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The first cave occurrence of orpiment (As_2S_3) from the sulfuric acid caves of Aghia Paraskevi (Kassandra Peninsula, N. Greece)

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Abstract:

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Orpiment, tamarugite and pickeringite occur in close association above the surface of thermal water cave pools in the active sulfuric acid caves of Aghia Paraskevi on the Kassandra peninsula, northern Greece. Gypsum also occurs as small interstitial crystals or encrustations. Orpiment is of high significance since it has not previously been reported as a cave mineral. In addition, tamarugite and pickeringite rarely occur in karst caves. Water from a borehole and a spring is of Na-Cl type and contains traces of CO_2 and H_2S . The B/Cl ratios indicate seawater participation with a possible mixing with geothermal water of meteoric origin. Oxidation of fumarolic H_2S and incorporation of seawater is a possible cause for the deposition of tamarugite. Orpiment accumulated from vapors under sub-aerial conditions at low temperatures in acidic conditions through an evaporation-condensation process. Fluid cooling and/or acidification of the solution resulting from H_2S oxidation were responsible for orpiment precipitation. Oxidation of H_2S to sulfuric acid dissolved the limestone bedrock and deposited gypsum.

Keywords: Greece, Aghia Paraskevi, hypogene caves, orpiment, tamarugite, pickeringite, gypsum

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INTRODUCTION

The active sulfuric acid caves of Aghia Paraskevi are located in the western part of Kassandra Peninsula in Chalkidiki, 100 km southeast of Thessaloniki (Fig. 1). They are related to a geothermal system known as the "Aghia Paraskevi thermal springs". Although these caves have been known for several decades, only limited studies concerning their origin were conducted. The first investigations by Sotiriadis (1969) concerned the thermal-water chemistry of the caves. This author suggested that the thermal water originated from seawater, which convected through a fault system. Sotiriadis (1969) and Sotiriadis et al. (1982) concluded that the caves were developed during an early karst event, before the formation of the Thermaikos Gulf graben (Fig. 1).

A new investigation of the Aghia Paraskevi area from the perspective of hypogene speleogenesis began in 2006 and is still in progress. Apart from the already known caves of the area, several other smaller caves

and cavities of interest have been found, either close to base level or in the vadose zone. In total, eight caves and cavities were discovered in Aghia Paraskevi. In two of these caves (WTG1 and WTG2, Fig. 1 and 2) the study of the mineralogy revealed that three samples (PAR-B1, PAR6, PAR7) contain orpiment (As_2S_3) associated with tamarugite $[\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$, pickeringite $[\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$ and gypsum $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$.

Orpiment is an arsenic sulfide and has a typical yellow and sometimes orange-yellow color. According to our knowledge it has not previously been documented in caves (C.A. Hill, P. Forti, B.P. Onac, personal communications, 2010). However other arsenic minerals have been found in karst settings, where they are mainly associated with low-temperature hydrothermal-geothermal environments.

Realgar (As_4S_4) has been reported from the Chauvai Hg-Sb ore deposit in Kyrgyzstan (Hill & Forti, 1997) and arsenolite and claudetite (As_2O_3) from Arizona, USA (Onac et al., 2007). In addition ten arsenates are known as cave minerals: arseniosiderite, beudantite, conichalcite, hörnesite, manganderzelitite, mimetite, olivenite, pharmacolite, strashimirite and talmessite (Hill & Forti, 1997; Onac et al., 2007).

This occurrence in the caves of Chalkidiki, Greece, is the first report of orpiment as a cave mineral.

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Fig. 1. Map of Greece with the Kassandra peninsula depicted (upper left corner). The Kassandra Peninsula and the study area (right upper corner). Geological sketch-map of the "Loutra of Aghia Paraskevi" area (lower), including the location of the caves, the thermal springs and the thermal-water borehole.

