The taranakite – francoanellite dehydration reaction: new data and possible implications for minerogenetic processes in cave environments

Yuri Galliano (1), Cristina Carbone (1), Fabio Bellatreccia (2), Jo De Waele (3)

(1) Department of Earth, Environmental and Life Sciences, University of Genoa, C.so Europa 26, Genoa, Italy

(2) Department of Sciences, University Roma Tre, Viale G. Marconi 446, Rome, Italy

(3) Department of Biological, Geological and Environmental Sciences, Alma Mater University of Bologna, Via Zamboni 67, Bologna, Italy, jo.dewaele@unibo.it (corresponding author)

Abstract

Taranakite ($K_3Al_5(PO_3OH)_6(PO_4)_2 \cdot 18H_2O$, *trigonal*, *R3C*) is a hydrated phosphate occurring in caves as a reaction product between bat guano and detrital silicates. Its presence has been documented widely throughout the world (HILL & FORTI, 1997). Previous experimental work has determined its high sensitivity to temperature change, which can lead to the loss of part of its structural water and the formation of the lower hydrate form francoanellite. The latter has also been proven to form in nature by BALENZANO et al. (1976), transforming taranakite into francoanellite ($K_3Al_5(PO_3OH)_6(PO_4)_2 \cdot 12H_2O$, *trigonal*, *R3C*). The name derives from Franco Anelli, former Italian karstologist and discoverer of the Castellana Caves (Apulia, Italy), where the first occurrence of the mineral was documented. With this contribution, we present a new occurrence of taranakite from the Pollera Cave (Liguria, Italy) and new experimental data regarding its thermally induced dehydration and consequent formation of francoanellite. Hence, we discuss a possible genetic mechanism for this rare and seldom investigated cave mineral both in natural (wild) caves and in show caves (such as in Castellana Cave, where the mineral was first discovered).

1. Introduction

The generally simple chemical systems which characterize the majority of known karst hypogean environments can be greatly complicated by the introduction of bat guano. Bat guano is very rich in P, S and N, which are released in the fluids and gases liberated by the degradation of organic matter driven by microbial activity. This triggers intense variations in the physico-chemical conditions of guano-influenced environments, such as pH values as low as 3, increase in CO2 partial pressure and increase in temperature. Therefore, the presence of bats and of their metabolic products leads to the onset of biocorrosion processes (DANDURAND et al., 2019) and to the formation of a rich variety of phosphate and sulphate minerals (HILL & FORTI, 1997; AUDRA et al., 2019).

The mineral assemblage is influenced by the nature of the material interacting with guano-derived fluids; where detrital or paragenetic siliciclastic deposits are involved, K-Al-Fe hydrated phosphates are the most common reaction products. In this context, taranakite is one of the most commonly observed phases and can form powdery surface aggregates, nodules and veinlets crosscutting sediments admixed with guano. On the other hand, the occurrence of francoanellite has been reported from a very limited number of sites (BALENZANO et al., 1976, 1979; CANCIAN, 1985; CHIORBOLI, 1985; DELL'ANNA et al., 1989; ONAC & VEREŞ, 2003).

The first to observe that the prolonged exposure of taranakite to a temperature of 95°C led to its degradation and the formation of a lower hydrate, characterized by a strong X-ray diffraction line at 13.8 Å, were SMITH & BROWN (1959). Further work was directed at studying the thermal behaviour of taranakite using thermogravimetric analysis and X-ray diffraction on the quench products after prolonged heating (ARLIDGE et al., 1963; SAKAE & SUDO, 1975; FIORE & LAVIANO, 1991).

It was only at the end of last century that DICK et al. (1997) and DICK & ZEISKE (1998) conducted single crystal X-ray diffraction and neutron powder scattering analyses on taranakite and francoanellite to solve their crystal structures.

2. Site description

The taranakite samples used for this study were collected in the Pollera Cave (Liguria, Italy). The cavity is hosted in the Pietra di Finale Fm. (Miocene), and actively controls part of the water runoff in the area with a subsurface stream (Rio Montesordo) which comes to light at the Arma del Buio resurgence and forming a tributary to the Aquila Stream (Figure 1). It is also a site of significant archaeological interest, due to the discovery of a plethora of artifacts attributed to the Bronze Age (DEL LUCCHESE & STARNINI, 2013) and of skeletal remains dated to the Neolithic, which were object of palaeopathological investigations (SPARACELLO et al., 2017). In its overall extension of more than 2 km, the cave also includes fossil passages characterized by collapse deposits and morphologies. One of the collapse rooms (Saloni Bensa) hosts a subfossil guano deposit, whose degradation has generated a varied phosphate-sulphate assemblage, which was the object of this study.

