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Precious and critical metal phases in the Agios Filippos high-sulfidation epithermal system, Kirki, Thrace, NE Greece

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Geologic setting

The Agios Filippos (Kirki) high-sulfidation epithermal deposit is located in Thrace, NE Greece, approximately 19 km to the NNW of Alexandroupolis city. The mineralization is hosted in the Eocene-Oligocene rock sequences of SE Evros county, and is associated to orogenic calc-alkaline to shosonitic magmatism as a result of subduction of the African plate below the Eurasian plate. The deposit is developed between two sub-parallel faults forming the western and the eastern part of the open pit (Skarpelis, 1999), and the low-grade ore body is hosted within a rhyolite dyke and the nearby hydrothermally altered volcano-sedimentary and sedimentary formations.

Sampling – Analytical methods

Drill core samples down to depths of approximately 180m from the surface were selected and used for the mineralogical investigation of primary epithermal mineralization, hydrothermal alteration assemblages and supergene mineral phases. Scanning electron microscopy was performed using a Jeol JSM 5600 scanning electron microscope combined with energy dispersive X-ray spectrometry (OXFORD ISIS Link electron microprobe) and equipped with a Jeol Analytical back-scattered electron detector at the Laboratory of Economic Geology and Geochemistry, Department of Geology and Geoenvironment, University of Athens. Operating conditions for the SEM were 20 kV accelerating voltage and 0.5 nA beam current. Counting time for each analysis was 50 sec, with 15-sec dead time.

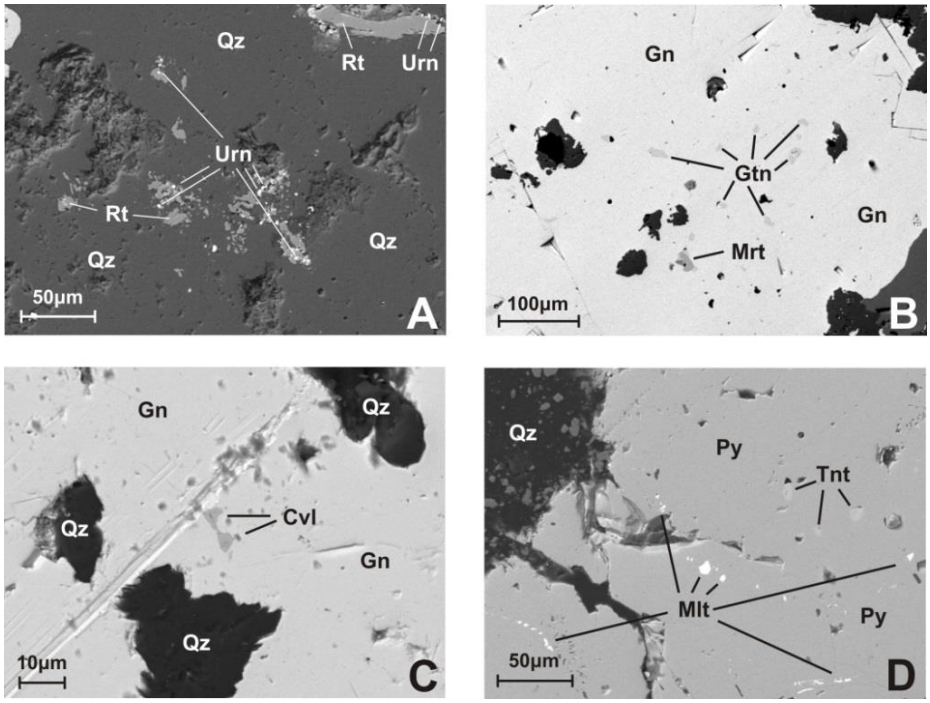

Figure 1. Back-scattered electron SEM images from the Agios Filippos high sulfidation epithermal system. A. Disseminated fine-grained uraninite (Urn) in association with anhedral rutile (Rt) in silicified host-rock. B. Anhedral gratonite (Gtn) and marrite (Mrt) inclusions in galena (Gn). C. Anhedral cervelleite (Cvl) inclusions in galena (Gn). D. Anhedral tennantite (Tnt) and matildite (Mlt) inclusions in pyrite (Py). Abbreviations for quartz, uraninite, rutile, galena, tennantite and pyrite after Whitney and Evans (2010).

