Revision_1

The dark color of the *Ploutonion* at *Hierapolis of Phrygiae* (Turkey)

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Abstract

The dark color of some excavated architectural elements of *Ploutonion*, in the archaeological site of Hierapolis of Phrygiae (Turkey), was investigated. The *Ploutonion*, visited by numerous ancient writers, such as Cicero and Strabo, was a sanctuary dedicated to Pluto and Kore, constructed during the early Imperial period above the entrance to a natural cave, from which thermal waters and poisonous gases emerge. It was used for sacred rituals: sacrifices, incubation, healing.

A multi analytical approach (X ray diffraction, X ray fluorescence, optical and electronic microscopy, chemical analyses of the thermal spring water) was used in order to define the composition and origin of darkening phenomena of some architectural elements of the *Ploutonion*.

Keywords: dark color, *Ploutonion*, Hierapolis, Mn oxides, ~~rancieite~~ ranciéite, birnessite, todorokite, X-ray diffraction, Turkey

Introduction

The archaeological site of Hierapolis of Phrygiae, one of the main Hellenistic and Roman cities in Western Asia Minor (modern Turkey), lays in a highly seismic region, in the N basin where the grabens of the Maeander and Gediz rivers meet (Alçiçek *et al.*, 2007). A SW-dipping normal fault system mainly consisting of two fault segments (the Hierapolis and Akköy segments; Altunel and Hancock, 1993~~a~~) separates the Palaeozoic and Mesozoic successions from the Neogene and Quaternary continental sediments filling the basin (Şaroğlu *et al.*, 1987, 1992; Çakir, 1999; Hancock *et al.,* 1999; Koçyiğit, 2005), and plays a fundamental role in the hydrothermal circulation and fluid upwelling. The Quaternary faults and fissures that are common in carbonate bedrock along the margins of the graben are natural pathways that allow meteoric waters to descend into the subsurface and hydrothermal fluids to come to the surface (Minissale *et al*., 2002; Dilsiz, 2006). The Pamukkale travertine plateau, where the ancient Hierapolis was built, is bounded by two SW-dipping faults. Offsetting of Roman artefacts along the Hierapolis segment provides further evidence of fault activity in the Pamukkale area (Altunel and Hancock, 1993~~a~~). The ancient city of Hierapolis, instead, was damaged several times by earthquakes (Altunel and Barka, 1996; Piccardi, 2007; Kumsar *et al.*, 2016) with magnitudes up to 6.0 (Hancock *et al*., 2000) that were triggered by normal faulting and extension of the basin (Kaypak and Gökkaya, 2012). Most of these earthquakes had focal depths of 5 to 15 km. Local seismicity of the Denizli Basin strongly depends on the deep and shallow geothermal systems in the region (Kaypak and Gökkaya, 2012).

In this archaeological site, environmental factors together with the microstructural characteristics of the typologies of marble play a fundamental role on the durability and the state of conservation of the materials. The hardness of the environmental factors is due to the closeness of the monuments with respect to the seismogenic faults and thermal waters.

During the antiquity Hierapolis was a famous pilgrimage, centre of cult, because of the *Ploutonion*, the sanctuary dedicated to Hades-Pluto and his wife Kore-Persephone, visited also by Cicero and Strabo (D’Andria, 2013).

During the last years the excavation conducted by the Italian Archaeological Mission, brought to light the entire sanctuary of Pluto, discovering the grotto and the theatre, described by the literary sources (D'Andria, 2013; D'Andria et al., 2016) (Fig. 1a).

The sanctuary was constructed during the early Imperial period (1st century B.C. – 1st century A.D.) exactly above the entrance to a natural cave, from which thermal waters and poisonous gases emerge. In the centre of a monumental travertine facade with Ionic half-columns, over which ran an inscription with a dedication to Pluto and Kore, was an arched opening allowing access to the sacred cave (Fig. 1a), while a huge rectilinear theatre, in limestone blocks, housed the spectators participating to the sacred rituals. Strabo's account (XII, 4, 14) stands out among them all with its reference to a grotto emitted gases, which were toxic to the animals that approached it: goats and bulls showed sign of suffocation in front of entrance to the grotto, finally dying after a short time, while the Galli, the eunuch priests of the goddess Cybele, miraculously entered the cave and remained inside without any harm, demonstrating their supernatural power (D'Andria, 2013; D'Andria *et al.* 2016; Bozza, 2016).