GEOLOGICAL SETTING

The Kassandra peninsula (Fig. 1) is part of the Vardar geotectonic zone of the internal Hellenides (Mountrakis, 2010). Sediments consist mainly of Neogene and Quaternary deposits with a thickness of about 500 m. At the southern part of the peninsula, Paleocene molassic sediments, including conglomerates and marls, overlie limestones and an ophiolite complex (Guy & Bornovas, 1969; Aidona et al., 2001).

The Aghia Paraskevi caves are located at the Loutra area, 3 km SW of the Aghia Paraskevi village, and are developed in strongly fissured and fractured *Calpionella* bearing limestones of Late Jurassic age (Guy & Bornovas, 1969). These limestones were unconformably deposited on top of the Mesozoic ophiolites of the Vardar zone, and are restricted in a narrow zone (150-200 m wide) along the steep coast (Fig. 1).

CAVES OF AGHIA PARASKEVI

Sulfuric acid speleogenesis is well known in several areas of the world (e.g., Gunn, 2004; Culver & White, 2005; Hose & Macalady, 2006; Ford & Williams, 2007; Klimchouk, 2007; Palmer, 2007). The Aghia Paraskevi area is considered to be an ideal example of sulfuric acid speleogenesis in Northern Greece coastal areas, due to the combination of active and relict hydrothermal caves. These caves were previously thought to have typical karst origin (Sotiriadis, 1969; Sotiriadis et al., 1982), but are now interpreted to be hypogene, related to the geothermal fields in the area. Caves located above base level comprise uplifted branches caused by rising thermal water.

In the Aghia Paraskevi area a total of eight caves or relict passages have been found. A "water table" group of three caves (WTG1-3) along the steep seacoast present thermal water cave pools, which are close to

the sea level. They display common morphological characteristics, such as pendants, cupolas and other small-scale solutional patterns (Fig. 1, 2). However, their entrances open at various altitudes, from 1 to 10 m asl. These water-table sulfuric acid caves are of ramifying horizontal pattern and the most typical indicators of the speleogenesis type in Aghia Paraskevi.

Orpiment-bearing samples presented in this study come from the larger two caves of this group (WTG 1 & 2, ~30 m and ~15 m of total passage length, respectively). It is noticeable that they are directly related to relict rising passages above the base level, indicating an uplifting movement of the cave-bearing limestone. Orpiment and the associated mineral assemblage form a layer up to 5 cm thick (Fig. 3a, b) covering part of the wall above the surface of the thermal cave pool. The occurrence covers an area more than one meter horizontally and less than one meter vertically. This is the only group of water-table caves that has been found in the area.

Apart from these caves, another group of three caves (QG1-3: "Quarry Group") is located to the east (Fig. 1) at about 25 m asl, in an abandoned quarry. Due to damages by the quarry works, only small sediment-filled passages are preserved, lined with calcite crystals or alunite deposited previously by the rising thermal water. These caves are vertically developed and fracture guided, forming well-shaped cupolas. They display a typical morphology originated from hypogene speleogenesis, below the water table.

A third group of two relict cavities in Aghia Paraskevi, a pothole and a horizontal one, is located at the top of the hill (BRCG 1 & 2; "Breakdown Relict Caves"). The pothole (Fig. 1; BRCG1) is about 10 m deep and forms a sinkhole due to cave ceiling collapse. Ceiling breakdown also forms the entrance of the horizontal cave (Fig. 1; BRCG2), which is partially filled by allochthonous clastic sediments and presents phreatic morphological features. The latter have been considered to be of supergene origin (Sotiriadis et al., 1982), but a hypogene speleogenesis seems more likely, considering the general evidence from the area and common morphological features, such as pendants, cupolas etc.

Fig. 2. Plan of the cave WTG1 (left). Plan, cross-sections, and longitudinal section of the cave WTG2. Location of samples PAR-6, PAR-7 and PAR-B1 are depicted on the cave plans.