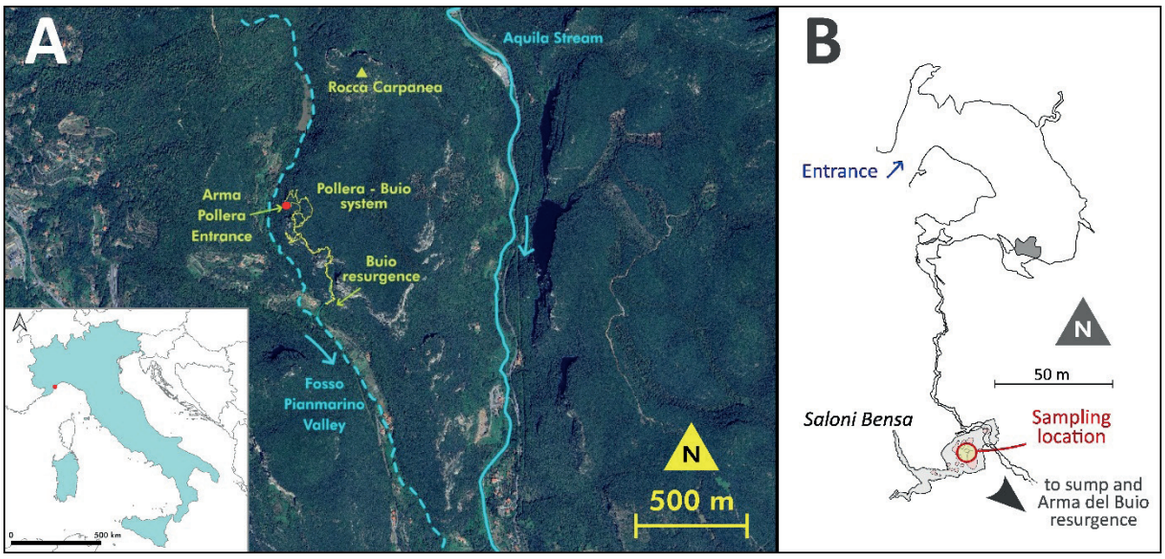

Figure 1: (A) Location of the Pollera Cave on Google Earth imagery. The yellow lines show the plain view of the Pollera – Buio system survey, acquired from the regional speleological database and developed by the members of Progetto Carpeneam. The inset shows the location of the cave in Italy. (B) Simplified map of the Pollera Cave, with the sampling location highlighted by a red circle.

3. Methods

Sampling for mineralogical investigation was conducted while trying to respect cave conservation criteria; it did not involve complex speleothems but was limited to rock surfaces and loose aggregates. Samples for mineral identification were collected in small quantities (~ 5 mg) and stored in Eppendorf - type flasks and in sealed plastic bags, to preserve the natural state of humidity until the day of examination.

The taranakite sample was checked for purity under a stereoscopic microscope and lightly ground in an agate mortar. After a preliminary analysis at ambient conditions, the powder was then subdivided into 5 aliquots and heated at different temperatures for different periods of time, cooled to room temperature and subjected to X-ray diffraction analysis.

Powder X-ray diffraction (PXRD) measurements were performed at the Department of Earth, Environmental and Life sciences of the University of Genoa. Data collection was carried out using a Philips PW 3710 diffractometer equipped with a Co anode and a point detector at 40 KV and 20 mA, using 0-background Si-crystal sample holders, in the angular range 3-40 °2θ, with a step size of 0.02 °2θ and a scan time per step of 1 s; PXRD data interpretation was carried out with X'pert High Score and Profex. Thermogravimetric – Differential Thermal Analysis (TG-DTA) was performed at the Department of Chemistry and Industrial Chemistry of the University of Genoa using a LabsysEvo 1600–Setaram. The sample (untreated taranakite) was placed in a closed alumina crucible and heated in a dry atmosphere (60 mL min–1) from 30°C to 250°C, with a heating rate of 10°C/min.

