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FIRST ALPINE EVIDENCE OF *IN SITU* COARSE CRYOGENIC CAVE CARBONATES (CCC_{COARSE})

Abstract: Colucci R.R., Luetscher M, Forte E., Guglielmin M., Lenaz D., Princivalle F. & Vita F., *First alpine evidence of in situ coarse cryogenic cave carbonates (CCC_{coarse}). (IT ISSN 0391-9839, 2017).*

A layer of coarse cryogenic cave carbonate (CCC_{coarse}) is documented within a subsurface ice outcrop (*in-situ*) in a cave of the Julian Alps (southeastern Alps). This original finding, representing the first alpine evidence of *in-situ* CCC_{coarse} and the first occurrence from the southern side of the Alps, provides a unique opportunity to better understand the processes associated with the formation of CCC_{coarse} with respect to the cave ice mass balance.

Here, we discuss first considerations on the shape and characteristics of CCC_{coarse} samples and their potential for palaeoclimate reconstructions in the southern Alps. In the light of accelerated climate change, we emphasize the need for scientific actions to exploit the available physical, chemical, isotopic and biological records from still untapped and fragile cryospheric archives such as ice caves.

Key Words: cryogenic cave carbonates, paleoclimate, climate change, ice caves, Alps

Riassunto: Colucci R.R., Luetscher M, Forte E., Guglielmin M., Lenaz D., Princivalle F. & Vita F., *Prima evidenza alpina di calcite criogenica grossolana in situ (CCC_{coarse}). (IT ISSN 0391-9839, 2017).*

In questo lavoro si documenta il ritrovamento di un deposito di calcite criogenica grossolana (CCC_{coarse}) trovato all'interno di una sezione di ghiaccio permanente (*in situ*) in una cavità delle Alpi Giulie (Alpi sudorientali).

Questo ritrovamento, che rappresenta la prima evidenza a livello alpino di CCC_{coarse} *in situ* oltre il primo ritrovamento per il versante meridionale delle Alpi, fornisce una importante opportunità per una migliore comprensione dei processi associati alla formazione della CCC_{coarse} in relazione al bilancio di massa di una grotta di ghiaccio. In questo lavoro si riportano alcune prime considerazioni sulla forma e le caratteristiche dei campioni di CCC_{coarse} ed il loro potenziale per una ricostruzione paleoclimatica nelle Alpi meridionali. In presenza di un cambio climatico accelerato, si vuole enfatizzare la necessità di azioni scientifiche atte a studiare i record fisici, chimici, isotopici e biologici di questi fragili ed ancora intatti archivi criosferici rappresentati dalle grotte di ghiaccio.

Termini Chiave: carbonato criogenico di grotta, paleoclima, cambiamento climatico, grotte di ghiaccio, Alpi.

INTRODUCTION

Ice caves are natural cavities in bedrock which contain perennial accumulations of ice (Perşoiu & Onac, 2012). Because cave ice is typically older than two years, ice

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RRC found the CCC_{coarse} deposits in the Leupa ice cave and wrote the manuscript together with ML. DL and FP performed X-ray diffractometer analyses. FV performed the electron microscope analysis. EF collected and analyzed the geophysical data and with MG participated in the discussion and revised the final version of the manuscript.

caves are commonly considered as sporadic permafrost phenomena (e.g., Holmlund & *alii*, 2005; Luetscher & *alii*, 2005, 2013; Hausmann & Behm, 2011; Kern & *alii*, 2011). The presence of ice deposits in caves is closely linked to cold climates, although they do also exist at altitudes or latitudes with outside mean annual air temperatures (MAAT) several degrees above the freezing point (e.g., Luetscher & *alii*, 2005; Colucci & *alii*, 2016). Ice caves are typically classified according to their thermodynamic characteristics (Luetscher & Jeannin, 2004). In particular, the presence of one or more cave entrances allows to distinguish between dynamic ice caves, subject to forced convection (i.e. chimney effect), and static ice caves, exposed to density-driven air flows during the winter season (Thury, 1861; Balch, 1900).

