The first cave occurrence of orpiment (As$_2$S$_3$) 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$_2$S. The B/Cl ratios indicate seawater participation with a possible mixing with geothermal water ofmeteoric origin. Oxidation of fumarolic H$_2$S 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$_2$S oxidation were responsible for orpiment precipitation. Oxidation of H$_2$S to sulfuric acid dissolved the limestone bedrock and deposited gypsum.

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

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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; Klimechouk, 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 a.s.l. 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 a.s.l, 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.
**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 CuKα 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° 2θ, start angle: 3°, end angle: 63° and scan speed: 0.02° 2θ/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     |

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 δ¹³C 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...
conductivity is 33.3 mS. The aluminum content is \(5 \times 10^{-3}\) 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 \(1.7 \times 10^{-4}\) 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 \(\text{As}_2\text{S}_3\) intergrown with tamarugite \([\text{NaAl(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}]\), pickeringite \([\text{MgAl}_2\text{SO}_4\text{)}_4 \cdot 22\text{H}_2\text{O}]\) and gypsum \([\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]\), cemented to each other (Fig. 3c, d).

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.

| 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 \(\text{Al}_2\text{O}_3\) ranging from 12.30 to 15.19 wt% and \(\text{Na}_2\text{O}\) 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%).

|       | Tamarugite | Pickeringite |
|-------|------------|--------------|
| wt%   | B1-1       | B1-2         |
| MgO   | bdl        | 2.22         |
| Na₂O  | 5.30       | 7.04         |
| Al₂O₃ | 15.19      | 12.12        |
| FeO   | bdl        | 1.14         |
| SO₃   | 49.72      | 39.94        |
| Total | 70.21      | 55.41        |

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 Agbia 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 $\text{H}_2\text{S}$ oxidation, were responsible for orpiment precipitation through an evaporation-condensation process. Oxidation of $\text{H}_2\text{S}$ to sulfuric acid dissolved the limestone bedrock and deposited gypsum.

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