SAMPLING AND ANALYTICAL METHODS

Three samples (PAR-B1, PAR6, PAR7) were collected from the caves (Fig. 2), focusing on those occurrences that contained multiple mineral phases. The samples were studied under a stereoscopic microscope to distinguish the various mineralogical phases in each sample. Powders of the samples were processed by X-ray diffraction (XRD). The XRD analyses were performed using a Philips PW1710 diffractometer with Ni-filtered CuK α radiation at the Department of Mineralogy, Petrology, Economic Geology, Aristotle University of Thessaloniki (A.U.Th), Greece. The counting statistics were: step size: 0.01° 2 θ , start angle: 3°, end angle: 63° and scan speed: 0.02° 2 θ /sec.

Chemical analyses were carried out in the Scanning Microscope Laboratory, A.U.Th., using a JEOL JSM-840A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) with 20 kV accelerating voltage and 0.4 mA probe current. Pure Co was used as an optimization element. For SEM observations, the samples were coated with carbon - to an average thickness of 200 Å - using a vacuum evaporator JEOL-4X.

For the purposes of this study, one water sample from the pool of the WTG1 cave was analyzed for arsenic content. The water sample was collected in a 1 L polyethylene bottle and preserved at low temperature during transportation. The concentration of As was determined by inductively coupled plasma mass spectrometry (ICP-MS), at the Agro Lab in Thessaloniki, Greece.

WATER CHEMISTRY

The water chemistry in the area of Aghia Paraskevi was evaluated for a better understanding of the hydrological context of the caves. For this reason two water analyses were used: one of a sample from the thermal cave pool of WTG1 cave (Lambrakis & Kallergis, 2005), and one of a sample from a borehole at the “Aghia Paraskevi thermal springs” provided by the Municipal Company of the Aghia Paraskevi Baths (DELAP) and performed by the Institute of Geology and Mineral Exploration of Greece (IGME).

On the basis of major ion data plotted on the Piper diagram (Fig. 4), the water from the borehole and from the spring is of Na-Cl type (Table 1) with concentrations of 10,994 mg L⁻¹ (Na⁺) and 19,467.54 mg L⁻¹ (Cl⁻). Boron (B) concentration is 12.5 mg L⁻¹ in the borehole water sample and 43 mg L⁻¹ in the spring water (Sotiriadis, 1969). The ratio B/Cl is 6.6x10⁻⁴ for the borehole water and ~22x10⁻⁴ for the spring water, whereas seawater has a value of 2x10⁻⁴. This may indicate seawater participation with a possible mixing with geothermal water of meteoric origin (Herrmann et al., 1973).

Table 1. Physical parameters of the Aghia Paraskevi waters. The water type is based on the chemical analyses in the references cited (Sotiriadis, 1969; I.G.M.E.-DELAP)

Locality	pH	T °C	TDS mg L ⁻¹	Water type	Reference
Spring	7.00	39.0	36.183	Na-Cl	Sotiriadis (1969)
Spring	6.35	39.2	35.964	Na-Cl	I.G.M.E.-DELAP
Spring2	6.45	35.0	38.600	Na-Cl	I.G.M.E.-DELAP
Borehole	6.88	-	43.521	Na-Cl-F	I.G.M.E.-DELAP

Fig. 3. Sampling site and samples of orpiment and associated minerals from Aghia Paraskevi caves a. Cave wall covered by orpiment above the water table; b. Cave wall covered by orpiment; c. Orpiment (orp) intergrown with tamarugite (tam); d. Fibrous pickerite (pick) associated with orpiment (orp).

Dotsika et al. (2006) recognized two main groups of thermal waters with respect to boron and chloride in Greece. The elevated boron concentration in continental Greece is attributed to geothermal fields, whereas in the islands and coastal areas it is due to elevated temperatures and intrusion of marine water, or of marine water mixed with fresh water. Considering the B and Cl concentrations and the B/Cl ratio, the Aghia Paraskevi water is comparable both to waters from the islands and from the geothermal fields.

