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New data on minerals of the hidalgoite-philipsbornite series from the Guatomo mine near Tham Thalu, Yala Province (Thailand)

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Abstract

The chemical composition of three samples of minerals of the hidalgoite-philipsbornite series from the central part of the Guatomo mine pit was studied in detail by EMPA-WDS. They form yellowish-green, light green to pale blue microcrystalline crusts or hollow pseudomorphs after prismatic hexagonal crystals of mimetite in fractures of strongly altered granite or quartz. All studied samples show relatively strong, irregular to oscillatory chemical zoning in BSE, caused by S *versus* As substitution on *T*-site. Most of the zones are corresponding to hidalgoite, with only minor, outer zones represented by S-rich philipsbornite. Besides of dominant contents of Pb, Al, As and S also minor amounts of K (up to 0.11 *apfu*), Na (up to 0.05 *apfu*), Cu (up to 0.22 *apfu*), Fe (up to 0.09 *apfu*) and P (up to 0.04 *apfu*) were detected in studied samples.

Key words: *hidalgoite, philipsbornite, alunite supergroup, supergene minerals, chemical composition, Guatomo mine, Tham Thalu, Thailand*

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Introduction

The Guatomo lead-tin mine in southern Thailand is considered as one of the classic localities of mimetite worldwide. A very little was known about this locality as a source of fine mineral specimens before the late 1990s when Italian mineral collectors Marco P. Sacchi and Danilo Bernasconi visited this mine and collected several hundreds of excellent mimetite specimens (Bode 1998; Sacchi 2017). Sacchi (2017) described except of mimetite also abundant presence of Pb dominant members of the alunite supergroup, which were tentatively identified by Raman spectroscopy as philipsbornite and segnitite, but were never analysed quantitatively.

In this short paper, we present new quantitative data on chemical composition of three samples of minerals of the hidalgoite-philipsbornite series from the Guatomo mine, which were collected by the first author (MŠ) during the detailed geological mapping of the mine site in May/June 2019.

Geological setting and occurrence

The Guatomo open-pit mine is located next to the Buddhist temple Wat Tham Thalu, around 10 km west of Bannang Sata town, Yala Province, southern Thailand close to the border with Malaysia. GPS coordinates of the Guatomo mine are: 6°15'26.54'' N and 101°9'53.12'' E. Samples with minerals of the hidalgoite-philipsbornite series were collected in the central part of the Guatomo mine pit, very close to the area which Sacchi (2017) described as philipsbornite trench.

The Guatomo lead-tin mine (also known as Tham Thalu mine or The Great mine) was considered in 1880s as one of the richest ore deposits in the Thai-Malay Peninsula (King 2007). The deposit was primarily exploited by open-pit method with some minor exploration shafts and adits (Brown et al. 1951; Goodwin, Vimolset 1981; Sacchi 2017). Monthly production of low-grade Sn concentrate was 5 to 30 tons in early 1980s. The concentrate also contained up to 37% of cerussite and Pb-Sn alloy was produced during smelting (Goodwin, Vimolset 1981; Suthakorn 1992; Whitbread-Abrutat et al. 1999; Ridd et al. 2011). Mining ceased after the collapse of world tin prices in 1985 (Natchakunlasap 2004).

The Guatomo/Tham Thalu deposit is skarn type Pb-Sn deposit. Skarn orebodies are developed at the contact zone between intrusion of Jurassic-Triassic porphyritic biotite-rich granite and Permian Ratburi limestone, with extensive supergene zone/gossan developed at the subsurface parts of orebodies. The dominant primary minerals are magnetite, garnets, cassiterite, arsenopyrite and pyrite. Galena was mostly completely replaced by cerussite or minor anglesite and goethite is principal mineral in gossan zone (Goodwin, Vimolset 1981; Suthakorn 1992; Whitbread-Abrutat et al. 1999; Malaysian-Thai Working group 2009; Ridd et al. 2011). Sacchi (2017) except of frequent mimetite described also other supergene minerals like carminite, cesàrolite, philipsbornite, plattnerite and segnitite. Števko et al. (2020) recently published detailed study of chemical composition of various morphological types of mimetite, some of them turned to be pyromorphite. They also provided brief description of other supergene minerals such as cerussite, anglesite or plattnerite and mentioned presence of malachite and linarite.

