

Seasonal isotopic imprint in moonmilk from Caverne de l'Ours (Quebec, Canada): implications for climatic reconstruction

Denis Lacelle, Bernard Lauriol, and Ian D. Clark

Abstract: Moonmilk, which is often seen coating walls in temperate caves, is a porous secondary calcite deposit composed of an aggregate of microcrystalline calcite and water. This study, based on moonmilk deposits found in Caverne de l'Ours, Ottawa Valley region, proposes a model for its formation based on the calcite and water isotope chemistry and evaluates its use as a climatic proxy. In Caverne de l'Ours, non-calcitic mineral inclusions protrude from the bedrock (Grenville marble) into the moonmilk, while others are entirely enclosed within the moonmilk. This observation suggests a mechanism of bedrock dissolution and reprecipitation for the formation of moonmilk, which is controlled by the changing seasonal climate in the cave. The $\delta^{18}\text{O}$ of the moonmilk interstitial water indicates that the condensation of water vapour occurs mostly in winter and spring. The condensation of water vapour on the surface of the walls allows for the dissolution of the Grenville marble and releases ions necessary for the precipitation of moonmilk. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of calcite and $\delta^{18}\text{O}$ of the moonmilk interstitial water indicate that precipitation of moonmilk occurs during summer and fall. During these seasons, the relative humidity in the cave decreases resulting in moonmilk growth through the slow evaporation of calcite-saturated water. A comparison of the $\delta^{18}\text{O}$ record of moonmilk from caves in Gaspésie (Canada) and from Aven d'Orgnac (France) shows that this material retains temperature information valuable for paleoclimatic reconstructions.

Résumé : Le mondmilch qui couvre souvent les parois des cavernes, est un dépôt poreux de calcite secondaire formé d'un mélange d'eau et de calcite microcristalline. Cette étude traite des dépôts de mondmilch de la caverne de l'Ours, située dans la région de la vallée de l'Outaouais et propose un modèle pour sa formation basé sur les isotopes de la calcite et de l'eau et évalue son potentiel pour des reconstructions climatiques. Dans la caverne de l'Ours, des inclusions de minéraux non-calcitiques extrudent de la roche-mère (le marbre de Grenville) et pénètrent dans le mondmilch tandis que d'autres sont entièrement enrobés de mondmilch. Cette observation suggère un mécanisme de dissolution de la roche-mère suivi d'une reprecipitation pour la formation du mondmilch, laquelle est contrôlée par les changements saisonniers du climat de la caverne. Les valeurs isotopiques de l'eau interstitielle du mondmilch indiquent que la condensation de la vapeur d'eau est la principale source d'eau pour le mondmilch. La condensation de la vapeur d'eau en hiver et au printemps sur la surface des murs provoque la dissolution du marbre et relâche les ions nécessaires à la précipitation du mondmilch. Les valeurs isotopiques de la calcite ($\delta^{18}\text{O}$ et $\delta^{13}\text{C}$) et de l'eau interstitielle ($\delta^{18}\text{O}$) du mondmilch indiquent que ce dernier se forme en été. Comme l'humidité relative dans la caverne décroît en été, un peu d'eau du mondmilch s'évapore lentement et il en résulte une précipitation de la calcite. Une comparaison des valeurs de $\delta^{18}\text{O}$ de mondmilch récolté dans des cavernes de Gaspésie (Canada) et de l'Aven d'Orgnac (France) permet de conclure que ce matériel contient des informations précieuses pour des reconstructions paléoclimatiques.

Introduction

Moonmilk (or mondmilch) is a porous speleothem composed of an aggregate of microcrystalline carbonate crystals and water often seen coating walls in caves (Bernasconi 1961; Fisher 1988). Moonmilk can be formed of CaCO_3

polymorphs (calcite, aragonite, vaterite), monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), magnesite (MgCO_3), hydromagnesite ($\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Onac and Ghergari 1993; Hill and Forti 1997). Calcite moonmilk is a term reserved to describe moonmilk

Received 4 March 2004. Accepted 8 September 2004. Published on the NRC Research Press Web site at <http://cjes.nrc.ca> on 14 December 2004.