Lambrakis & Kallergis (2005) reported concentrations of 719 mg L⁻¹ for CO₂ and 101.64 mg L⁻¹ for H₂S, respectively. A stable isotopic study focusing on $\delta^{13}\text{C}$ in CO₂ discharges in the geothermal fields of Greece showed that the CO₂ is related to the thermal metamorphism of the marine limestones (Barnes et al., 1986).

The thermal water of the pool in the WTG1 cave has a temperature of 39.20°C, a pH of 6.38, and its

Fig. 4. Piper diagram illustrating the Na-Cl type of the Aghia Paraskevi thermal waters.

Fig. 5. Scanning Electron Microscope (SEM) images of orpiment, tamarugite and pickeringite from Aghia Paraskevi caves a. Orpiment grains (orp) overgrowing tabular tamarugite crystals (tam); b. Orpiment short prismatic crystals (orp) with tamarugite crystals (tam); c. Orpiment (orp) on tamarugite crystals (tam); d. Tabular tamarugite crystals (tam) along with fibrous pickeringite crystals (pick).

conductivity is 33.3 mS. The aluminum content is 5×10^{-3} mg L⁻¹ (analysis of IGME). The arsenic content is 3.4 mg L⁻¹, which is significantly higher than the common values for seawater (e.g. Welch et al., 1988) as well as the 10 µg L⁻¹ threshold value for drinking water established by the EC legislation in 1998 (EC, 1998) and adopted by the Greek legislation in 2001 (O.G.G., 2001). Generally in geothermal fields, As and Cl show a positive correlation due to a common behavior, but not a common source. Arsenic derives mainly by host rock leaching (Webster & Nordstrom, 2003) whereas Cl originates from the hydrothermal fluids or the seawater. The As/Cl ratio (1.7×10^{-4}) of Aghia Paraskevi is also indicating a possible mixing of geothermal water with seawater (e.g., Aiuppa et al., 2006).

MINERALOGY AND MINERAL CHEMISTRY

The samples PAR-B1, PAR6 and PAR7 collected from WTG1 and WTG2 caves consist of orpiment (As₂S₃) intergrown with tamarugite [NaAl(SO₄)₂·6H₂O], pickeringite [MgAl₂(SO₄)₄·22H₂O] and gypsum (CaSO₄·2H₂O), cemented to each other (Fig. 3c, d).

Fig. 6. X-ray diffraction (XRD) pattern of sample PAR-B1 showing the presence of tamarugite and orpiment.

Orpiment is common as orange yellow or yellow soft crumbly grains. It forms aggregates of crystals up to 2 µm (Fig. 5a-c) and is mainly found as coatings and minute crystalline encrustation over tamarugite (Fig. 5a-c) and sometimes over pickeringite (Fig. 3d) or gypsum. The XRD patterns show that orpiment occurs in smaller amounts than tamarugite (Fig. 6) and pickeringite, and relative abundances vary, depending on the sample site. At high SEM magnification, short prismatic crystals are observed (Fig. 5b). Samples that contain orpiment have a typical yellow color, sometimes resembling sulfur.

Four EDS analyses of orpiment from Aghia Paraskevi show As ranging from 60.24 to 61.32 wt% and S between 38.92 and 39.90 wt% (Table 2). No trace elements were found in orpiment.

Table 2. SEM-EDS micro-chemical analyses of orpiment (wt%).

wt%	B1-2	B1-3	B1-6	B1-7
As	60.07	61.10	61.32	60.24
S	39.90	39.54	38.92	39.34
Total	99.97	100.64	100.24	99.58

Tamarugite occurs as a semi-transparent colorless or white mineral, forming aggregates of tabular crystals in association with orpiment and pickeringite (Fig. 5a-d). It commonly occurs as globular encrustations of thin frail crystals. The XRD diagrams of the encrustations show well-developed patterns for tamarugite (Fig. 6). Observations with the SEM show that it is abundant in the encrustations, forming thin euhedral platelets. Alterations or inclusions were not observed. Chemical analyses of tamarugite (Table 3) show a typical chemical composition with Al₂O₃ ranging from 12.30 to 15.19 wt% and Na₂O from 5.30 to 9.06 wt%.