The progressive freezing of water more or less saturated with respect to calcium carbonate results in the segregation of solutes (e.g. Gross & *alii*, 1977; Petrenko & Withworth, 1999) and subsequent precipitation of cryogenic cave carbonates (CCC; Žák & *alii*, 2012; Luetscher, 2013; Spötl & Cheng, 2014). Whether precipitation occurs in an open or closed system with respect to carbon determines the stable isotope signature (e.g. Žák & *alii*, 2004) and the crystal size and habit of the precipitates. Fine crystalline powders (CCC_{fine}) which are commonly associated with rather rapid freezing of a thin water layer at the ice surface are subject to large kinetic isotope fractionation (e.g. Lacelle, 2007). In contrast, coarse crystalline cave carbonates (CCC_{coarse}) precipitate essentially during the slow freezing of a water pool. CCC_{coarse} typically ranges between a few hundreds of micrometers to several centimeters in size.

Observations in Alpine ice caves suggest that CCC_{fine} is more common, but to our knowledge published reports only exist for Monlesi, a small ice cave in the Swiss Jura Mountains (Luetscher & *alii*, 2007), Eisriesenwelt in Salzburg, Austria (Spötl, 2008; May & *alii*, 2011) and Leclanché Cave, Switzerland (Luetscher & *alii*, 2013). In contrast, CCC_{coarse} has been widely documented from presently ice-free Central European caves located in the so-called periglacial corridor during the late Pleistocene, between the Scandinavian ice sheet and the Alpine glacier network (e.g., Žák & *alii*, 2004, 2012; Richter & *alii*, 2010, 2013). In the Alps, the presence of CCC_{coarse} has been reported from three cave sites (fig. 1), and in most cases the loose CCC_{coarse} crystals deposited on the cave floor were found in presently ice-free cave sections (Richter & *alii* 2009; Luetscher & *alii*, 2013; Spötl & Cheng, 2014). Despite the presence of numerous ice caves in the world no documented evidence of CCC_{coarse} findings within ice layers (*in-situ*) exists. The lack of modern analogues therefore severely limits a profound understanding of the processes leading to the formation of CCC_{coarse}. It is only recently that *in-situ* CCC_{coarse} were reported from a Pyrenean ice cave (Bartolomé & *alii*, 2015) and we present here the first finding from an ice cave in the Alps.