Analytical methods

Paragenetic and textural relationships as well as chemical zoning of minerals of the hidalgoite-philipsbornite series were studied in BSE mode using a JEOL JXA-8530FE electron microprobe (Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica, Slovak Republic).

The chemical analyses of minerals of the hidalgoite-philipsbornite series were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic) operating in the wave-dispersive (WDS) mode (15 kV, 5 nA and 3 to 5 µm wide beam). The following standards and X-ray lines were used to minimize line overlaps: albite (Na*K*α), apatite (Ca*K*α, P*K*α), baryte (Ba*L*α), Bi (Bi*M*α), celestine (Sr*L*β, S*K*α), clinoclase (As*L*α), Co (Co*K*α), Cr_2O_3 (Cr*K*α), $CuFeS_2$ (Cu*K*α, S*K*α), diopside (Mg*K*α), halite (Cl*K*α), hematite (Fe*K*α), LiF (F*K*α), rhodonite (Mn*K*α), sanidine (Al*K*α, K*K*α, Si*K*α), scheelite (W*L*α), vanadinite (V*K*α), wulfenite (Pb*M*α, Mo*L*α) and ZnO (Zn*K*α). Contents of the above-listed elements, which are not included in the tables, were analysed quantitatively, but their contents were below the detection limit (ca. 0.03 - 0.05 wt. % for individual elements). Raw intensities were converted to the concentrations of elements using automatic "PAP" matrix-correction procedure (Pouchou, Pichoir 1985).

Results

Minerals of the hidalgoite-philipsbornite series occur in fractures of strongly altered granite or hydrothermal quartz veins, often associated together with mimetite. They form yellowish-green, light green to pale blue microcrystalline crusts or hollow pseudomorphs after prismatic hexagonal crystals of mimetite (Figs. 1-2). All three studied samples of minerals of the hidalgoite-philipsbornite series

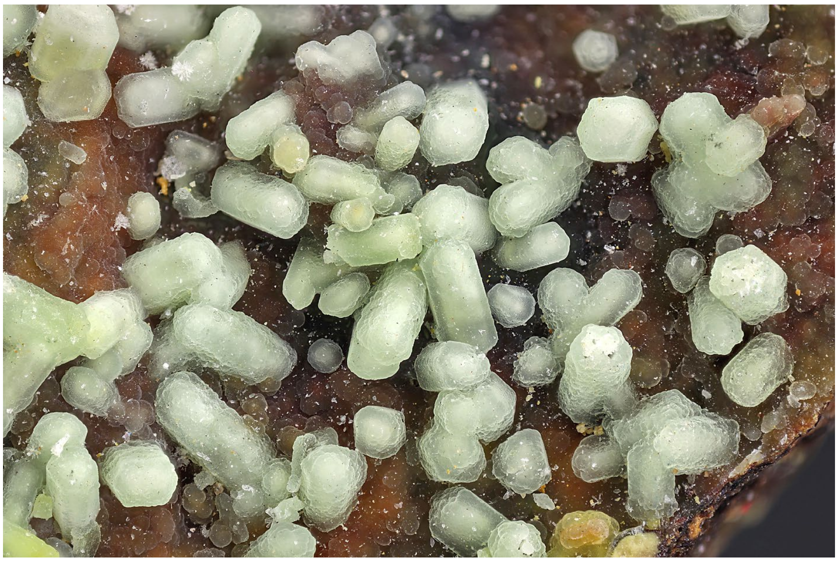

Fig. 1 *Pale green microcrystalline pseudomorphs of minerals of the hidalgoite-philpsbornite series after mimetite crystals. Field of view is 5.3 mm. Photo by L. Hrdlovič.*

Fig. 2 *Pale green microcrystalline pseudomorphs of minerals of the hidalgoite-philpsbornite series after mimetite crystals. Field of view is 5.4 mm. Photo by L. Hrdlovič.*