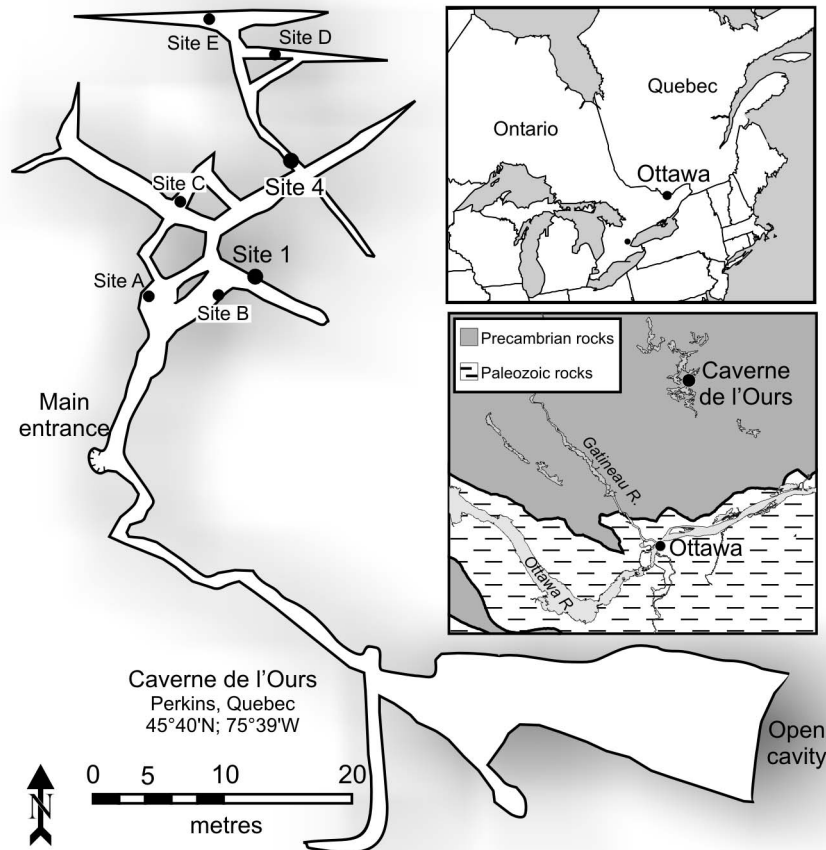
Paper handled by Associate Editor D. Lavoie.

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Fig. 1. Location and topography of Caverne de l'Ours showing location of moonmilk samples.



that has > 90% calcite in its solid phase (Fisher 1992, 1993). The water content of active moonmilk varies considerably. Under its normally hydrated phase (40%–70% gravimetric water content), active moonmilk is spongy and wet. According to Istvan et al. (1995), the water retaining capacity of active moonmilk can be attributed to its porous network of calcite fibers.

Many hypotheses for the genesis of this quite-ordinary substance have been proposed since the first description made by Nicolas Lanh in 1708 (in Bernasconi 1976). Some envisage moonmilk as being the result of biogenic processes of cave microorganisms (Bertouille 1972; James et al. 1982). Other attributes its origin to physico-chemical processes similar to speleothem formations (Bernasconi 1961; Melon and Bourguignon 1962; Geze 1976). More recently, moonmilk has been attributed to a combination of both physico-chemical and biogenic processes (Basillais 1997; Onac and Ghergari 1993). Although there are a number of studies on the isotopic composition of fluid inclusion in stalagmites and stalactites (Gascoyne 1992; Genty et al. 2002), no investigations exist of the isotopic composition of the interstitial water of moonmilk and of its calcite.

Caves in the Ottawa Valley – St. Lawrence Lowland region are abundant in moonmilk, but poor in stalagmites and stalactites. In European caves, moonmilk is considered a destructive agent, degrading prehistoric cave paintings and

cultural features. This study focuses on active moonmilk deposits found in Caverne de l'Ours, Ottawa Valley region, with the objectives of (1) determining the origin of the water in moonmilk based on the stable isotope of water (^{18}O and D); (2) examining the equilibrium conditions of the isotope exchange in the calcite–water system; (3) proposing a model for the formation of moonmilk based on its calcite C–O isotope chemistry (^{13}C , ^{14}C , and ^{18}O); and (4) comparing the $\delta^{18}\text{O}$ of moonmilk from various geographical regions to evaluate its use as a proxy for paleoclimatic reconstructions.

Caverne de l'Ours

Caverne de l'Ours (45°40'N; 75°39'W) is located 25 km north of Ottawa, near the eastern limit of the Canadian Shield (Fig. 1). The cave is situated in a region characterized by large seasonal temperature variations and relatively high precipitation. The mean annual air temperature recorded in Ottawa is 6 °C (January temperature $T^{\circ}\text{mean}$: –11 °C; July $T^{\circ}\text{mean}$: 21 °C), and the area receives a total of 1100 mm of precipitation annually, of which one-third falls as snow (Environment Canada 2003). Caverne de l'Ours is found in a mixed-deciduous forest composed of spruce (*Picea*), hemlock (*Tsuga*), cedar (*Thuja*), birch (*Betula*), and maple (*Acer*), which is characteristic of the middle Ottawa zone of the Great Lakes – St. Lawrence forest region (Rowe 1972).

The cave was probably scoured into Precambrian Grenville marble outcrop by subglacial meltwater flowing from the Laurentide ice sheet. The Grenville marble consists of metamorphosed limestone ($\text{CaCO}_3 > 95\%$), with $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of -7.9‰ and 2.3‰ , respectively (Kretz 1980, 2001). This marble is highly soluble and contains numerous inclusions of quartz, gabbro, garnet, and feldspar (Dresser and Denis 1946; Prévost and Lauriol 1994).