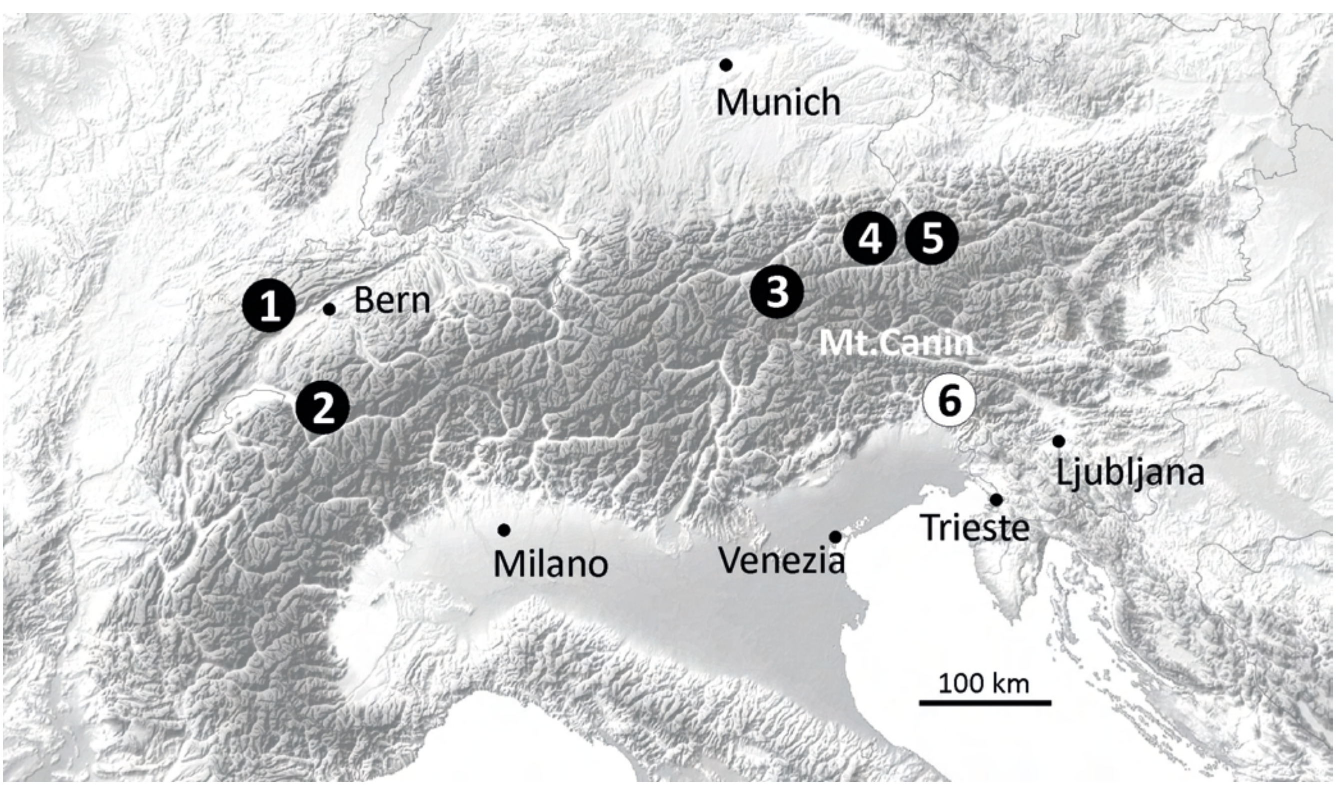

Fig. 1 - The Alpine region (open access map, courtesy Scilands GMBH http://www.scilands.de/) highlighting the known locations of CCC_{fine} (1: Monlesi cave; 2: Leclanché cave; 5: Eisriesenwelt) and CCC_{coarse} (2: Leclanché cave; 3: MSK Cave; 4: Glaseis Cave). Location 6 is the Leupa ice cave (Mt. Canin) where, for the first time, CCC_{coarse} is described *in situ* (this study).

This paper aims to: i) document *in-situ*-crystals of CCC_{coarse} in a cave located in the southern Alps, ii) report shape and characteristics of the loose crystals deposited recently on the cave floor, and iii) discuss the potential of the discovery of *in-situ* CCC_{coarse} for a better understanding of the processes involved in the precipitation of cryogenic carbonate.

STUDY AREA

The Mt. Canin massif (46°21' N, 13°26' E; 2587 m) is located in the Julian Alps (southeastern European Alps). The average (1981-2010) MAAT at 2,200 m is 1.1±0.6 °C according to Colucci & Guglielmin (2015), while the 1981-2010 mean annual precipitation (MAP) equals 3,335 mm. High precipitation also determines the mean winter snow accumulation which reaches about 7 m at 1,800 m a.s.l. Few small glaciers, glacierets and ice patches still persist in the area, representing some of the lowest glaciers in the European Alps (Triglav Čekada & *alii*, 2014; Salvatore & *alii*, 2015; Colucci, 2016; Colucci & Žebre, 2016). This is primarily due to the important role of avalanches, which allow the existence of permanent snow fields even on sunny slopes (Colucci & *alii*, 2014). Besides several active pronival ramparts, a relict rock glacier at 1,150 m a.s.l. is the only permafrost-related evidence in the area (Colucci & *alii*, 2016). Glaciokarst (sensu Žebre & Stepišnik, 2015) is however widespread. The Canin massif hosts more than 2,000 known caves with a density of up to 250 caves km^{-2} (Muscio & *alii*, 2011).