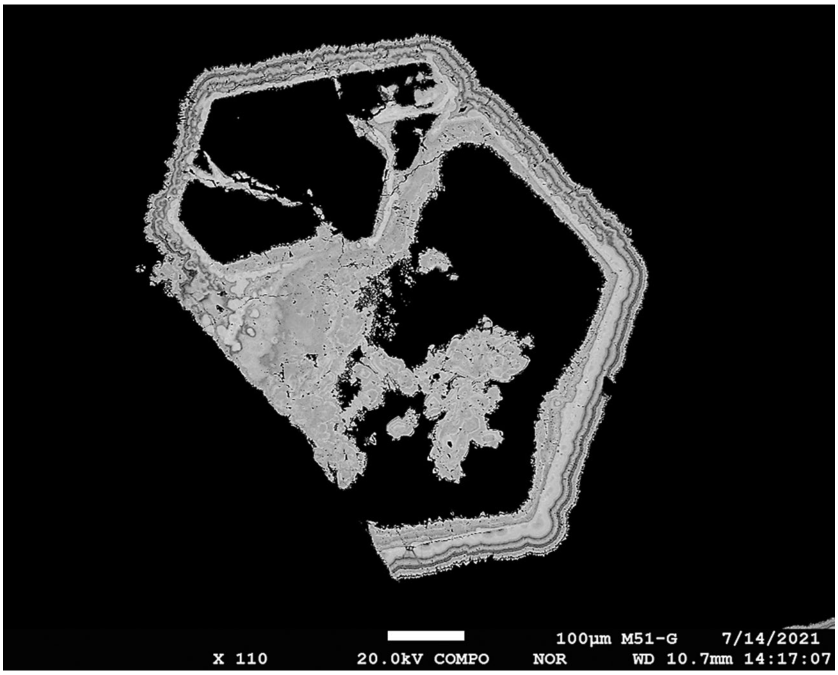

Fig. 3 *Cross section through a hollow pseudomorph of minerals of the hidalgoite-philipsbornite series after hexagonal crystals of mimetite. BSE image by T. Mikuš.*

from the Guatomo mine show relatively strong, irregular to oscillatory chemical zoning in BSE (Figs. 3-5).

The members of the hidalgoite-philipsbornite series represent a small part of the large supergroup of compounds with alunite-type structure. The chemical composition of minerals of the alunite supergroup can be expressed by the general formula $AB_3(TO_4)_2X_6$, where *A*-site is occupied by monovalent (Na^+, K^+, Ag^+, Tl^+, NH_4^+ or H_3O^+), divalent (Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} or Hg^{2+}) or trivalent (Ce^{3+}, La^{3+}, Nd^{3+} or Bi^{3+}) or tetravalent (Th^{4+}) cations or vacancy. The *B*-site is occupied by divalent (Cu^{2+}, Zn^{2+}, Mg^{2+}), trivalent (Al^{3+}, Fe^{3+}, V^{3+}, Cr^{3+} or Ga^{3+}) and tetravalent (Sn^{4+}) cations, *T*-site can be occupied by Si^{4+}, P^{5+}, As^{5+}, Sb^{5+}, S^{6+} or Cr^{6+}. The hydroxyl groups $(OH)^-$ dominate in the *X*-site over Cl^-, F^- or H_2O. Extensive substitutions/solid-solutions are known, especially on *A*-, *B*- or *T*-site. For $A^{2+}B^{3+}T^{5+}$ members of the alunite supergroup protonation of TO_4 anions is required (e.g. Scott 1987; Rattray et al. 1996; Jambor 1999; Kolitsch, Pring 2001; Sato et al. 2008; Mills et al. 2008; Sejkora et al. 2009; Bayliss et al. 2010; Mills

Fig. 4 *Detail on chemical zoning of minerals of the hidalgoite-philipsbornite series from the Guatomo mine. BSE image by T. Mikuš.*