The main entrance to Caverne de l'Ours is located at 200 m above sea level and consists of a 2-m vertical shaft. A second entrance, located 10 m below the main entrance, consists of an open cavity at the same level of a small closed-basin lake adjacent to the cave. The cave measures 250 m in length with narrow (<1 m) subhorizontal passages that reach a few meters in height. A perennial stream flows on the floor of the cave.

In Caverne de l'Ours, moonmilk covers ~20% of the walls. Today, about ~80% of all moonmilk in Caverne de l'Ours is inactive, while active moonmilk is restricted to a few locations in the cave (i.e., sites 1 and 4; Fig. 1). In Caverne de l'Ours, active moonmilk is characterized by its cauliflower-like appearance, white colour, and wet and spongy texture. Inactive moonmilk is white, hard, and crumbly with a porous texture and sometimes covered by a thin clay coating. At site 1, located 10 m from the main entrance, moonmilk is found ~1 m above the floor and is about 5 cm thick. A film of water is often observed along its surface in the winter and spring. At site 4, located in the distant portion of the cave, moonmilk is found 1.8 m above the floor in a narrow side fissure where it reaches a thickness of 5 cm. The active moonmilk sampled in Caverne de l'Ours has a water content (total weight of the liquid/solid phase) varying from 40% in summer to 80% in winter.

Methodology

The microclimate of Caverne de l'Ours was monitored throughout the year 2002. Air temperature was recorded using temperature data loggers (Hobo H8 Pro™), from which daily averages were computed, while relative humidity was measured on a monthly basis using a manual psychrometer. The CO_2 concentration of the cave's atmosphere was measured in situ with CO_2 gas detector tubes (Sensidyne™). The analytical precision of this device is ± 5 ppm. The cave's atmosphere was sampled using pre-evacuated 2 L gas bottles for $\delta^{13}\text{C}$ analysis of the CO_2 . The $^{13}\text{C}/^{12}\text{C}$ ratio was measured with a Gas Bench II interfaced with a Finnigan Mat Delta XL mass spectrometer at the G.G. Hatch Laboratory (University of Ottawa, Ottawa, Ontario).

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition of the moonmilk calcite was measured to establish the geochemical conditions during the formation of moonmilk. The $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios of calcite were determined with a VG SIRA-12 isotope mass spectrometer at the G.G. Hatch Laboratory on CO_2 gas released by the powdered calcite reacting with 100% phosphoric acid (H_3PO_4). Stable isotope data for C and O are expressed in δ -notation, where δ represents the per mil relative difference of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ in a sample with respect to the Vienna Pee-Dee Belemnite (VPDB) standard. Analytical reproducibility is $\pm 0.15\text{‰}$.

The source of carbon for moonmilk has been constrained

by radiocarbon measurements. The ^{14}C activity and ^{14}C age measurements were made at Université Laval (St-Foy, Quebec) by benzene synthesis and beta counting. The ^{14}C activities are presented as pMC (percent Modern Carbon). Radiocarbon ages are presented as uncalibrated ^{14}C years BP using Libby's half-life (5568 years).

The water associated with active moonmilk was collected at the beginning of every month in 2002 to determine the origin of the water in moonmilk and to examine the isotope equilibrium of the calcite–water system. The moonmilk was cored by pressing a glass amber tube through it, which was then tightly sealed. This allowed the samples to be kept in stable conditions until analyses. The moonmilk interstitial water (MIW) was extracted in the laboratory using a porewater press. The $^{18}\text{O}/^{16}\text{O}$ ratio of MIW was determined on CO_2 isotopically equilibrated with the water at 25 °C (analytical reproducibility of $\pm 0.1\text{‰}$). The D/H ratio of MIW was measured on H_2 isotopically equilibrated with the water at 25 °C using a Pt based catalyst (analytical reproducibility of $\pm 1.5\text{‰}$). Both stable isotope measurements were made on the same sample using a Gas Bench II interfaced with a Finnigan Mat Delta XL mass spectrometer at the G.G. Hatch Laboratory. Results are presented using the δ -notation, where δ represents the per mil relative difference of $^{18}\text{O}/^{16}\text{O}$ or D/H in a sample with respect to Vienna Standard Mean Ocean Water (VSMOW).