The fibrous mineral intergrown with orpiment and tamarugite is identified as a member of the halotrichite-pickeringite series (Fig. 3d, 5d). As shown in Table 3, magnesium content (2.22-7.11 wt%) exceeds that of iron (0.39-1.89 wt%), leading to the identification of the mineral as pickeringite. Due to the Fe content it can be characterized as a ferro-pickeringite.

Gypsum in the studied samples is found either as small interstitial crystals or as encrustations.

DISCUSSION

Tamarugite was identified as a cave mineral in a volcanic cavity more than a century ago, when Zambonini (1907) recorded it in Grotta dello Zolfo, Italy. It has also been described from Alum Cave (Sicily, Italy) by Forti et al. (1996) and Ruatapu Cave (New Zealand) by Rodgers et al. (2000). Forti (2005) suggested that tamarugite in volcanic environments is deposited by aerosols and vapors during low temperature (50-100°C) degassing, conditions which are favorable for the formation of sulfates and halides. It commonly forms under arid conditions by the oxidation of sulfides in aluminous and alkali-rich environments. Tamarugite was first reported in a true karst setting from Diana Cave (Romania), where it resulted from the reaction between alkali-type sulphidic thermal waters and kaolinite and clay minerals from marls (Onac et al., 2009).

Table 3. SEM-EDS micro-chemical analyses of tamarugite and pickeringite (wt%).

wt%	Tamarugite					Pickeringite				
	B1-1	B1-4	B1-5	B1-6	B1-7	B1-2	B1-3	B1-8	B1-9	B1-10
MgO	bdl	bdl	bdl	bdl	bdl	2.22	7.04	7.11	4.33	4.32
Na ₂ O	5.30	8.60	7.48	8.65	9.06	bdl	bdl	bdl	bdl	bdl
Al ₂ O ₃	15.19	14.25	12.30	14.29	14.45	12.12	11.68	11.31	11.90	11.66
FeO	bdl	bdl	bdl	bdl	bdl	1.14	0.39	0.59	0.92	1.89
SO ₃	49.72	45.47	45.04	45.98	46.61	39.94	36.09	34.95	37.98	37.40
Total	70.21	68.32	64.81	68.93	70.12	55.41	55.20	53.95	55.13	55.27

Tamarugite in Aghia Paraskevi must have been derived by aerosols and vapors from the Na-rich thermal water of the cave pools, under oxidizing conditions. Sulfide oxidation is excluded as a mechanism for tamarugite formation, as there is not field evidence of sulfide minerals in the rocks surrounding the Aghia Paraskevi caves.

Pickeringite has been identified first at the Diana Cave, Romania (Diaconu & Medesan, 1973) and at Grotta dello Zolfo, Italy (Hill & Forti, 1997). At the latter site, minerals of the halotrichite - pickeringite group were formed through evaporation of alkali-type sulfate solutions that reached the surface of the marly limestones by capillary action. Pickeringite from the Diana Cave has a higher Fe content than the samples from the WTG1 Cave in Aghia Paraskevi. Capillarity and evaporation are unlikely mechanisms for pickeringite and tamarugite precipitation in the WTG1 and WTG2 caves, since the limestone is not significantly porous.

The presence of gypsum crusts in the caves of Aghia Paraskevi is the result of oxidation of H₂S to sulfuric acid, which in turn, dissolves the limestone bedrock and deposits gypsum. Oxidizing conditions are extremely favorable for the precipitation of sulfates. This is consistent with the presence of tamarugite and pickeringite in the association. However, gypsum crusts form larger deposits at WTG1 Cave, covering the southeast cave walls where the thermal water is shallow or the passage is dry. Orpiment, tamarugite and pickeringite do not occur in these crusts.