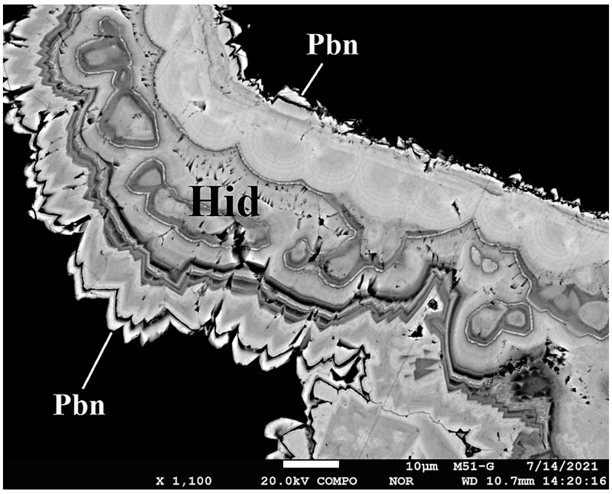

Fig. 5 *Detail on chemical zoning of minerals of the hidalgoite-philipsbornite series from the Guatomo mine. Majority of the aggregate is corresponding to hidalgoite (Hid) and only very thin, light outer zone is represented by S-rich philipsbornite (Pbn). BSE image by T. Mikuš.*

Table 1 *Chemical composition of minerals of the hidalgoite-philipsbornite series from the Guatomo mine (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Hid	Pbn	Pbn
Na_2O	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00
K_2O	0.00	0.68	0.00	0.61	0.42	0.00	0.19	0.79	0.00	0.00	0.39	0.00	0.00	0.65	0.23
PbO	35.83	33.13	35.48	34.02	33.12	38.46	36.57	29.44	36.92	36.45	32.70	36.79	36.39	33.06	37.17
CuO	1.49	1.41	2.66	1.50	0.44	0.64	2.34	1.52	0.60	0.56	1.07	1.32	0.66	0.39	0.47
Fe_2O_3	0.00	0.28	0.29	0.36	1.09	0.30	0.27	0.38	0.31	0.00	1.02	0.00	0.42	0.33	0.00
Al_2O_3	20.08	21.93	19.58	21.29	21.13	19.30	19.23	23.03	20.10	20.20	21.08	19.68	19.71	22.36	21.93
As_2O_5	20.59	17.46	18.23	20.50	16.89	23.11	16.76	14.64	22.04	24.82	16.06	21.21	22.70	26.24	27.90
P_2O_5	0.00	0.00	0.20	0.00	0.00	0.12	0.23	0.03	0.19	0.20	0.00	0.29	0.29	0.46	0.36
SO_3	9.25	14.05	11.22	11.40	13.65	7.03	12.23	15.03	8.09	6.53	13.64	9.09	6.42	5.27	4.20
total	87.24	88.94	87.66	89.88	86.74	88.96	87.82	84.86	88.25	88.76	86.18	88.38	86.59	88.76	92.26
Pb^{2+}	1.089	0.907	1.054	0.950	0.935	1.186	1.086	0.836	1.120	1.087	0.945	1.091	1.157	0.985	1.109
Na^+	0.000	0.000	0.000	0.040	0.000	0.000	0.000	0.000	0.000	0.000	0.046	0.000	0.000	0.000	0.000
K^+	0.000	0.088	0.000	0.081	0.056	0.000	0.027	0.106	0.000	0.000	0.053	0.000	0.000	0.092	0.033
Σ *A*-site	1.089	0.995	1.054	1.071	0.991	1.186	1.112	0.942	1.120	1.087	1.044	1.091	1.157	1.077	1.142
Al^{3+}	2.673	2.628	2.547	2.604	2.611	2.606	2.499	2.863	2.668	2.638	2.667	2.555	2.744	2.918	2.865
Fe^{3+}	0.000	0.021	0.024	0.028	0.086	0.026	0.022	0.030	0.026	0.000	0.083	0.000	0.038	0.028	0.000
Cu^{2+}	0.127	0.108	0.222	0.118	0.035	0.055	0.195	0.121	0.051	0.047	0.087	0.110	0.059	0.033	0.039
Σ *B*-site	2.800	2.757	2.793	2.749	2.732	2.687	2.716	3.015	2.746	2.685	2.836	2.665	2.840	2.978	2.904
As^{5+}	1.216	0.928	1.052	1.112	0.926	1.384	0.966	0.807	1.298	1.438	0.901	1.222	1.402	1.519	1.617
P^{5+}	0.000	0.000	0.019	0.000	0.000	0.012	0.021	0.003	0.018	0.019	0.000	0.027	0.029	0.043	0.034
S^{6+}	0.784	1.072	0.929	0.888	1.074	0.604	1.012	1.190	0.684	0.543	1.099	0.751	0.569	0.438	0.349
Σ *T*-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
OH^-	5.236	5.137	5.194	5.039	5.161	4.981	5.165	5.891	5.109	4.727	5.509	4.818	5.345	5.402	5.273