METHODS

CCC_{coarse} were sampled in the cave using tweezers and a small brush and were transported in Eppendorf® tubes to the laboratory where individual crystals and aggregates were photographed and measured. The samples were sputter coated with gold in a Edwards S150A apparatus (Edwards High Vacuum, Crawley, West Sussex, United Kingdom) and examined with a Leica Stereoscan 430i scanning electron microscope (Leica Cambridge Ltd., Cambridge, United Kingdom). The instrument is equipped with an energy-dispersive X-ray system (Oxford Instruments SEM-EDX Si(Li) detector).

X-ray powder diffraction (Siemens diffractometer equipped with a STOE D500 goniometer) was used to characterize the mineralogy of the samples. The following conditions were used: monochromatic CuKα radiation; detection angle from 5 to 70 degree 2θ, step 0.05° 2θ steps, 2s counting time per step. The stable carbon and oxygen isotope composition was analysed at University of Innsbruck using an online continuous-flow system (GasBench II) coupled to a Thermo Fisher $Delta^{plus}XL$ isotope ratio mass spectrometer.

RESULTS AND DISCUSSIONS

Leupa Cave (LC) is located at 2,300 m on the northern flank of the Canin massif (Italy) and opens with a 13 m-wide and 4 m-high entrance. The cave hosts a ca. 600 m^3 subhorizontal ice body, averaging ca. 3 m in thickness. Due to a complex air flow system between two or more cave entrances, LC is classified as a dynamic ice cave. Temperature recording performed in 2011 and 2012 reveals a MAAT in the cave of -1.4 °C with seasonal minima reaching up to -12 °C. The increased occurrence of extreme weather events characterized by warmer and more intense rainfall (Colucci & *alii*, 2016) over the last two decades is seen as a possible cause for rapid cave ice degradation.

The LC ice deposit is characterized by several internal structures highlighted using ground penetrating radar (GPR, Colucci & *alii*, 2016) which also allows estimation of maximum ice thickness to 4.5 m. A multiyear monitoring campaign (2 to 3 observations per year) was launched in 2011 and includes the measurement of the distance to the cave ice at fixed marks. Following a 2-year-period of rather stable mass balance the cave ice is showing evidence of rapid melt. Accordingly, the topographic ice surface has lowered by about 35 cm since 2011 of which 27 cm were ablated over the last 3 years. Warm air inflows through debris accumulated at the base of the ice deposit have resulted in the progressive widening of a dome-shaped melting cavity underneath the ice body (fig. 2).

CCC_{coarse} samples were found *in situ* in November 2015 in a vertical ice outcrop about 2.5 m beneath the topographic ice surface. The deposit is enclosed within a ca. 10 cm thick, highly reflective ice stratum characterized by numerous air inclusions. The lower boundary of this ice layer is marked by an erosional unconformity with denser cave ice underneath. The CCC_{coarse} are located few centimeters above this boundary and form a 1 to 3 cm thick detrital layer which can be traced laterally for about 3 m (fig. 2a). The crystal aggregates are evenly distributed and do not show any apparent spatial grading (fig. 2b). Overall, the CCC_{coarse} layer follows the general ice structure which is slightly dipping towards the inner part of the ice body. At the vertical of this overhanging outcrop, loose CCC_{coarse} crystals were found on the cave floor spread over an area of ca. 1 m^2 (fig. 2c). Unlike regular speleothems, the loose CCC_{coarse} crystals are found on debris and boulders suggesting that they were gradually released by the slowly retreating ice wall. The proximity of the modern ablation front suggests that this process must have occurred very recently.

Two populations of crystals are observed macroscopically. Whitish crystals are generally predominant with respect to the brownish-coloured ones. The crystals are mostly represented by aggregates 1-3 mm in size, with individual crystals ranging between few hundreds of micrometers and several millimeters. X-ray diffraction analysis and chemical composition obtained by the SEM-EDX reveal that both crystal populations consist of pure calcite. Quartz, mica, clay minerals or heavy mineral characteristic of clastic cave deposits in the area (Velicogna & *alii*, 2011) have not been observed.