In front of the cave, a marble circular building (*tholos*) was flanked by two rectangular pools for the warm thermal water flowing from the grotto.

The grotto is opened along the eastern side of a large fissure of the ground that was produced by the seismic fault that crossed all the urban area of Hierapolis. The natural agents characterizing the site (i.e. carbonatic hot-thermal waters and gases rich in CO_2), important for the ancient cult rituals, are responsible for critical conservation of the architectural structure of the *Ploutonion*.

Several marble and travertine blocks (column bases, capitals, elements of frieze architrave of porticos – Fig. 1b, c, d), belonging all to architectonics elements of the *Ploutonion* and extracted, since 2013 during the excavation campaign, from wet ground and water between the entrance of the grotto and the byzantine wall, are affected by thick black crusts and deposits. Also the internal walls of the natural cave are entirely blackened and covered by these encrustations (Fig. 1e).

In order to characterize them some samples were taken and analysed using a multi analytical approach. The role of thermal waters was also investigated, where the underground springs of Hierapolis, characterized by an intense circulation, emerge to the surface in front of the entrance of the *Ploutonion*.

Figure 1 a) The entrance of the grotto in the *Ploutonion* sanctuary during the restoration (2014). Some blocks from which black encrustations were sampled: b) H14_PN3; c) H14_PA1; d) TRAV3. Black encrustations on the internal walls of the natural cave.

Materials and Methods

Samples were collected from the marble and travertine blocks by using a scalpel, after the excavation of blocks (Tab. S1 and Fig. 1b, c, d, e). Since 1957, when archaeological excavations in Hierapolis ancient city were initiated (D'Andria, 2003), relics of historical earthquakes are abundant (Kumsar *et al.*, 2016). In particular, the archaeologists reconstructed that the original structure of the *Ploutonion* collapsed due to an earthquake in the fifth century AD and that the blocks were affected by other earthquakes in mid-seventh, X-XI and mid-fourteenth century (Kumsar *et al.*, 2016; D'Andria *et al.*, 2016).

Encrustations, of centimeter thickness, were diffusely present. Some of these were soft and with a subspherical structure in the superficial part, while in the inner one, at the direct contact with the stone substrate of not altered marble/travertine, were hard and adherent.

A detailed mineralogical and chemical characterization of these encrustations was realized. Polycrystalline X-ray diffraction data were collected (at room conditions) on an X'Pert Pro PANalytical diffractometer equipped with an X'Celerator detector and using a Ni-filtered Cu-$K\alpha$ radiation source. The X-ray tube was operated at 40 kV and 40 mA. The diffraction patterns were collected with: 2-theta range 0-70°, step size 0.033°, total time per pattern of 16 min 27 s. Soller and anti-scatter slits were used on the incident and diffracted beam; a divergent slit was used on the incident beam.

Chemical semi quantitative analysis was performed on a Rigaku Primus II with wavelength dispersive X-ray fluorescence (WDXRF) spectrometer with a Rh tube, automatic sample changer, Detectors Scintillation counter for heavy elements and Flow proportional counter for light elements. Powder pellets were prepared from four samples (TRAV3, H14_PA1, H14_PA3 and H14_BP1) mixed with a binding agent; analysis were performed in the elemental range from F to U in vacuum. Polished cross sections of H14_PN1 and TRAV1 samples were prepared embedding the sample in a bi-component epoxy resin (Epofix, Struers *DK*). The cross sections were then observed with optical microscope, a Nikon Eclipse E600.

Semi-quantitative micro-chemical analyses on the black deposits of H14_PN1 and TRAV1 were obtained by means of a SEM-EDS electronic microscope (ZEISS EVO MA 15) with an analytical system in dispersion of energy and W filament. The measurements were performed with an acceleration potential of 20 kV. Backscattered electron images at high magnification (from 200X to 400X) and elemental analysis were carried out using an Oxford Instruments INCA 250 analyser. For semi-quantitative microanalysis, internal standards were used, and then normalized using INCA 250 algorithms.