calculated empirical formulae are based on sum of (P+As+S)=2 *apfu*

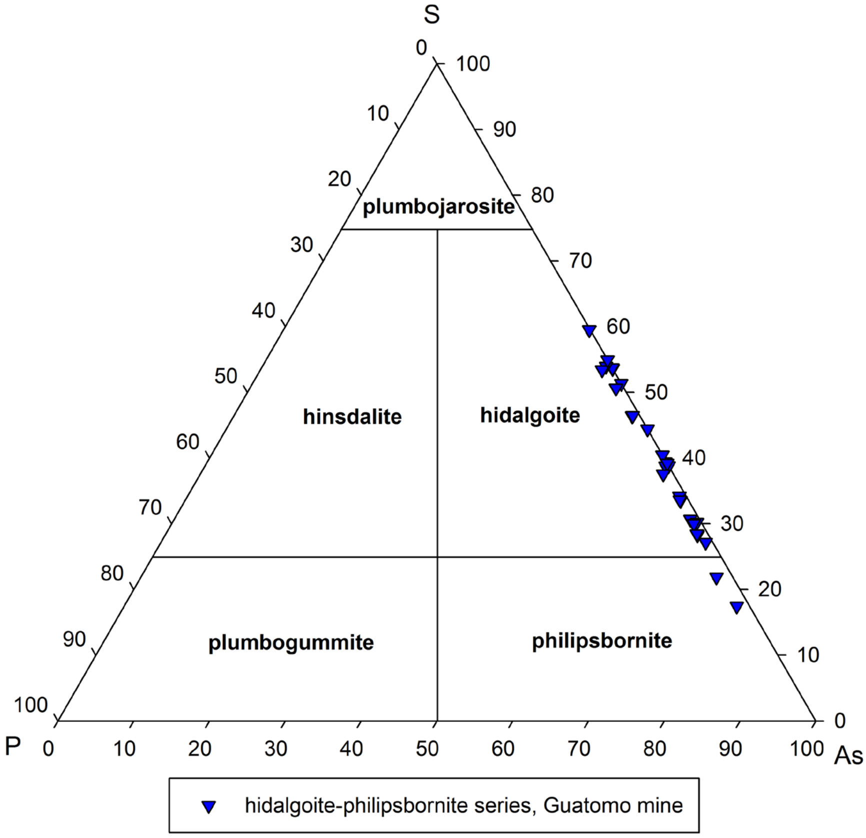

Fig. 6 *Chemical composition of minerals of the hidalgoite-philipsbornite series in ternary As-S-P diagram.*

et al. 2014; Vrtiška et al. 2019).

Representative chemical analyses of minerals of the hidalgoite-philipsbornite series from the Guatomo mine are shown in Table 1 (all 29 analyses are available in supplementary file). The *A*-site in the studies samples is almost exclusively occupied by Pb (ranging between 0.84 to 1.19 *apfu*), accompanied only by minor amounts of K (up to 0.11 *apfu*) and Na (up to 0.05 *apfu*). Aluminium is the dominant element on the *B*-site (ranging between 2.50 to 2.92 *apfu*) and it is substituted by minor amounts of Cu (up to 0.22 *apfu*) and Fe (up to 0.09 *apfu*). Chemical zoning observed in BSE is caused by relatively strong S *versus* As substitution on *T*-site (Fig. 6). The major parts of the zones/aggregates are represented by hidalgoite, with S contents ranging between 0.54 to 1.19 *apfu* and As contents ranging between 0.81 to 1.44 *apfu*. Only very thin, light external zones of aggregates are corresponding to S-rich philipsbornite, with S contents reaching up to 0.44 *apfu*. Minor amounts of P (up to 0.04 *apfu*) were also detected.

Conclusions

The chemical composition of three samples of minerals of the hidalgoite-philipsbornite series from the Guatomo mine was studied in detail. All three studied samples are compositionally corresponding to hidalgoite with only minor outer zones represented by S-rich philipsbornite.

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