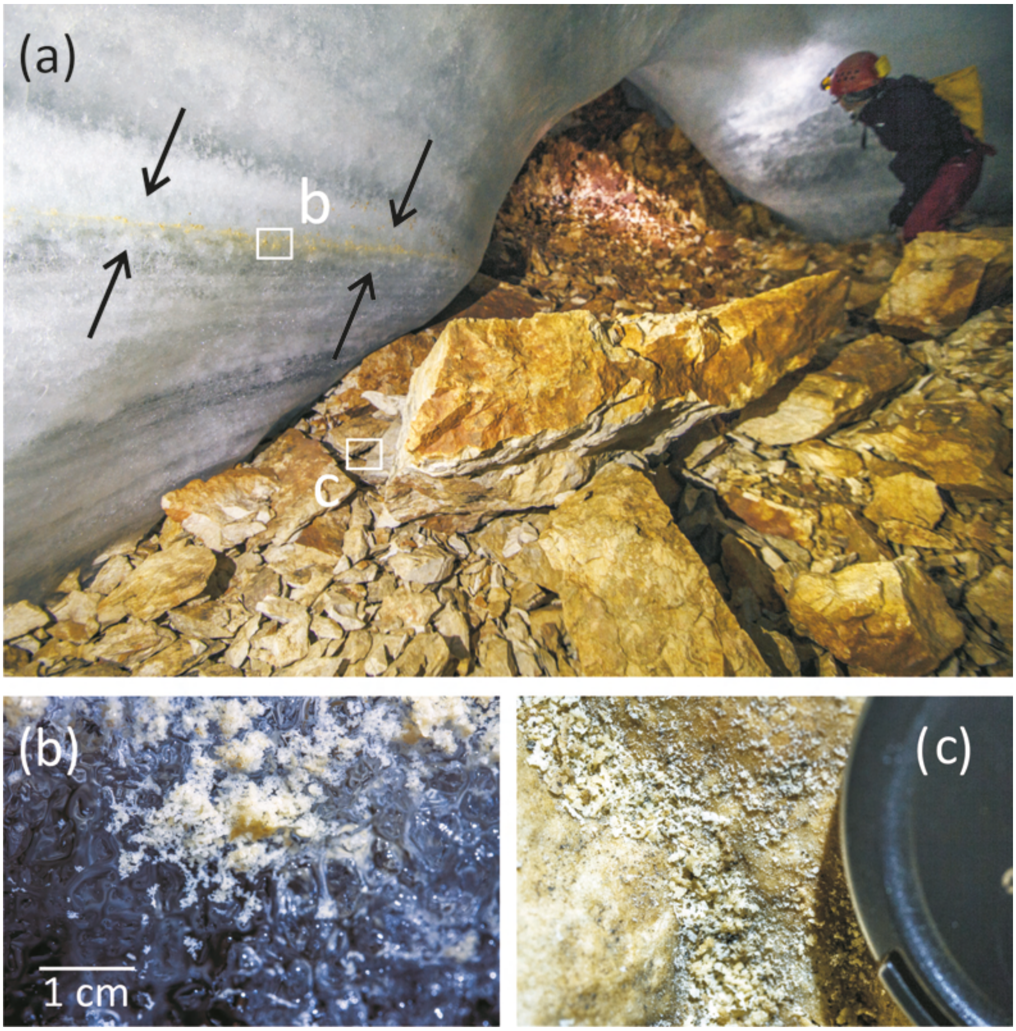

FIG. 2 - The cavity underneath the permanent ice deposit in the Leupa ice cave. The internal layer of CCC_{coarse} is highlighted by arrows in (a). Details of the *in-situ* crystals of coarser cryogenic calcite in (b) and loose crystals deposited recently on clastic sediments in (c). Photographs by R.R. Colucci.