4. Results and Discussion

During preliminary investigations, combined PXRD, SEM-EDS, Raman and FTIR analyses confirmed that (i) apatite, ardealite, brushite and gypsum constitute the reaction products on top of the surfaces of collapsed limestone blocks while (ii) taranakite and leucophosphite have formed at the contact between guano and a ***terra rossa*** deposit (Figure 2). Here, taranakite appears as white powdery nodules and veins that cut through the clay deposit, while leucophosphite forms purplish-brown crusts and botryoidal aggregates.

The results of thermogravimetric analysis on taranakite (displayed in Figure 3), in line with previous work (e.g., FIORE & LAVIANO, 1991; MARINCEA & DUMITRAŞ, 2003) demonstrated that, at a heating rate of 10°C/min, the mass loss starts at T ≈ 95°C. The weight of the sample shows a steady decrease up to about 160°C, where an inflection in the TG curve suggests that pretty much all of the taranakite has now dehydrated to form francoanellite.

Figure 2: The subfossil guano deposit and associated mineralisation. The surfaces of collapsed limestone blocks are altered in a Ca-phosphate assemblage; in the position marked by the yellow arrow, the terra rossa deposit is evidently transformed into a K-Al-Fe phosphate assemblage.

The mass loss of 7.38 % is close to the 8.05% expected for the loss of ~ 6 H2O molecules from the theoretical formula of taranakite. This corresponds to the loss of interlayer water from the structure. The relative DTA endothermic peak is centred at ~ 152°C. The next dehydration step observed in the inspected T range, marked by the endothermic peak in the DTA curve at ~ 187°C, is due to the complete loss of structural water and amorphization of the material, which is completed at T > 250°C.

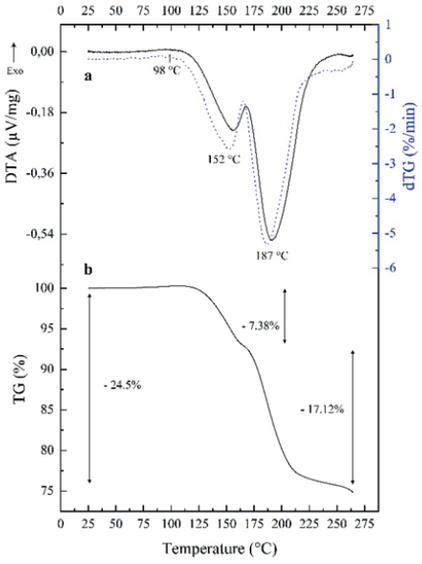

Figure 3: *Results of the thermogravimetric analysis conducted on the Pollera Cave taranakite. In the upper part of the graph (a), differential thermal analysis (DTA – black solid line) and the first derivative of the thermogravimetric curve (dTG – blue dotted line) are reported. In the lower part of the graph (b), the thermogravimetric curve (TG) is reported.*

However, heating taranakite ex-situ in isothermal conditions using a static oven results in quite different temperatures for the onset of the dehydration. As can be seen in Figure 4, signs of taranakite degradation and consequent formation of francoanellite start to be evident at temperatures as low as 55°C, if this condition is maintained for 68 hours. If taranakite is left at 60°C for 76 hours, francoanellite becomes the predominant phase, and the same result is achieved at 65°C for 65 hours, and at 85°C for as short as 8 hours. It is also worth mentioning that the heating of taranakite in isothermal conditions at temperatures between 55 and 65°C for prolonged periods generates powders with a characteristic diffraction peak at ~ 14.7 Å, about halfway between the distinctive peaks of taranakite (at 15.7 Å) and francoanellite (at 13.8 Å), which hints at the possible presence of a phase with intermediate state of hydration in the sample.

As evidenced in this set of measurements, the temperature for the onset of the taranakite – francoanellite dehydration reaction resulting from thermogravimetric experiments conducted at a constant heating rate, be it moderately high (as in our case) or slow (e.g. FIORE & LAVIANO, 1991), is definitely higher than the one that can be achieved in case of isothermal heating. With the timespans available in normal laboratory settings (i.e., some tens of hours at a time), it was possible to trigger the start of taranakite dehydration at temperatures as low as 55°C.