Temperature, pH, and electrical conductivity (EC in ms cm^{-1}) of the thermal water, in front of the entrance of the natural cave, were measured directly on site using a multiparameter PCe-PHD1 probe. Total alkalinity (HCO_3^-) was analyzed via acidimetric titration with 0.01 N HCl using a Metrohm 794 automatic titration unit. The main anions (Cl^-, SO_4^{2-}, NO_3^-, Br^-, and F^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) were analyzed by ion chromatography (Metrohm 761 and Metrohm 861, respectively). The analytical error for major water constituents was ≤ 5%. Fe and Mn content were analyzed in laboratory using a Perkin Elmer Optima 8000 ICP-OES instrument.

Results and discussion

The phase identification of the polycrystalline samples of this study, based on their X-ray diffraction patterns, was performed using the X'Pert HighScore (PANAlytical TM) program and its database. The identification was not trivial because some of the crystalline phases, in particular the Mn-bearing minerals (which are the dominant/major phases, Table 1), were affected by a severe broadening due to their low crystallinity and structural disorder (*e.g.*, Post and Bish, 1988; Post and Veblen, 1990; Ertl *et al.*, 2005). In addition, shape and average intensity of the background of the diffraction patterns suggest the presence of an X-ray amorphous phase in all the samples. The identified crystalline phases were: calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2), birnessite (ideally $(Na, Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$), ranciéite (ideally $(Ca,Mn^{2+})Mn^{4+}_4 O_9 \cdot 3H_2O$), and todorokite (ideally $(Mn^{2+},Ca,Na,K)(Mn^{4+},Mn^{2+},Mg)_6O_{12} \cdot 3H_2O$) (*e.g.* Fig. 2). Birnessite and ranciéite have the main Bragg peaks with close 2-theta angles (*i.e.*, with similar inter-planar distances). In the diffraction patterns of this study, the Bragg peaks of these two Mn-minerals were substantially overlapped as their full-width-at-half-maximum (FWHM) were significantly high (FWHM > 0.5-0.6° in 2-theta), in response to their poor crystallinity. In order to prove the presence of the two phases (*i.e.*, one of the two or the co-presence of both), their "calculated" diffraction patterns were generated on the basis of the structural models available in the literature (Post and Veblen, 1990; Ertl *et al.*, 2005) by Rietveld method (Rietveld, ~~1968~~ 1969; Altomare *et al.*, 2017) using the GSAS package (with a pseudo-Voigt profile function and a Chebyshev-type polynomial to model the background curves, Larson and Von Dreele 1994) and a combination of both, with ranciéite fraction higher than that of birnessite, showed the best fit with the "observed" diffraction patterns. This finding proved that ranciéite and birnessite co-exist in all the samples of this study (Table 1). However, a conventional and robust quantitative phase analysis was not possible due to the poor crystallinity of the mineralogical components. In this light, the phase concentration is given in Table 1 only at a first approximation (*e.g.*, as "dominant or major", "subordinate", "minor or very minor"). An additional Mn-bearing phase was observed in some of the samples: a todorokite-like phase, which is one of the dominant/major phases for the samples TRAV_1 and TRAV_3 (Table 1).

The aforementioned Mn-bearing phases are known to guest metal ions that are not considered in the ideal chemical formula. Todorokite, for example, exhibits a microporous structure and Mg, Mn, Cu, Ni, Co, Fe and other metals in their ionic forms can lie in the large structural tunnels running parallel to the [010] axis (Post and Bish, 1988), along with H_2O molecules. On the other hand, even in birnessite and ranciéite (defined as "phyllomanganates") other metals in their ionic forms can replace Mn in the layers of the (Mn^{4+}, Mn^{3+})O_6 octahedra or in the intercalated atomic sites connected with H_2O molecules (Post and Veblen, 1990; Ertl *et al.*, 2005). This can explain why the chemical analyses show the presence of Co, Ni, Cu and Zn along with Mn (Tab. S2). As shown in table S2, in fact, four samples were analyzed with X-ray Fluorescence to identify the elements present. All samples are rich in Mn (74, 594 ÷ 84,721 % in weight) and Ca (8,579 ÷ 12,942 % in weight), also show a significant percentage of Co, Ni, Cu and Zn accordingly with X-ray powder diffraction data.

Table 1. Crystalline phase identification of the samples of this study based on the X-ray diffraction data.

Figure 2. X ray powder diffraction pattern of H14_PN1. The identified crystalline phases are reported: * = calcite; # = quartz; ° = dolomite; £ = ranciéite; $ = birnessite; § = todorokite.