Microclimate

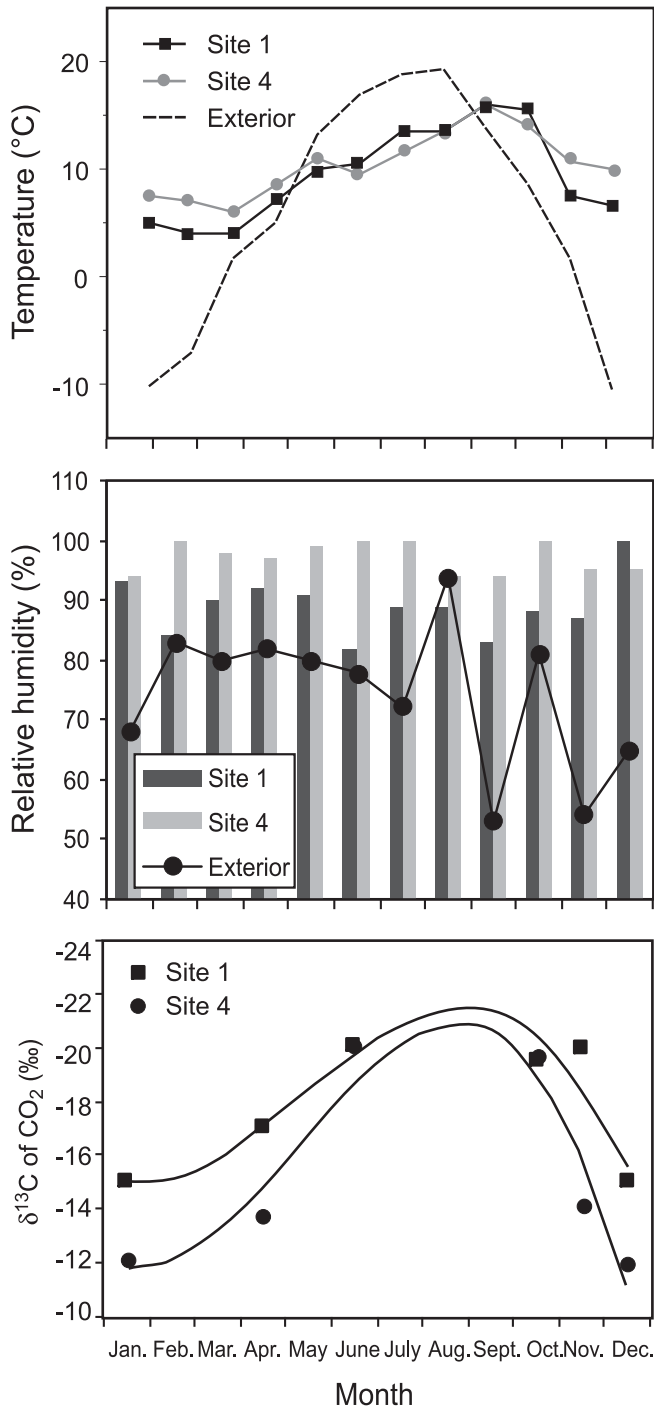
Temperature, relative humidity, and CO_2

The monthly air temperatures, relative humidity, and CO_2 time series in Caverne de l'Ours are presented in Fig. 2. The mean annual air temperature at sites 1 and 4, respectively, were 9.5 ± 4 °C and 10.5 ± 3 °C. These values are higher than the long-term mean annual air temperature recorded in Ottawa (6.3 ± 0.8 °C; Environment Canada 2003) but are only slightly higher than the recorded temperature in 2001 (7.6 ± 2.4 °C; Environment Canada 2003). This is due to the fact that Caverne de l'Ours is a shallow and thermally responsive cave, characterized by a large range in annual air temperature. The difference in air temperature between both sites reflects their location in the cave. Site 1, located near the main entrance of the cave, experiences the largest seasonal temperature variations (ΔT (°C) = 8), while site 4, located in the distant section, experiences smaller seasonal temperature variations (ΔT (°C) = 5).

Relative humidity in the cave approaches the dew point ($93 \pm 5.7\%$). At site 1, the relative humidity averaged $89 \pm 5\%$, with lower values in the summer (85%–90%) (Fig. 2). Site 4 was nearly continuously saturated with water vapour throughout the year ($96 \pm 3\%$). In general, the relative humidity at both sites is slightly lower in summer than in winter because of the increasing hygrometric capacity of warmer air.

The $\delta^{13}\text{C}$ of CO_2 time series exhibits an annual cycle related to the seasonal fluctuations associated with the growing season (Fig. 2). In winter, the $\delta^{13}\text{C}$ of the CO_2 in the cave is enriched (-15‰ to -12‰) over the summer $\delta^{13}\text{C}$ values (-20‰ to -17‰). During the growing season, the decay of plant material that uses the C_3 photosynthetic pathway, which is what the local vegetation uses, produces $\delta^{13}\text{C}$ values in the

Fig. 2. Air temperature, relative humidity, and CO₂ levels time series from sites 1 and 4 for 2002. Measurements were taken 1.5 m above the floor of the cave.