The crystals, although imperfectly developed, show the rhombohedra and scalenohedra morphology under the SEM (fig. 3a,b) including various fan-like and lath-shaped forms (roses; e.g. fig. 3e). Raft-like crystal aggregates, similar to the floating calcite crystals commonly observed in pools of ice-free caves, are also present (fig. 3c). Single calcite scalenohedra elongated along the vertical axis represent the most common habitus, which is typical of cryogenic rafts (Žák & *alii*, 2012). Their presence suggests a progressive freezing of water pools located at the surface of the ice (Žák & *alii*, 2004, Richter & Riechelmann, 2008). The occasional occurrence of spheroids also points to rather slow crystallization rates (Luetscher & *alii*, 2013). The freezing of these water pools likely preceded a period of positive cave ice mass balance as suggested by the ca. 2.5 m-thick cave ice overlying the CCC_{coarse} layer.

Preliminary stable isotope analyses (n=4) of two crystal aggregates show compositions of between 6.6‰ and 6.9‰ for $\delta^{13}C$ and -11.8 ‰ and -12.0 ‰ for $\delta^{18}O$, respectively. Although somewhat enriched for typical CCC_{coarse} samples these values are still very close to some of the aggregates found in MSK cave (Spötl & Cheng, 2014).

In contrast to observations from other caves where CCC_{coarse} formed predominantly in the deep interior at stable thermal conditions (Žák & *alii*, 2012, Richter & *alii*, 2009), CCC_{coarse} at LC was found close to the cave entrance, in a similar setting as in the Pyrenees (Bartolomé & *alii*, 2015). This may either point to a different cave geometry at the time of CCC precipitation favoring more stable conditions, or to a phase of positive cave ice mass balance following extreme hydrologic recharge. Besides a crystal habitus showing many similarities to previously described alpine CCC_{coarse} samples, in particular at Mitterschneidkar Eishöhle (MSK) in the Zillertal Alps, Austria (Spötl & Cheng, 2014), the undisturbed *in-situ* layer of LC reveals a higher concentration of brownish crystals in the upper part of the layer, with whitish crystals predominant in the lower section. This pattern is consistent with the raft-type morphology described at MSK and suggests that the brownish samples may have formed at the favor of a higher concentration of organic material during the final stages of freezing.

Ice coring across the CCC layer was performed in November 2016 in the frame of the C3 project (www.c3project.