The thermal water, sampled in front of the entrance of the *Ploutonion*, was characterized by relatively high total dissolved solids (TDS) (2710 mg L^{-1}) and a sulphate – bicarbonate - calcium (Ca^{2+}- HCO_3^-, SO_4^{2-}) composition (Ca^{2+}, HCO_3^- and SO_4^{2-}concentrations were 507, 1296 and 704 mg L^{-1}, respectively) (Tab. S3). The Fe and Mn analysis revealed that the concentration values of these elements were very low, under the Detection Limit (DL) and 2.163 μg L^{-1} respectively (Tab. S3).

Previous studies on thermal waters in the Denizli area showed a lacking of Mn ions (Ulcay *et al.*, 2012). The travertine deposits in the Çukurbağ fissure-ridge (Pamukkale, Turkey) are generally lacking of Mn inside the crystal lattice. Fe and Mn values of the calcite are lower in the light coloured travertines (e.g., ~280 ppm Fe, 70 ppm Mn, in the white crystalline calcite travertine precipitated on the slope facies of Pamukkale) (Özkul *et al.*, 2013). Residual materials of Fe and Mn oxides were observed on banded travertine, and their presence was attributed to meteoric or soil-related Mn-rich parent water (Brogi *et al.*, 2014).

The main aquifer supplying hot and mineralized water to the Pamukkale thermal springs is the Paleozoic and Mesozoic limestone (Şimşek *et al.*, 2000). The waters, in the Pamukkale area, are typical of a karst aquifer, and their chemical composition is almost constant from place to place (Şimşek, 2003). High mountains to the north and south are the main recharge areas for the hydrothermal system (Özler, 2000) and the deep- and shallow sourced waters in the basin are mainly of meteoric origin (Özkul *et al.*, 2013). As the thermal waters ascend to the surface, they mix with the shallow cool groundwater (Dilsiz, 2006; Crossey *et al.*, 2009). The CO_2 involved in travertine precipitation comes from thermometamorphic processes associated with magmatic sources in the area (e.g., Kele *et al.*, 2011). Thermal waters that come to the surface derive from deeply sourced waters, i.e. endogenic waters mixed with meteoric water in different ratios (Crossey *et al.*, 2006; Fórizs *et al.*, 2011), and have high water temperature, high amounts of free CO_2, and high saturation levels (Özkul *et al.*, 2013). In the Büyük Menderes Graben the highest mantle-CO_2 with the highest sediment-derived CO_2 (that is an input of carbon derived from organic sediments) proportion is found at Pamukkale. Such contribution may suggest varying input of atmospheric component for CO_2, probably by mixing with fresh groundwaters during the ascent of thermal water from the reservoir (Karakuş and Simsek, 2013).

Black shale series-hosted manganese deposits of Cretaceous age, for example, that are economically the most important deposits of Turkey, are especially concentrated at the Ulukent region (Tavas – Denizli) (Kuşcu and Gedikoğlu, 1989). However, the precise determination of any particular source over another for manganese deposits, as well as to know about processes that are able to put Mn into solution are difficult to distinctively assess (Pracejus *et al.*, 1988; Roy, 1997). Water and a good drainage system seem to be fundamental requisites: all dissolution and precipitation processes depend directly on the presence of water. The intense and deep thermal water circulation system in the Büyük Menderes Graben together with meteoric waters and groundwaters may have mobilized Mn that may have been transported also for thousands of kilometres from the original site up to precipitate again.

Scanning electron microscopy observations revealed two different morphologies of these Mn-based encrustations: (i) the branched morphology (Fig. ~~2~~ 3A) and (ii) the straight multilayered deposition (Fig. ~~2~~ 3B).

Both types of manganese deposition that were observed in our samples are multilayered, suggesting a cycling of the favorable conditions of their formation attributable to the presence of microorganisms in the process of manganese oxide deposition. The presence of organic matter and of microbial biofilms in the water and on the solid stone surfaces is varying according to nutrient supply, climatic conditions. The organic matter and microbial biofilms are ideal places for metal ions entrapping and activation of different bio-chemical reactions. The formation of solid manganese oxides phases could be a result of these type of processes. At higher SEM magnifications, traces of microorganisms were observed with spherical morphology (Fig. ~~3~~ 4) as observed in Kilias *et al.*, 2007 for the Vani Mn deposit in Milos (Greece). Also in the case of *Ploutonion* of Hierapolis we can suppose that photosynthetic cyanobacteria with sheath, and other manganese-oxidizing bacteria, have contributed to the formation of Mn encrustation by promoting chemical oxidation of Mn^{2+} and precipitation of Mn-oxides through the release of molecular oxygen and/or enzymatic metabolic activities. This process was surely facilitated by opportune environmental parameters (i.e. water temperature, pH, Eh) of thermal waters in which the blocks were submerged.