–26‰ to –20‰ range (Clark and Fritz 1997). The biogenically depleted ¹³C of CO₂ is transferred to the cave's atmosphere by diffusion through the fissural network in the bedrock and by the biological respiration of plants in the root zone. For this reason, the δ¹³C in the cave is depleted in summer (–20‰ to –17‰) compared with winter δ¹³C CO₂ values (–15‰ to –12‰).

Air circulation

The seasonal pattern of air circulation in Caverne de l'Ours is shown in Fig. 3. In summer, the cave behaves as a cool environment (i.e., cold trap) since the temperature outside the cave is warmer than inside the cave. During winter, the cave's air temperature is warmer than the temperature outside the cave causing the cold dense air to penetrate inside the warmer cave. This convective air exchange reduces the cave's air temperature and dilutes the biogenically depleted ¹³C of CO₂ in the cave to δ¹³C values near –14‰ with atmospheric CO₂ (~–8‰). In addition, the cold dry air that enters the cave in winter rapidly warms as it flows over the stream and increases its humidity to values near 100%. As the warm humid air rises in the cave, it is replaced by cold air drawn into the cave, creating a strong vertical thermal stratification. In some instances, the warm air escapes the cave through narrow chimneys. As the cold ground surface cools the roof and upper walls of the cave by thermal conduction, the warm air rising condenses at the contact with the surface of the walls. Condensation is a common process in thermally responsive caves (Tarhule-Lips and Ford 1998; De Freitas and Schmekel 2003). Evidence of condensation in the cave is observed in winter as a film of water on the surface of the walls and hoar ice on the walls near both entrances. In summer, the surface of the walls is dry, as thermal conduction transfers heat from the ground surface to the cave's roof and walls.

Moonmilk

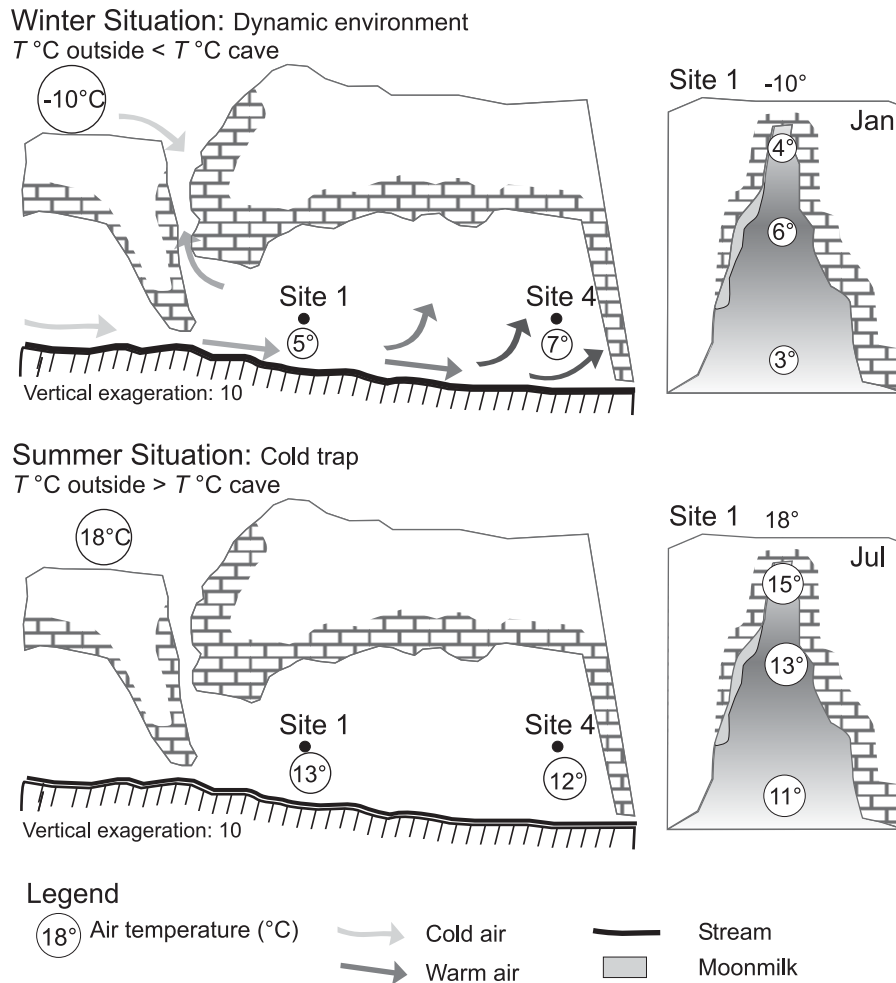
Mineralogical and microscopic descriptions

Moonmilk in Caverne de l'Ours is invariably dominated by calcite (CaCO₃), with trace amount of aragonite (CaCO₃) and kutnohorite (CaMn(CO₃)₂). According to Vigneault (1999), who examined speleothems in caves in the Ottawa Valley region, the presence of the latter is difficult to explain. Many studies indicate that it is a rare mineral (Ness 1991; Deer et al. 1992) and that it is only common in martian meteorites (Lane and Christensen 1997).