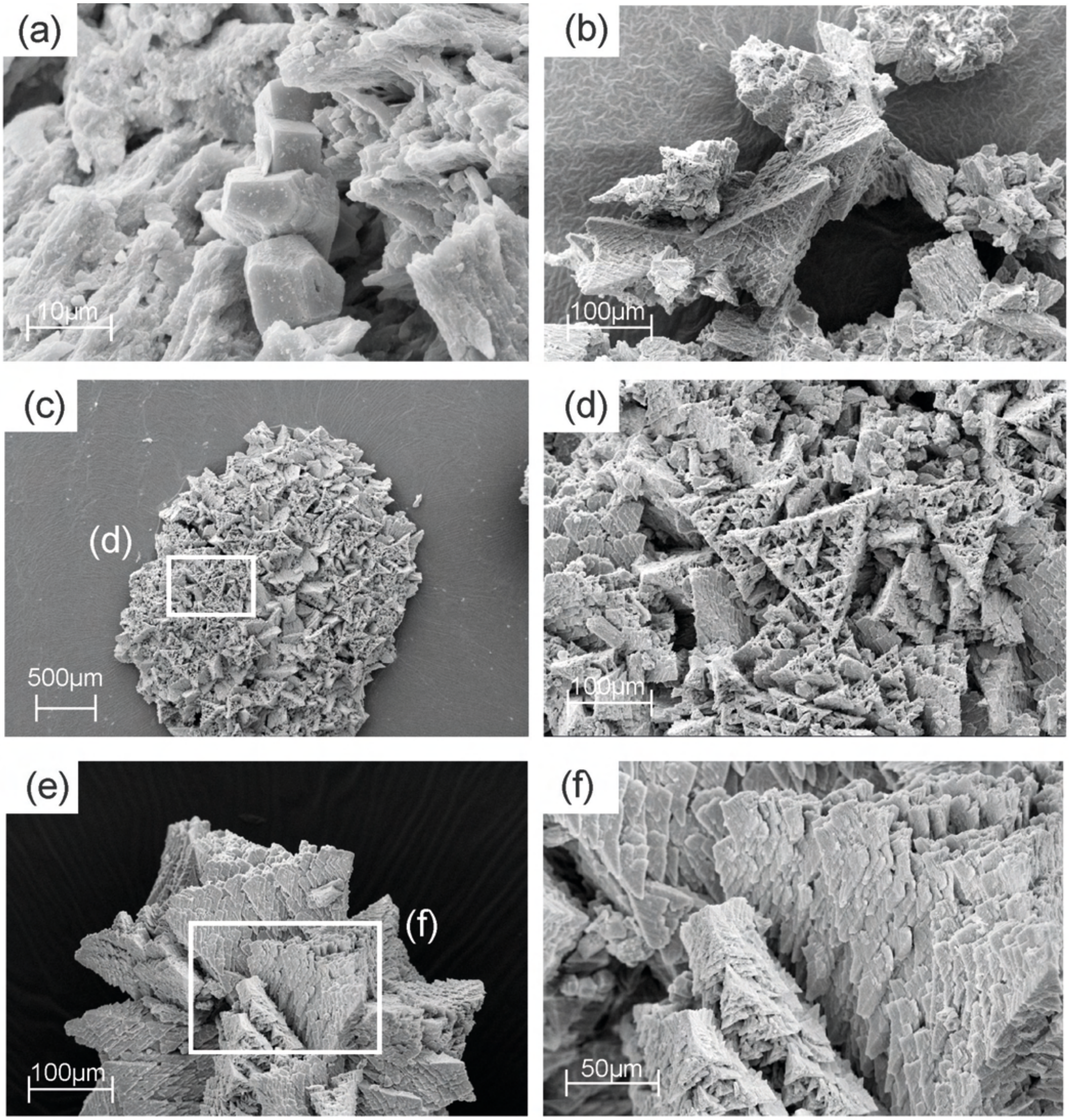

FIG. 3 - Morphology of calcite crystals as seen under SEM-EDX. (a) Detail of euhedral (rhombohedral) crystals; (b) Detail of euhedral (scalenohedral) crystals; (c) raft-like calcite aggregate consisting of calcite scalenohedra sometimes elongated in the direction of the vertical axis; (d) close-up of (c) showing a distribution of individual scalenohedral crystals with stepped faces; (e) fan-like aggregate (calcite rose) with various intergrowths of scalenohedral crystals; (f) close-up of (e) showing stepped crystal growth over the crystals surface.

net). A high-resolution chemistry profile will possibly give more insights into the processes involved in the formation of these peculiar carbonates, especially with respect to the final stages of freezing when the supersaturation is highest. Moreover, dating of the CCC layer is currently performed to constrain the timing of subsurface climate conditions when the cave ice deposit may have been even smaller than today. Previous results from an ice cave in the western Swiss Alps linked the formation of CCC_{coarse} to phases of warmer climate during the Medieval and the Roman

Period (Luetscher & *alii*, 2013). Interestingly, a recent finding of CCC_{coarse} from a deglaciated cave in the Austrian Alps (Spötl & Cheng, 2014) did not correlate with any warmer periods of the Holocene questioning a simple relationship between climate and the formation of CCC_{coarse}.

The precise conditions leading to CCC_{coarse} formation are still poorly understood. This new discovery from the Southern Alps is an important new addition to the database of Holocene CCC precipitates in high mountain permafrost regions and, thus, will allow to compare results to other regional paleoclimate records. The rare occurrence of ice containing *in-situ* CCC_{coarse} crystals provides the opportunity for more sophisticated analyses, e.g. of microbial communities, which may be associated (passively or actively) with the precipitation of these carbonates.

CONCLUSIONS

We documented the first *in-situ* evidence of CCC_{coarse} from an Alpine ice cave, which is also the first occurrence of CCC_{coarse} reported from the southern side of the Alpine chain. This discovery is crucial given the current accelerated warming which is going to rapidly destroy this important paleoclimatic archive, and will possibly provide an opportunity to better understand the processes associated with the formation of CCC_{coarse}.

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