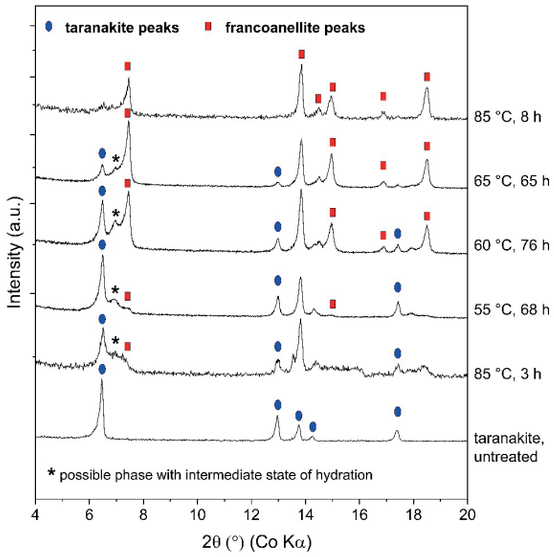

Figure 4: *PXRD data of taranakite treated at different temperatures and for different times; h : hours spent at given temperature. The peaks are assigned after ICDD-00-029-0980 (francoanellite) and ICDD-00-029-0981 (taranakite).*

The question that would naturally arise after observing these data, is whether these conditions are achievable in nature, and if the heating of taranakite could be considered a viable mechanism for the formation of francoanellite in cave environments. It is also important to consider that there is one more condition regarding the maximum temperature, which should not exceed ~ 150°C, so as not to trigger complete dehydration. For this reason, we should discard guano-combustion events (ONAC & FORTI, 2011). However, by taking into account that the degradation of organic matter by microbial action happens predominantly through exothermic reactions, it is possible to hypothesize that, in a limited number of cases, the temperatures reached inside guano deposits experiencing bacterial decay, or the temperature reached during the diagenesis of sediments admixed with guano, might be sufficiently high to cause the dehydration of taranakite, but not as high as to cause the amorphization of newly formed francoanellite.

5. Conclusion

Taranakite, a hydrated K-Al phosphate typical of cave sediments altered by fluids generated from bat guano degradation in damp conditions, is present in the phosphate-sulphate mineral assemblage of the Pollera Cave in proximity to a subfossil guano deposit. Thermogravimetric data, in accordance to the available literature, suggest that its thermal degradation should start at ~ 95°C. However, probably due to the slow kinetics of this dehydration reaction, experiments conducted in isothermal conditions confirmed that the destabilization of taranakite and consequent gradual formation of francoanellite can take place at temperatures much lower than previously thought. At present, it is difficult to assess whether the mild heating provided by the decay of organic matter in actively degrading guano deposits could provide the necessary conditions for the formation of francoanellite. This would explain most of the natural occurrences of francoanellite in wild caves. In Castellana Cave, high temperatures might have occurred close to powerful spotlights. Further mineralogical, geomorphological and microbiological observations in these contexts might aid in better understanding the processes regulating the thermal evolution of degrading guano deposits and the transformation taking place in their surroundings.

Acknowledgments

The authors wish to thank the members of the Speleological Group CAI Bolzaneto for their support during fieldwork, the Ligurian Speleological Delegation (DSL) and the members of Progetto Carpeneam for the survey of the Pollera Buio system, available on the Ligurian Speleological Registry (Catasto Speleologico Ligure). Marco Fortunato, Ph.D. student at the Department of Chemistry and Industrial Chemistry of the University of Genoa at the time of data collection, is acknowledged for conducting the thermogravimetric analysis on taranakite. Dr. Tudor Tămaş is thanked for reviewing the manuscript and improving its quality.

References

ARLIDGE E. Z., FARMER V. C., MITCHELL B. D., MITCHELL W. A. (1963) Infra-red, X-ray and thermal analysis of some aluminium and ferric phosphates. Journal of applied chemistry 13(1):17-27.

AUDRA P., DE WAELE J., BENTALEB I., CHROŇÁKOVÁ A., KRIŠTŮFEK V., D'ANGELI I.M., CARBONE C., MADONIA G., VATTANO M., SCOPELLITI G., CAILHOL D., VANARA N., TEMOVSKI M., BIGOT J.-Y., NOBÉCOURT J.-C., GALLI E., RULL F., SANZ-ARRANZ A. (2019) Guano-related phosphate--rich minerals in European caves. International Journal of Speleology 48(1):75-105.