Chemical analyses (X-ray fluorescence) show that the moonmilk consists primarily of CaO (55%), while other constitutive elements (Al₂O₃, MgO) never reached 2%, except SiO₂ (6.7%) at site 4 (Table 1). Traces of clays found in the moonmilk at site 4 account for the higher SiO₂ concentration. When the mineral constituents of the moonmilk are dissolved in a weak acid (5% HCl), a transparent yellowish organic residue remains (5%–10%). The presence of this organic residue is common in moonmilk, but its origin is still debated (e.g., Boston et al. 2001).

Petrographically, the moonmilk is composed of calcite needles forming intertwined meshes (Fig. 4), a structure typical of moonmilk (Verrecchia and Verrecchia 1994; Basillais 1997; Borsato et al. 2000). The calcite needles are 0.5–2 μm wide and ~10 μm long and can be characterized as either single or paired monocrystalline rods, which sometimes have a serrated edge. These crystal morphologies are commonly associated with organic material or calcified bacteria, which inhibit lateral growth of calcite during precipitation (Verrecchia and Verrecchia 1994). In cut section, the moonmilk has a laminated internal structure with organic elements

Fig. 3. Theoretical air circulation in Caverne de l'Ours. In summer, the cave behaves as a cold trap since the cave's air temperature is colder than outside. In winter, the cave behaves as a dynamic environment as the cave's air temperature is warmer than outside. The cold dry air that enters the cave rapidly warms as it flows over the stream. As this warm humid air rises, it is replaced by cold air drawn in the cave, creating a vertical thermal stratification.



and non-calcitic mineral inclusions. Some of these minerals protrude from the Grenville marble into the moonmilk, while others are entirely enclosed within the moonmilk (Fig. 4).

^{13}C and ^{18}O values of calcite

The $\delta^{13}\text{C}$ values of actively growing moonmilk are in the -7.5‰ to -6.5‰ range at site 1, and slightly more enriched at site 4, with $\delta^{13}\text{C}$ values in the -5.7‰ to -4.4‰ range (Table 2). The $\delta^{18}\text{O}$ values of the moonmilk remain fairly constant, fluctuating between -10.7‰ and -8.9‰ at site 1, and between -10.7‰ to -10.1‰ at site 4 (Table 2). Active and inactive moonmilk from five other sites in the cave (sites A–E, Fig. 1) have their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values within the same range of the moonmilk from sites 1 and 4 (Table 2). This suggests that the conditions controlling moonmilk growth are similar throughout the cave.

^{14}C activities and ages of calcite

The surface of inactive moonmilk in Caverne de l'Ours has a corrected ^{14}C activity in the 55–63 pMC range (Table 3). By contrast, the surface of active moonmilk at site 1 yielded a corrected ^{14}C activity of 87 pMC (Table 3). At site 4, the

corrected ^{14}C activity of moonmilk varies between 58 pMC near the contact with the host bedrock (Grenville marble) and 80 pMC at the surface. The reason why the ^{14}C activities from the surface of active moonmilk are < 100 pMC may be attributed to the input of dead carbon derived from the Grenville marble, which is ^{14}C free and dilutes the ^{14}C activities of active moonmilk to values < 100 pMC.

Many studies indicate that modern speleothems contain about 85 pMC (Hennig et al. 1983; Genty and Masseault 1997; White 2004), a proportion similar to the one observed at the surface of active moonmilk. According to Brook and Nickman (1996), radiocarbon dating modern speleothems with the assumption of 85 pMC gives good results. Using a dilution factor of 0.87 for the moonmilk in Caverne de l'Ours, inactive moonmilk yielded ^{14}C ages between 3791 BP (UL-2701) and 2668 BP (UL-2699), while active moonmilk yielded modern ^{14}C ages from 0 BP (site 1; UL-2702) to 693 BP (site 4; UL-2784). Borsato et al. (2000) also found that, in caves in the Italian Alps, active moonmilk had apparent ^{14}C ages of < 2000 years BP and that inactive moonmilk ^{14}C ages were > 2000 years BP. This may be a response to modifications of microclimatic conditions in the cave or, alterna-

Fig. 4. (A) Cross-section of moonmilk showing non-calcitic mineral inclusions extruding from the Grenville marble into the moonmilk while others are entirely enclosed within the moonmilk. (B) Cryo-SEM (scanning electron microscopy) photograph of porous moonmilk microfibers forming intertwined meshes. (C) The calcite crystals are 0.5–2 μm wide and $\sim 10 \mu\text{m}$ long and can be characterized as either single or paired monocrystalline rods, which sometimes have a serrated edge.