Figure ~~2~~ 3 Back scattering SEM images at high magnification of sample A) TRAV 1 (microchemical analyses are reportedd in Table 2) and B) H14 PN1(microchemical analyses are reported in Table 3).

Figure ~~3~~ 4 High magnification of branched morphology of sample TRAV 1 with traces of spherical microorganisms.

The presence of microorganisms in the process of manganese oxide deposition is crucial (Miura and Hariya, 1997). ~~Rancieite~~ Ranciéite is characteristically found, for example, in Ca-rich environments such as travertines, limestones or marbles (Nimfopoulos *et al.*, 1997), but in the case of the thermal spring water of the *Ploutonion* the Ca concentration is not the main factor in determining the precipitation of ~~rancieite~~ ranciéite mineral phase rather than birnessite or todorokite. The mineral species in manganese wad precipitated from hot-spring water is therefore dependent on the presence or absence of microorganisms (Miura and Hariya, 1997). They could influence this process by modifying the local redox and pH conditions in the water environment and by releasing metabolic products able to oxidize Mn^{2+} (Tebo *et al.*, 2004). The acidic water favour reactivity of Mn^{2+}which can be easily oxidized by the microbiota, especially by the one containing extracellular polymeric substances (EPS) (Tebo *et al.*, 2004). The water from Pamukkale contains a great biodiversity of cyanobacteria and bacteria able to form sheats and biofilms containing EPS (Altunöz *et al.*, 2016; Cuzman *et al.*, 2016). The microorganisms containing EPS are able to entrap and use as an energy source a wide range of metal ions, if necessary, being influenced by the close related environmental conditions (pH, O_2 content, temperature, Eh, ecc.). As these reactions occur on an immersed colonized surface, they may to the formation of Mn oxides lead in appropriate conditions. In the case of Pamukkale, the water presents a little content of Mn^{2+} and a great TDS value, which indicates the presence of organic substances as well beside of the inorganic matter. The organic matter is another place where the reactivity and mobility of metal ions is very high. The Mn^{2+} is microbially oxidized in an acidic water, as in the case of Pamukkale where the value of pH is about 6, forming manganese biooxides. These bioproducts could sorb along Mn other metals (Co, Ni, Cu and Zn) originating new oxides in two possible forms: (i) freely moving particulates and (ii) cemented black crusts of manganese oxides (todorokite, ranceite) that entrap also other metals. Microchemical analyses performed by SEM EDS (Tabs. 2 and 3) confirm the capability of Mn oxides to trap heavy metal elements, such as Ni and Co. This trapping depends on the crystal structure of individual Mn oxide species: todorokite, for example, contains the highest amount of trace elements (Miura and Hariya, 1997). The TRAV 1 sample, instead, characterized by dominance of todorokite phase, show the maximum amount of Co (13.85 wt%).

Table 2. Micro-chemical point analyses of TRAV1 sample by SEM-EDS in wt% (see Figure 2A).

Table 3. Micro-chemical point analyses of H14_PN1 sample by SEM-EDS in wt% (see Figure 2B).

Conclusions

Mn oxides were responsible of dark color of some architectural blocks excavated from *Ploutonion* in the archaeological site of Hierapolis of Phrygiae (Turkey). The mineralogical investigation confirm the presence of birnessite (ideally $(Na, Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$), ranciéite (ideally $(Ca,Mn^{2+})Mn^{4+}_4 O_9 \cdot 3H_2O$), and todorokite (ideally $(Mn^{2+},Ca,Na,K)(Mn^{4+},Mn^{2+},Mg)_6O_{12} \cdot 3H_2O$). The thermal water, in which these blocks were buried, has a sulphate – bicarbonate - calcium composition with a very low concentration of Mn (2.163 μg L^{-1}). The temperature is about 35°C and the pH is 6.07.

