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Isotope signature of sand calcites in the Paris Basin: a proxy for permafrost/groundwater paleoconditions

Médard Thiry [a], Christophe Innocent [b], Christine Franke [a]

[a] Géosciences Center, MINES ParisTech, 35 rue St Honoré, 77305 Fontainebleau, France
[b] BRGM / LAB-ISO, 3 avenue Claude Guillemin BP 6009, 45060 Orléans cedex 2

Abstract

Sand calcites occurring as rhombohedral crystals and spherolitic concretions in several Tertiary sandstone formations in the Paris basin have been dated to the cooling periods of the four last glacial stages, using ^{14}C and U-Th methods. Sand calcites constitute a novel proxy to estimate paleo-groundwater levels and the extension of permafrost conditions. The $\delta^{13}C$ and $\delta^{18}O$ compositions of sand calcites are a function of precipitation depth in relation with the warming of surface water during infiltration. Sand calcites appear as precious markers for Pleistocene paleo-landscape reconstructions.

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Keywords: sand calcite; datation; isotopes; paleo-groundwater; paleo-permafrost; Fontainebleau; France;

1. Introduction

Calcite crystallizations within sandstones (sand calcites or sand crystals) have attracted for a long time the interest of naturalists and collectors [1]. In contrast, geologists were hardly interested by these objects and their potential as environmental markers has not yet been explored.

Such crystallizations are present in all Tertiary sandstone formations in the Paris Basin. However, the extension of this kind of crystallizations is much more widespread, as one can appreciate in the numerous web sites dedicated to mineral collections. Similar calcite crystallizations are known in Central Europe, USA, Morocco …

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2. Description

In the Paris basin, three main sand crystal habits are found.

- Aesthetic group of rhombohedral calcite crystals forming cristallarias called "Calcite de Fontainebleau" grown in the presence of white sand. Individual crystals may reach several centimeters.
- Calcitic sandstone spheres with size varying from decimeter concretions to millimeter granules. The concretions either are scattered through the sand, or form plurimetric heaps. The concretions are often zoned, with a relative "smooth" surface, or in contrary radially arranged small rhomboehedral calcite crystals.
- Translucent, centimeter sized, euhedral calcite crystals are sometimes associated with the previous sand calcite type. They develop as dissolution features associated to limestone layers or fossils.

The crystal habitus is always the inverse rhomb ($02\bar{2}1$). The spherolites and the cristallarias are of poecilitic texture formed of large calcite crystals engulfing quartz grains of the host sandstone. The calcite proportion of the sand crystals varies between 20 and 35%, according to the porosity of the weakly compacted sandstone.

Sand crystals and spherolites are arranged with respect to particular levels in the sandstone. The cristallarias may combine and stick together to form 10 cm thick sub-continuing layers extending laterally over several tens of meters. However, most frequently cristallarias are scattered within the sandstone according to poorly-defined levels of about 1 m thickness. These distributions and modes of occurrence are consistent with paleo-water table positions.

Often cristallarias show geopetal dispositions with dissolution cupules at the summit, larger crystals at their periphery, and finally smaller crystals at the lower face. These arrangements resemble vertical infiltrations with progressive equilibration of the solutions and calcite precipitation, likely as in karst stalagmites.

The large accumulations of spherolitic concretions also display a vertical profile with dissolution features on top, followed by dense cross-laminated layers that cement the spherolites, and finally weakly connected spherolithes towards the base. The spherolitic accumulations are arranged according to vertical bodies of several metres in diameter, which often reach down to 6-7 m depth. These complexes seem to record particular infiltration zones where large amounts of water circulate forming large volumes of precipitated calcite.

3. Age dating

The ^{14}C and U-Th ages of a total of 19 sand calcite samples from various sandstone formations in the Paris Basin all resulted in Pleistocene ages [2]. The ages are distributed over 4 periods that coincide with cooling periods (Fig. 1). Calcite precipitation is linked to climate and to the sandstones. The youngest ages (< 20 000 years) match with particular spherolites occurring at the upper surface of quartzite pans. No age difference was evidenced between the euhedral and the spherolitic sand crystals.

