey arsenopyrite (typical appearance). Photo: Š. Ferenc.

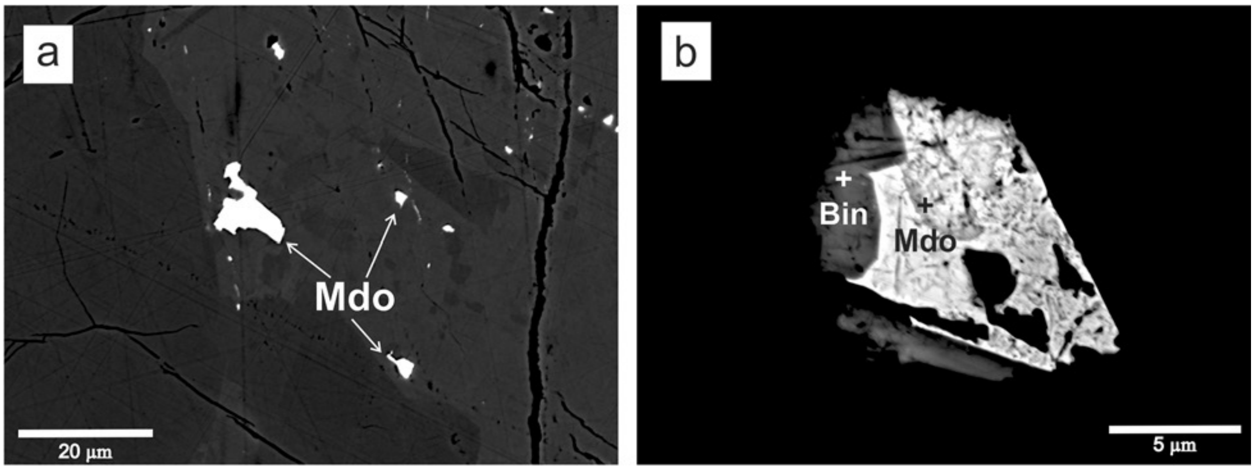

Fig. 4 *Maldonite (Mdo) in arsenopyrite (dark; a), rarely intergrowth of maldonite (Mdo) with bismuthinite (Bin; black is arsenopyrite, b). BSE images, photo: T. Mikuš.*

Table 2 *Chemical composition of maldonite from Henclová*

anal.	1	2	3	4	mean
Au	61.59	61.87	61.69	60.69	61.46
Ag	0.03	0.02	0.02	0.04	0.03
Fe	1.52	1.48	1.62	1.25	1.47
As	0.30	0.19	0.35	0.28	0.28
Sb	0.09	0.05	0.12	0.09	0.09
Bi	35.16	35.47	35.04	37.01	35.67
S	0.16	0.23	0.26	0.34	0.25
Se	0.15	0.00	0.00	0.01	0.04
Σ wt. %	98.98	99.32	99.12	99.71	99.28
apfu					
Au	1.805	1.810	1.793	1.767	1.794
Ag	0.002	0.001	0.001	0.002	0.001
Fe	0.157	0.153	0.166	0.128	0.151
Σ Cat.	1.963	1.964	1.960	1.897	1.946
As	0.023	0.015	0.027	0.022	0.021
Sb	0.004	0.003	0.006	0.004	0.004
Bi	0.971	0.978	0.960	1.015	0.981
S	0.028	0.041	0.047	0.061	0.044
Se	0.011	0.000	0.000	0.001	0.003
Σ An.	1.037	1.036	1.040	1.103	1.054

atomic proportions were calculated on the basis of 3 atoms

Discussion and conclusions

In Slovakia, maldonite was first found in the frame of hydrothermal vein U-sulphidic mineralization in Early Palaeozoic rhyolite metatuffs of the Gemeric Unit. It occurs here strictly in arsenopyrite, it was also rarely found overgrown with bismuthinite (Fig. 4a, b). Gold minerals are very rare in Slovakia. From the overview in Table 1, it is clear, that most locations with gold-bearing minerals are connected to epithermal hydrothermal systems related to Neogene volcanism. As for occurrences in Palaeozoic and Mesozoic rocks: Zlatá Idka (Pršek, Lauko 2009) and Smolník – Spišská baňa deposits represent aurostibite occurrences within metamorphic-hydrothermal quartz--stibnite vein mineralization related to the Alpine shear zones (Hurai et al. 2008); in the case of Rochovce site (Radková et al. 2019), the connection of mineralization with aurostibite to the hydrothermal systems in the vicinity of Cretaceous granite body (Rochovce granite) is obvious (mineralization of granitoid intrusion exocontact). The occurrence at Henclová has the same geological (not timing) position like Rochovce. The apophyse of the Permian (Gemeric) S - type granite rises to the surface about 1.2 km to the W of the studied locality, but according to the data of Šefara et al. (2017), the roof of the Gemeric granite pluton in the given location is located at an altitude of about 500 - 600 m, i.e., at a depth of 200 - 300 m below the studied occurrence (or below the current surface). Based on this position, it is possible to consider the hydrothermal influence of Gemeric granite on the overlying rocks ("granite", "perigranitic" or "intrusion" related type of vein U deposits; sensu Ruzicka 1993). In situ dating of uraninite by CHIME proved the contemporarity of hydrothermal vein U-Mo-(Pb, Bi, Te) mineralization in the Majerská dolina near Čučma with the Permian Gemeric granites (Ferenc et al. 2021), as well as the uraninite in U-sulphidic mineralization at Henclová (authors' unpublished data). For this reason, within the detailed study of origin of ore mineralization at Henclová, it is possible to consider the model in the sense of Rojkovič (1997) and Rojkovič et al. (1997, 1999). These authors consider hydrothermal U-Au±REE mineralization in the Gemeric unit as a Hercynian (although without any dating), whereby the Permian Gemeric granites presumably provided fluids and thermal energy. The hydrothermal effect of granites could have caused a mobilization of P, REE and U from the surrounding Lower Paleozoic graphitic phyllites, metalydites (both types of rocks are present at the studied locality) and metaphosphates, and a subsequent concentration of these elements in the hydrothermal veins. Based on the microstructural relationships of ore minerals, it can be assumed that maldonite precipitated in the final stages of mineralization, when the temperature of the system decreased (after the crystallization of sulphoarsenides and löllingite). According to the phase diagrams, the Au_2Bi alloy is stable in the temperature range of 371 - 116 °C (Massalski et al. 1986), but in nature, maldonite is metastable (under certain conditions, it can also exist below 116 °C).

The presented contribution documents the first occurrence of maldonite - Au_2Bi within hydrothermal vein U-sulphidic, granite-related mineralization near Henclová. The authors hope that they have contributed at least a little to the expansion of knowledge about the mineralogy of gold and gold-bearing minerals in the area of the Slovak part of the Carpathians.

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