The morphology of Mn encrustation allows to identify the role of microorganism and identify this process as a biomineralization occurred after the collapse of these architectural elements (made of marble and travertine) of *Ploutonion* under water following the historical earthquakes and on the internal walls of the natural cave, emphasizing the suggestion of the mystery of this sanctuary.

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References

Alçiçek, H., Varol, B., Özkul, M., 2007, Sedimentary facies, depositional environments and palaeogeographic evolution of the Neogene Denizli Basin of SW Anatolia, Turkey, *Sedimentary Geology,* 202, 596–637.

Altunel, E., Hancock, P.L., 1993a, Morphology and structural setting of Quaternary travertines at Pamukkale, Turkey, *Geological Journal*, 28, 335-346.

Altunel, E., Barka, A., 1996, Evaluation of archaeoseismic damages at Hierapolis, *Geological Bulletin of Turkey*, 39, 65-74.

Altomare, A., Cuocci, C., Gatta, G.D., Moliterni, A., Rizzi, R., 2017, Methods of crystallography: powder X-ray diffraction, *European Mineralogical Union Notes in Mineralogy*, 19(2), 79–138 (DOI: 10.1180/EMU-notes.19.3).

Altunöz, M., Obali, O., Atici ,T., Arru, L., 2016, Seasonal monitoring of algal flora in the Pamukkale travertines and thermal springs (Denizli/Turkey), *Biological Diversity and Conservation*, 9, 116-127.

Bozza, S., 2016, The Ionic Portico of the Ploutonion in Hierapolis in Phrygia, in Ismaelli, T., Scardozzi, G. (eds.), *Ancient quarries and building sites in Asia Minor. Research on Hierapolis in Phrygia and other cities in south-western Anatolia: archaeology, archaeometry, conservation*, Edipuglia, Bari, 373-385, ISBN 978-88-7228-819-1.

Brogi, A., Capezzuoli, E., Alçiçek, M.C., Gandin, A., 2014, Evolution of a fault-controlled fissure-ridge type travertine deposit in the western Anatolia extensional province: the Çukurbağ fissure-ridge (Pamukkale, Turkey), *Journal of the Geological Society*, 171, 425 –441.

Çakır, Z., 1999, Along-strike discontinuity of active normal faults and its influence on Quaternary travertine deposition: examples from western Turkey, *Turkish Journal of Earth Science*, 8, 67–80.

Crossey, L.J., Fischer, T.P., Patchett, P.J., Karlstrom, K.E., Hilton, D.R., Huntoon, P., Reynolds, A.C., 2006, Dissected hydrologic system at Grand Canyon: interaction between upper world and lower world waters in modern springs and travertine, *Geology*, 34, 25–28.

Crossey, L.J., Karlstrom, K.E., Springer, A., Newell, D., Hilton, D., Fisher, T., 2009, Degassing of mantle-derived CO2 and 3He from springs in the southern Colorado Plateau region-neotectonic connections and implications for groundwater systems, *Geological Society of America Bulletin,* 121, 1034-1053.

Cuzman, O.A., Leal, A.S., Schaffar, S., Vettori, S., Cantisani, E., 2016, Notes on the stone biodiversity of Hierapolis monuments, in Ismaelli, T., Scardozzi, G. (eds.), *Ancient quarries and building sites in Asia Minor. Research on Hierapolis in Phrygia and other cities in south-western Anatolia: archaeology, archaeometry, conservation*, Edipuglia, Bari, 609-618, ISBN 978-88-7228-819-1.

D'Andria, F., 2003, Hierapolis di Frigia (Pamukkale). Guida Archeologica/Hierapolis (Pamukkale), Arkeoloji Reheberi, Istanbul.

D'Andria, F., 2013, Il Ploutonion a Hierapolis di Frigia, in *Istanbuler Mitteilungen*, 63, 157-217.

D'Andria, F., Ismaelli, T., Panarelli, P., 2016, Initial data on the supply of marble for the Ploutonion, in Ismaelli, T., Scardozzi, G. (eds.), *Ancient quarries and building sites in Asia Minor. Research on Hierapolis in Phrygia and other cities in south-western Anatolia: archaeology, archaeometry, conservation*, Edipuglia, Bari, 365-372, ISBN 978-88-7228-819-1.