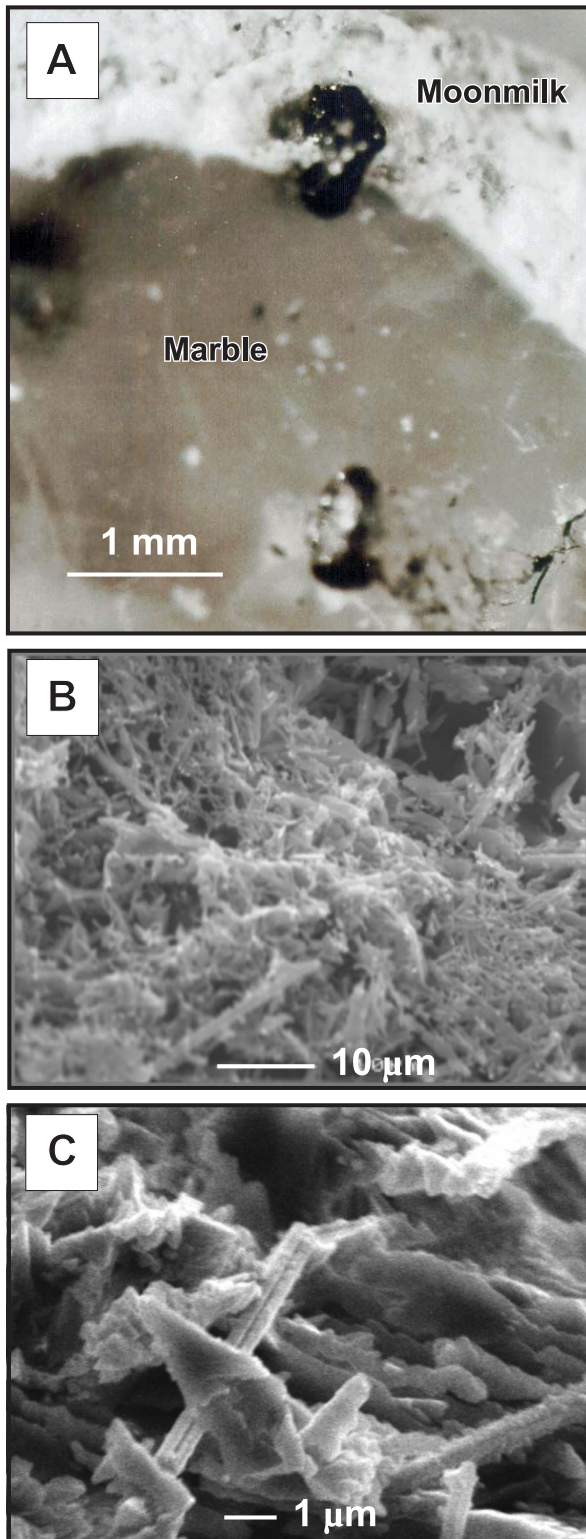


Table 1. Major (%) and trace element (ppm) chemistry of moonmilk in Caverne de l'Ours.

Mineral constituents	Caverne de l'Ours	
	Site 1	Site 4
CaO (%)	54.10	44.70
SiO ₂ (%)	0.99	6.68
Al ₂ O ₃ (%)	0.28	1.37
MgO (%)	0.12	0.66
Fe ₂ O ₃ (%)	0.14	0.64
K ₂ O (%)	0.05	0.25
P ₂ O ₅ (%)	0.03	0.09
TiO ₂ (%)	0.02	0.07
MnO (%)	0.00	0.01
Sr (ppm)	326.00	269.00
Ba (ppm)	26.00	122.00
Zr (ppm)	8.00	34.00
Cr (ppm)	8.00	16.00
Zn (ppm)	4.00	16.00
Nb (ppm)	3.00	4.00
Ni (ppm)	1.00	3.00
Rb (ppm)	0.00	5.00

Table 2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of calcite moonmilk from various locations inside Caverne de l'Ours and of the bedrock (Grenville Marble).

Location	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	<i>n</i>
Site 1	-7.1 ± 0.4	-9.9 ± 0.7	4
Site 4	-4.9 ± 0.6	-10.3 ± 0.3	4
Site A	-6.6	-9.4	1
Site B	-6.5	-8.9	1
Site C	-5.1 ± 0.7	-10.0 ± 0.5	4
Site D	-5.1	-9.4	1
Site E	-6.4	-9.5	1
Bedrock	-2.3	-7.9	1

Note: See Fig. 1 for locations.

tively, that moonmilk may remain active for up to 2000 years. However, due to the uncertainties in the contribution of ^{14}C -free carbon from the wall rock, the measured ^{14}C activities represent minimum values and the calculated ^{14}C ages represent maximum ages for moonmilk formation.