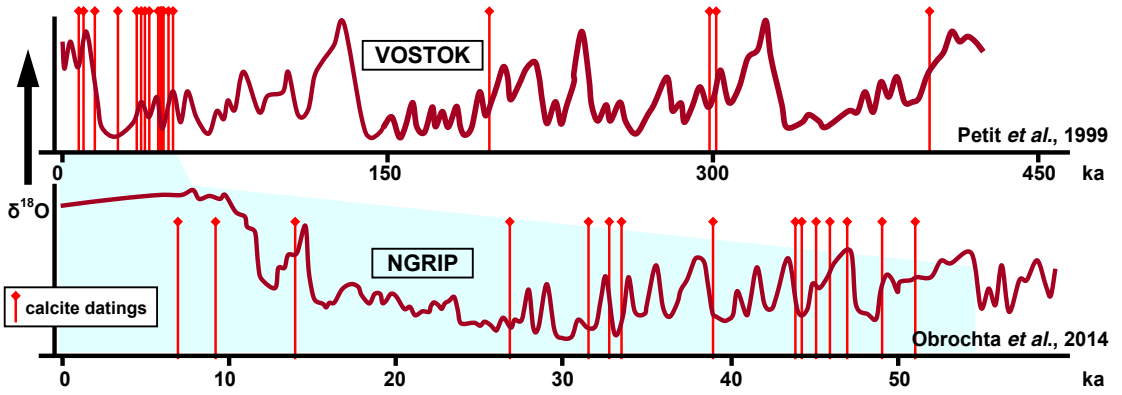


Figure 1 – Distribution of age estimates of the sand calcite in comparison to the time calibrated $\delta^{18}O$ record of the VOSTOK [3] and NGRIP [4] ice cores. The sand calcites are bound distinctively to the cooling periods of the last four glacial periods. Analytical errors present <± 10%.

4. Hydro-chemical model

Spatial distribution and morphological characteristics of the sand calcites show that their formation is related to infiltration of surface waters down to the water table. During the Pleistocene glacial periods, and more specifically during the cooling periods, a marked temperature gradient was established between the surface waters (near 0°C) and the deeper realm (aquifer and groundwater) because the deep zones need more time to record the temperature changes occurring at the surface. Under these conditions, the temperature of the subsoil at 10 or 20 m depth may have been equivalent to its current temperature around 12°C.

Yet, CO_2 and carbonates are more soluble in cold waters than in warm waters. When the water in equilibrium with the atmospheric CO_2 warms up from 0 to 12°C it looses approximately 1/3 of its dissolved CO_2 and more than 30 % of the dissolved calcite precipitates. During cold periods, the infiltrating water warms up in the subsoil, inducing CO_2 degasses subsequently leading to calcite precipitation (Fig. 2). Therefore, the permafrost thickness has to be limited and discontinuous to allow local infiltration. There is the link with the cooling periods.

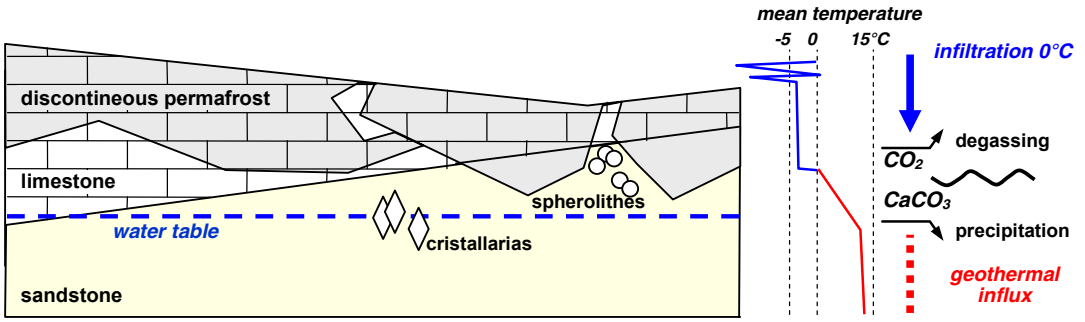


Figure 2 – Conceptual model of sand calcite precipitation. The temperature contrast at the base of the permafrost causes degassing of the infiltration water that in turn leads to the precipitation of the dissolved carbonate.

5. Isotopic composition

The stable isotopic compositions of bulk samples show variable $\delta^{13}C$ values ranging between -5 and -12‰ and $\delta^{18}O$ values ranging between -3 and -6‰ relative to PDB (Fig. 3). These results are similar to those of karst spelotherms of central and Western Europe [5,6] and very different from cryocalcites resulting from the super-saturation of freezing water [6,7].

There is a trend of increasing $\delta^{13}C$ values with depth of calcite precipitation (estimated from present day depth beneath the overall plateau level). Light $\delta^{13}C$ signature originating from organic carbon input is clearly bound to shallow samples (Fig. 3a). Furthermore, the "younger" samples have a lighter $\delta^{13}C$ signature, whereas the "older" samples show less influence of organic carbon (Fig. 3b). The younger and shallower calcite crystals are strongly influenced by organic carbon originating from the overlying soils whereas the older and deeper crystals are more influenced by regional groundwater. Nevertheless, younger and older calcites may coexist in a section because the sedimentary cover has been eroded between two stages of crystallization.

The stable isotope results distribute according to two trends within a $\delta^{18}O$-$\delta^{13}C$ diagram (Fig. 3c):

- a trend depicted by the positive slope arrow in graph (increasing $\delta^{18}O$ with decreasing $\delta^{13}C$) which highlights an evolution from near-surface samples enriched in CO_2 originating from organic carbon toward deeper samples fed by the groundwater with less influence of organic carbon;
- a trend depicted by the negative slope arrow in graph (increasing $\delta^{13}C$ with increasing $\delta^{18}O$), in agreement with precipitation mechanisms. The lower $\delta^{13}C$ values and higher $\delta^{18}O$ values are conform to kinetic isotope fractionation due to fast CO_2 degassing and calcite precipitation. For a given deposit, the values are relatively dispersed along the negative slope arrow due to changes of the precipitation conditions. There is also an evolution between the centre and the rim of a cristallaria corresponding to faster precipitation, reflected by the formation of multiple small crystals on the surface of the previous large single crystals.