Dilsiz, C., 2006, Conceptual hydrodynamic model of the Pamukkale hydrothermal field, southwestern Turkey, based on hydrochemical and isotopic data, *Hydrogeology Journal*, 14, 562-572.

Ertl, A., Pertlik, F., Prem, M., Post, J.E., Kim, S.J., Brandstätter, F., Alfschuster, R., 2005, ~~Rancieite~~ Ranciéite crystals from Friesach, Carinthia, Austria, *European Journal of Mineralogy*, 17, 163 – 172.

Fórizs, I., Gökgöz, A., Kele, S., Özkul, M., Deák, J., Baykara, M.O., Alçiçek, M.C., 2011, Comparison of the isotope hydrogeological features of thermal and cold karstic waters in the Denizli Basin (Turkey) and Buda Thermal Karst (Hungary), *Central European Geology*, 54 (1–2), 115-119.

Hancock, P.L., Chalmers, R.M.L., Altunel, E., Çakır, Z., 1999, Travitonics: using travertines in active fault studies, *Journal of Structural Geology*, 21, 903–916.

Hancock, P.L., Chalmers, R.M.L., Altunel, E., Çakir, Z., Becher-Hancock, A., 2000, Creation and destruction of travertine monumental stone by earthquake faulting at Hierapolis, Turkey, in McGuire, W.G., Griffiths, D.R., Hancock, P.L. Stewart, I.S. (Eds.), The Archaeology of Geological Catastrophes, *The Geological Society, London*. Special Publications, 171, 1-14.

~~H. Karakuş, Ş. ŞimşekTracing deep thermal water circulation systems in the E–W trending Büyük Menderes Graben, western Turkey~~

Karakuş, H., Şimşek, Ş., 2013, Tracing deep thermal water circulation systems in the E–W trending Büyük Menderes Graben, western Turkey, *Journal of Volcanology and Geothermal Research,* 252, 38-52.

Kaypak, B., Gökkaya, G., 2012, 3-D imaging of the upper crust beneath the Denizli geothermal region by local earthquake tomography, western Turkey, *Journal of Volcanology and Geothermal Research,* 211-212, 47-60.

Kele, S., Özkul, M., Gökgöz, A., Fórizs, I., Baykara, M.O., Alçiçek, M.C., Németh, T., 2011, Stable isotope geochemical and facies study of Pamukkale travertines: new evidences of low-temperature non-equilibrium calcite-water fractionation, *Sedimentary Geology,* 238, 191-212.

Kilias, S.P., Detsi, K., Godelitsas, A., Typas, M., Naden, J., Marantos, Y., 2007, Evidence of Mn-oxide biomineralization, Vani Mn deposit, Milos, Greece, in Andrew, C.J., (ed.) *Digging deeper: proceedings of the ninth biennial Meeting of the Society for Geology Applied to Mineral Deposits, Dublin, Ireland 20th-23rd August 2007.* Dublin, Ireland, Irish Association of Economic Geologists, 1069-1072.

Koçyiğit, A., 2005, The Denizli graben-horst system and the eastern limit of western Anatolian continental extension: basin-fill, structure, deformational mode, throw amount and episodic evolutionary history, SW Turkey, *Geodinamica Acta*, 18, 167–208.

Kumsar, H., Aydan, Ö., Şimşek, C., D'Andria, F., 2016, Historical earthquakes that damaged Hierapolis and Laodikeia antique cities and their implications for earthquake potential of Denizli basin in western Turkey, *Bulletin of Engineering Geology and the Environment,* 75(2), 519-536.

Kuşcu, M., Gedikoğlu, A., 1989, Ulukent (Tavas-Denizli) Güneyi Manganez Yataklarının Jeokimyasal Özellikleri, *Yerbilimcinin Sesi*, 17, 29-47.

Larson, A.C., Von Dreele, R.B., 1994, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR, 86-748.

Minissale, A., Kerrick, D.M., Magro, G., Murrel, M.T., Paladini, M., Rihs, S., Sturchio, N.C., Tassi, F., Vaselli, O., 2002, Geochemistry of Quaternary travertines in the region north of Rome (Italy): structural, hydrologic and paleoclimatologic implications, *Earth and Planetary Science Letters*, 203, 709-728.

Miura, H., Hariya, Y., 1997, The recent manganese deposit in Hokkaido, Japan, in Nicholson, in K., Hein, J.R., Buhn, B., Dasgupta, S. (eds.) Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, *Geological Society Special Publication*, 119, 281–299.