BALENZANO F., DELL´ANNA L., DI PIERRO M. (1976) Francoanellite, H6K3Al5(PO4)8·13H2O, a new mineral from the caves of Castellana, Puglia, southern Italy. Neues Jahrbuch für Mineralogie Monatshefte 2:49-57.

BALENZANO F., DELL´ANNA L., DI PIERRO M. (1979) Francoanellite from the Grotta della Rondinella in Apulia (Southern Italy): a new occurrence and new data. Neues Jahrbuch für Mineralogie Monatshefte 8:363-372.

CANCIAN G. (1985) I fosfati della Grotta ad Est di San Martino del Carso (Gorizia): brushite, idrossiapatite, francoanellite, taranakite. Atti 3 Convegno Triveneto di Speleologia: 19-26.

CHIORBOLI S. (1985) Dati mineralogici sulla Francoanellite della "Grotta Due Piani", San Martino del Carso (Gorizia). Min. Univ. Ferrara 1:1-6.

DANDURAND G., DURANTHON F., JARRY M., STRATFORD D. J., BRUXELLES L. (2019) Biogenic corrosion caused by bats in Drotsky's Cave (the Gcwihaba Hills, NW Botswana). Geomorphology 327:284-296.

DELL'ANNA L., FIORE S., LAVIANO R. (1989). I fosfati di cavità carsiche pugliesi: giaciture, natura e genesi. Atti XV Congresso Nazionale dei Speleologia, Castellana Grotte, 171-187.

DEL LUCCHESE A., STARNINI E. (2013) Aggiornamenti sull'età del Bronzo Liguria. Nuovi dati dall'assemblaggio della ceramica della Grotta Pollera (Finale Ligure, SV). Archeologia in Liguria 3:11-23.

DICK S., ZEISKE T. (1998) Francoanellit K3Al5HPO4) 6 (PO4) 2· 12H2O: Struktur und Synthese durch topochemische Entwässerung von Taranakit/Francoanellite K3Al5HPO4) 6 (PO4) 2· 12H2O: Structure and Synthesis by Topochemical Dehydration of Taranakite. Zeitschrift für Naturforschung B, 53(7), 711-719.

DICK S., GOBNER U., WEIB A., ROBL C., GROBMANN G., OHMS G., ZEISKE T. (1998) Taranakite—the mineral with the longest crystallographic axis. Inorganica chimica acta 269(1):47-57.

DICK S., GOBNER U., WEIB A., ROBL C., GROBMANN G., OHMS G., ZEISKE T. (1998) Taranakite—the mineral with the longest crystallographic axis. Inorganica chimica acta 269(1): 47-57.

FIORE S., LAVIANO R. (1991) Brushite, hydroxylapatite, and taranakite from Apulian caves (southern Italy): New mineralogical data. American Mineralogist 76(9-10):1722-1727.

HILL C.A., FORTI P. (1997) Cave minerals of the World, second ed. National Speleological Society, Huntsville, AL.

MARINCEA S., DUMITRAS D.G. (2003) The occurrence of taranakite in the dry Cioclovina Cave (Sureanu Mountains, Romania). Neues Jahrbuch für Mineralogie Monatshefte (3):127-144.

ONAC B. P., FORTI P. (2011) Minerogenetic mechanisms occurring in the cave environment: an overview. International Journal of Speleology 40(2):79-98.

ONAC B.P., VEREŞ D.S. (2003) Sequence of secondary phosphates deposition in a karst environment: evidence from Magurici Cave (Romania). European Journal of Mineralogy 15(4):741-745.

SAKAE T., SUDO T. (1975) Taranakite from the Onino-Iwaya limestone cave at Hiroshima Prefecture, Japan: A new occurrence. American Mineralogist: Journal of Earth and Planetary Materials 60(3-4):331-334.

SMITH J. P., BROWN W E. (1959) X-ray studies of aluminum and iron phosphates containing potassium or ammonium. American Mineralogist: Journal of Earth and Planetary Materials 44(1-2):138-142.

SPARACELLO V. S., ROBERTS C. A., KERUDIN A., MÜLLER R. (2017) A 6500-year-old Middle Neolithic child from Pollera Cave (Liguria, Italy) with probable multifocal osteoarticular tuberculosis. International Journal of Paleopathology 17:67-74.