Orpiment is a common mineral in low temperature hydrothermal veins, hot springs and fumaroles, but it has not previously been reported in caves. Orpiment precipitation has been observed where small H₂S-rich steam vents occur in the bed of hot spring-fed streams at the Waiotapu and Rotokawa geothermal fields in New Zealand (Webster & Nordstrom, 2003). In the absence of high levels of antimony and mercury in solution, As-rich precipitates in hot springs are commonly yellow orpiment (Webster & Nordstrom, 2003). Precipitation of orpiment under subaerial conditions is highly temperature dependant and may occur as a result of fluid cooling. Atmospheric oxidation does not present a direct adverse effect on orpiment solubility, whereas surface degassing of H₂S increases its solubility (Webster, 1990).

Orpiment is characterized by a wide range of stability conditions (Nordstrom & Archer, 2003) and is commonly associated with realgar (As₄S₄). Nordstrom & Archer (2003) suggested that realgar is rarely

found as a direct precipitate from sulfate solutions at temperatures less than 100°C and is stable over a narrow range of sulfur fugacity. Furthermore, realgar is an indicator of strongly reducing conditions, either acidic or alkaline, while orpiment occurs in less reducing conditions, mainly acidic but also alkaline (Vink, 1996). The exposure of realgar to light for long periods could produce the assemblage orpiment and arsenolite. Orpiment also derives from realgar through oxidation (Nordstrom & Archer, 2003).

Orpiment of Aghia Paraskevi caves could not have derived from realgar by exposure to light, since it commonly occurs in dark areas far from the cave entrances and arsenolite is absent from the association. Oxidation is also excluded since orpiment is not found coating realgar. The lateral extent of the orpiment-bearing assemblage in the Aghia Paraskevi caves is significant. The assemblage occurs only above the present level of thermal water in the cave pool, indicating sub-aerial formation.

Solubility data for As₂S₃ (amorphous) and orpiment indicate that in hot spring systems, temperature decrease and pH increase are the most likely factors for the removal of As from sulphate solutions and its deposition as arsenic sulfides (Eary, 1992). Orpiment precipitates from low-temperature (<100°C) hot spring fluids only when pH is less than 4 and the As content is lower than 5 mg L⁻¹. Such low pH values can occur at the water table, where oxidation of H₂S produces H₂SO₄ (Ballantyne & Moore, 1988). This suggests that acidification of the solution was required for orpiment deposition.

Based on the results of the present study we suggest that fluid cooling (*e.g.*, Webster, 1990; Eary, 1992) and/or acidification resulting from H₂S oxidation (*e.g.*, Ballantyne & Moore, 1988) are responsible for orpiment precipitation at the Aghia Paraskevi caves from vapor under sub-aerial conditions. The assemblage orpiment-tamarugite-pickeringite-gypsum commonly occurs closely above the surface of the thermal water, but can also be found higher, on the cave ceiling. Considering that all deposits are formed contemporaneously, a process of evaporation-condensation could be responsible for this selective deposition depending on the local climate conditions in the caves.

CONCLUSIONS

Orpiment occurs in the sulfuric acid caves of Aghia Paraskevi (WTG1 and WTG2) on the Kassandra Peninsula of Chalkidiki, Greece, and is documented as a cave mineral for the first time. This arsenic

sulfide is associated with tamarugite, pickeringite and gypsum, on cave-walls and ceilings of water-table caves, above the surface of the thermal water pools. The assemblage in the Aghia Paraskevi caves is a noteworthy occurrence since tamarugite and pickeringite are not commonly recorded in karst caves.

Orpiment, tamarugite and pickeringite must have accumulated under sub-aerial conditions from vapors at low temperatures in acidic conditions. As-bearing acidic fluids ascending from depth in hypogenic caves may have been of meteoric origin with a significant seawater component. In addition fluid cooling and/or acidification of the solution, resulting from H₂S oxidation, were responsible for orpiment precipitation through an evaporation-condensation process. Oxidation of H₂S to sulfuric acid dissolved the limestone bedrock and deposited gypsum.

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