Nimfopoulos, M.K., Michailidis, K.M., Christofides, G., 1997, Zincian ~~ranceite~~ ranciéite from the Kato Nevrokopi manganese deposits, Macedonia, northern Greece, in K., Hein, J.R., Buhn, B., Dasgupta, S. (eds.) Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, *Geological Society Special Publication*, 119, 339-347.

Özkul, M., Kele, S., Gökgöz, A., Shen, C.C., Jones, B., Baykara, M.O., Fórizs, I., Németh, T., Chang, Y.W., Alçiçek, M.C., 2013, Comparison of the Quaternary travertine sites in the Denizli extensional basin based on their depositional and geochemical data, *Sedimentary Geology,* 294, 179–204.

Özler, H.M., 2000, Hydrogeology and geochemistry in the Çürüksu (Denizli) hydrothermal field, western Turkey, *Environmental Geology*, 39, 1169-1180.

Piccardi, L., 2007, The AD 60 Denizli Basin earthquake and the apparition of Archangel Michael at Colossae (Aegean Turkey), in L. Piccardi, W.B. Masse (Eds.), *Geological Society*, London, Special Publications, 273, 95-105.

Post, J.E., Bish D.L., 1988, Rietveld refinement of the todorokite structure, *American Mineralogist,* 73, 861-869.

Post, J.E., Veblen, D.R., 1990, Crystal structure determinations of synthetic sodium, magnesium and potassium birnessite using TEM and the Rietveld method, *American Mineralogist*, 75, 477-489.

Pracejus, B., Bolton, B.R., Frakes, L.A., 1988, Nature and development of supergene manganese deposits, Groote Eylandt, Northern Territory, Australia, *Ore Geology Reviews*, 4, 71-98.

Rietveld, H.M., 1969, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography*, 2, 65-71.

Roy, S., 1997, Genetic diversity of manganese deposition in the terrestrial geological record, in K., Hein, J.R., Buhn, B., Dasgupta, S. (eds.) Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, *Geological Society Special Publication*, 119, 5-27.

Şaroğlu, F., Emre, O., Boray, A., 1987, Turkiye'nin diri faylari ve depremsellikleri, *Mineral Research and Exploration Institute of Turkey*, Rept. No. 8174.

Şaroğlu, F., Emre, O., Kuscu, I.,1992, The East Anatolian fault zone of Turkey, *Annales Tectonicae*, 6, 99–125.

Şimşek, Ş., 2003, Hydrogeological and isotopic survey of geothermal fields in the Büyük Menderes graben, Turkey, *Geothermics,* 32, 669-678.

Şimşek, Ş., Günay, G., Elhatip, H., Ekmekci, M., 2000, Environmental protection of geothermal waters and travertines at Pamukkale, Turkey, 29, 557-572.

Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004, Biogenic manganese oxides: properties and mechanism of formation, *Annual Review of Earth Planet Science*, 32, 287-328.

Ulcay, S., Kurt, O., Akcora, C.M., Ozturk, M., 2012, Environmental monitoring in the Kaklik Cave (Denizli, Turkey), *Natural Science*, 3, 159-165.

Figure captions

Figure 1 a) The entrance of the grotto in the *Ploutonion* sanctuary during the restoration (2014). Some blocks from which black encrustations were sampled: b) H14_PN3; c) H14_PA1; d) TRAV3. Black encrustations on the internal walls of the natural cave.

Figure 2. Back scattering SEM images at high magnification of sample A) TRAV 1 (microchemical analyses are reportedd in Table 2) and B) H14 PN1(microchemical analyses are reported in Table 3).

Figure 3. High magnification of branched morphology of sample TRAV 1 with traces of spherical microorganisms.

Table captions

Table 1. Crystalline phase identification of the samples of this study based on the X-ray diffraction data.

Table 2. Micro-chemical point analyses of TRAV1 sample by SEM-EDS in wt% (see Figure 2A).

Table 3. Micro-chemical point analyses of H14_PN1 sample by SEM-EDS in wt% (see Figure 2B).

Table S1. List and images of the investigated samples.

Table S2. Chemical analysis by XRF expressed in wt%.

Table S3. Temperature (°C), pH and chemical composition of water sample. Concentrations are in mg L^{-1} (ppm). TDS = total dissolved solids.