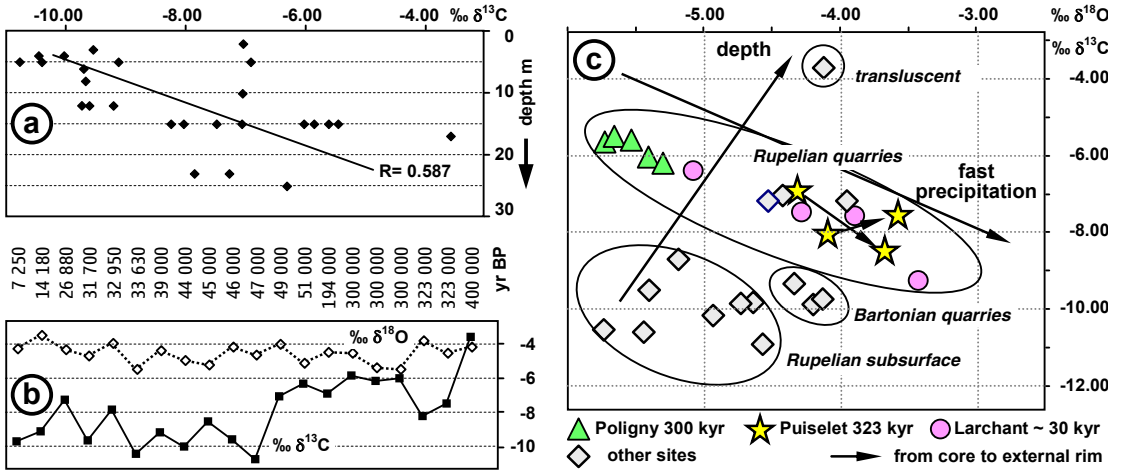


Figure 3 – Stable isotope composition of sand calcite. (a) correlation of $\delta^{13}C$ with depth of the precipitation sites; (b) relation ship between age and isotopic composition; (c) $\delta^{18}O$ vs. $\delta^{13}C$ diagram showing the dispersion of the values along the axes.

6. Prospective

Sand calcites appear as a novel proxy to reconstruct the characteristics of paleo-groundwaters and the extension of paleo-permafrost. Their presence within a rock section points out strong paleo-temperature gradients and thus serves as a tool to estimate the depth reached by freezing in periglacial environments.

Structure and habitus of the sand calcites give information on their position with respect to the land surface and the water table level. Spherolitic sand calcites form in particular settings of water infiltrating that correspond to thermokarsts and talik features. Individual cristallarias form in deeper parts of the sections and in zones where infiltration water gently seeps through. Sand calcites arranged in layers mark the position of a paleo-water table.

The variability of $\delta^{13}C$ isotopic composition of sand calcites as a function of precipitation depth emphasizes their importance for reconstructing Pleistocene paleo-landscape evolution. Thus, sand calcites may provide additional evidence for recent tectonic activity and/or erosion in a given area. Their current exposure above the present day water table holds important implications for the interaction between paleo-groundwater flow, climatic oscillation, landscape erosion, and river incision since the time they have formed. Their relatively precise dating allows reconstructing detailed landscape evolution and approaching differentiated erosion rates.

References

1 Lassone (de) JMF. Nouvelles observations sur les grès cristallisés, faisant suite du mémoire sur les grès, en général & particulièrement sur ceux de Fontainebleau. *Mémoire Académie Royale des Sciences* 1775;68-74.

2 Thiry M, Schmitt J-M, Innocent C, Cojan I. Sables et Grès de Fontainebleau : que reste-t-il des faciès sédimentaires initiaux ? In: 14ème Congrès Français de Sédimentologie, Paris 2013, Trois excursions géologiques en région parisienne, Livre d'excursions. *Publication ASF* 2013;**74**:37-90.

3 Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM, Basile I., ... & Stievenard M. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 1999;**399**:429-436.

4 Obrochta SP, Yokoyama , Morén J, Crowley TJ. Conversion of GISP2-based sediment core age models to the GICC05 extended chronology. *Quaternary Geochronology* 2014;20:1-7.

6 Couchoud I. *Etude pétrographique et isotopique de spéléothèmes du sud-ouest de la France formés en contexte archéologique. Contribution à la connaissance des paléoclimats régionaux du stade isotopique 5*. Thèse doct., Univ. Bordeaux I; 2006.

7 Zak K. Richter DK, Filippi M, Zivor R, Deininger M, Mangini A, Scholz D. Coarsely crystalline cryogenic cave carbonate – a new archive to estimate the Last Glacial minimum permafrost depth in Central Europe. *Climate of the Past* 2012;8:1821–1837.

8 Richter DK, Meissner P, Immenhauser A, Schulte U, Dorsten I. Cryogenic and non-cryogenic pool calcites indicating permafrost and non-permafrost periods: a case study from the Herbstlabyrinth-Advent Cave system (Germany). *The Cryosphere* 2010;**4**:501–509.