Results and discussion

Uraninite (UO_2) is reported for the first time in the Agios Filippos epithermal system and is identified at the upper part of the deposit, forming disseminated subhedral to euhedral crystals with size ranging between 2 and 10 μm. Uraninite is associated to TiO_2, pyrite and barite in silicified to advanced argillic altered sectors of the deposit (Figure 1A). Marrite ($PbAgAsS_3$) is identified in samples from the upper part of the Agios Filippos deposit, and in particular within the rhyolite intrusion at the eastern part of the mineralized zone**,** forming anhedral inclusions within galena crystals (Figure 1B, Table 1). Cervelleite (Ag_4TeS) is also identified for the first time in the Agios Filippos epithermal system, and in particular in

samples from the upper - eastern part of the deposit where bedded acidic tuffs have suffered silicic to advanced argillic alteration. Cervelleite is mainly found forming inclusions in galena (Figure 1C, Table 1), and based on semi-quantitative SEM-EDS analyses shows enrichment in Sn (up to 5.4 wt%). In Greece, cervelleite type phases are also reported in the vein-hosted Panormos Bay system in Tinos (Spry et al., 2006). Matildite ($AgBiS_2$) is identified in samples from the lower sector of the Agios Filippos deposit, and within bedded acidic tuffs. Matildite forms anhedral inclusions with size ranging between 1 and 10μm within pyrite (Figure 1D, Table 1). The presence of cervelleite, marrite and matildite in the Agios Filippos epithermal system may indicate evolution from early high-sulfidation state to late intermediate sulfidation state (Baksheev et al., 2018; Mehrabi et al., 2016). Cuprobismutite ($Cu_{10}Bi_{12}S_{23}$) is identified at the lower sector of the Agios Filippos deposit, and within bedded acidic tuffs. Cuprobismutite forms anhedral inclusions within pyrite and is closely associated to matildite. Based on SEM-EDS analyses, cuprobismutite shows enrichment in Ag up to 4.6 wt% (Table 1). Besides primary critical and precious metal bearing phases, Ga-bearing beudantite [endmember chemical formula $PbFe_3(AsO_4)(SO_4)(OH)_6$] is identified at the upper part of the oxidation zone. In the Agios Filippos system, beudantite is fine grained and its composition varies showing enrichment in Ga, In and Sb. The Ga content of beudantite crystals analyzed from the Agios Filippos epithermal system ranges from 1.2 to 5.6 wt% (as Ga_2O_3), and in several occasions In is also detected, ranging from 0.7 to 1.2 wt% (as In_2O_3), whereas the Sb content of beudantite (as Sb_2O_5) ranges from 3 to 5.9 wt% (Triantafyllidis, 2006).

Table 1: Representative semi-quantitative SEM-EDS analyses (in wt%) of critical and precious metal ore phases from the Agios Filippos high-sulfidation epithermal system.

Phase	**S**	**Fe**	**Pb**	**Te**	**Cu**	**Ag**	**Sn**	**Bi**	**As**	**Total**
Matildite	16.09	1.65	n.d.	n.d.	n.d.	27.61	n.d.	55.06	n.d.	100.41
Cuprobismuthite	18.01	3.15	n.d.	n.d.	10.10	4.58	n.d.	63.98	n.d.	99.82
Marrite	19.01	n.d.	44.37	n.d.	n.d.	21.43	n.d.	n.d.	15.38	100.19
Cervelleite	5.85	n.d.	n.d.	21.51	n.d.	66.96	5.44	n.d.	n.d.	99.76
	Molecular proportions									**No of ions**
Matildite	1.91	0.11	-	-	-	0.97	-	1.00	-	4.00
Cuprobismuthite	22.45	2.25	-	-	6.35	1.70	-	12.24	-	45.00
Marrite	2.94	-	1.06	-	-	0.98	-	-	1.02	6.00
Cervelleite	1.08	-	-	0.99	-	3.66	0.27	-	-	6.00
n.d.: not detected										

The Agios Filippos deposit has been a target of exploitation for base metals (Pb, Zn and Cu), and only in recent years the presence of elevated concentrations of Critical and Precious Metals was revealed (Skarpelis, 1995; Voudouris et al., 2005). In this study, mineralogical investigation of drill core samples from the Agios Filippos epithermal system revealed the presence of rare and uncommon Critical and Precious metal bearing phases including uraninite, cervelleite, marrite, matildite and cuprobismutite (Figure 1, Table 1), that could provide further insights on the mode of formation of the Agios Filippos deposit and its correlation with the Northern Greece metallogeny, as well as further information on the Critical and Precious Metal potential of Greek mineral deposits and mineralizations.

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