^{18}O and δD values of water

The $\delta^{18}\text{O}$ and δD values of the MIW allow an initial insight into its origin and into the calcite–water isotope equilibrium system (Fig. 5). At site 1, the MIW is characterized by monthly $\delta^{18}\text{O}$ time series ranging from -13.8‰ to -9.0‰ ($\delta^{18}\text{O} = -11.0 \pm 1.6\text{‰}$), and at site 4, the monthly MIW $\delta^{18}\text{O}$ record is in the -14.2‰ to -9.2‰ range ($\delta^{18}\text{O} = -11.1 \pm 1.9\text{‰}$). Both sites show similar trends with minimum $\delta^{18}\text{O}$ values reached in spring and summer. On a $\delta\text{D} - \delta^{18}\text{O}$ diagram, the MIW from both sites plot along a line with a slope of 7.9 (site 1: $\delta\text{D} = 7.9 \delta^{18}\text{O} + 12.3$; ($r^2 = 0.91$); site 4: $\delta\text{D} = 7.9 \delta^{18}\text{O} + 13.7$; ($r^2 = 0.92$)) that is significant at the 1%

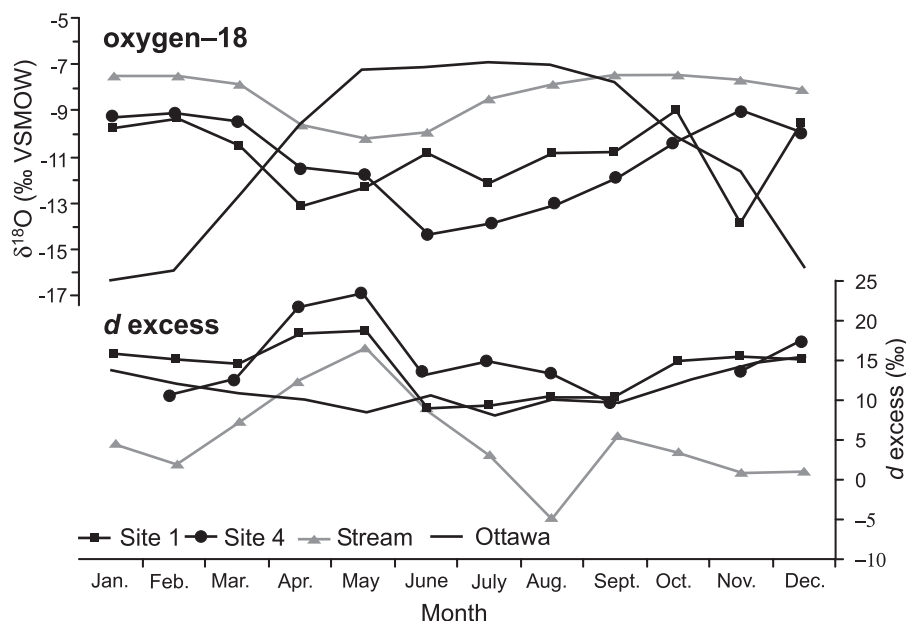
Table 3. Radiocarbon measurements and modeled age estimates of moonmilk in Caverne de l'Ours.

Location	Uncorrected ^{14}C activity (pMC) ^a	Corrected ^{14}C activity (pMC) ^b	Corrected ^{14}C age (years BP)	Modelled age q^c	Laboratory number
Site 1	90	87	1158±90	0	UL-2702
Site 4s	83	80	1808±60	693	UL-2700
Site 4b	60	58	4415±60	3352	UL-2698
Site D	65	63	3722±60	2668	UL-2699
Site B	61	58	4348±70	3352	UL-2703
Site C	57	55	4785±70	3791	UL-2701

^aAs reported from the laboratory.

^bAfter normalization for a $\delta^{13}\text{C}$ value of -6‰ .

^cUsing a dilution factor of 0.87 in the decay equation: $\text{age} = -\ln(a^{14}\text{C}/q \cdot 100) \cdot 8267$.

Fig. 5. Monthly $\delta^{18}\text{O}$ and d excess time series of moonmilk interstitial water from sites 1 and 4 compared with the $\delta^{18}\text{O}$ and d excess time series of precipitation recorded in Ottawa (IAEA/WMO 2001) and the stream flowing inside the cave.

level (Fig. 6). The deuterium excess value ($d = \delta\text{D} - 8 \delta^{18}\text{O}$; Dansgaard 1964) is a measure of the deviation of a given point from the meteoric water line and can indicate if non-equilibrium processes occurred. For comparison purposes, the d excess of precipitation in Ottawa averages 11.7‰ (IAEA/WMO 2001). At Site 1, the monthly d excess time series ranges from $9.1 \pm 0.7\text{‰}$ in summer to $16.9 \pm 2\text{‰}$ in winter (Fig. 5). Site 4 shows a similar trend with monthly d excess record, ranging from $11.9 \pm 2.6\text{‰}$ in summer to $19.4 \pm 6\text{‰}$ in winter (Fig. 5).

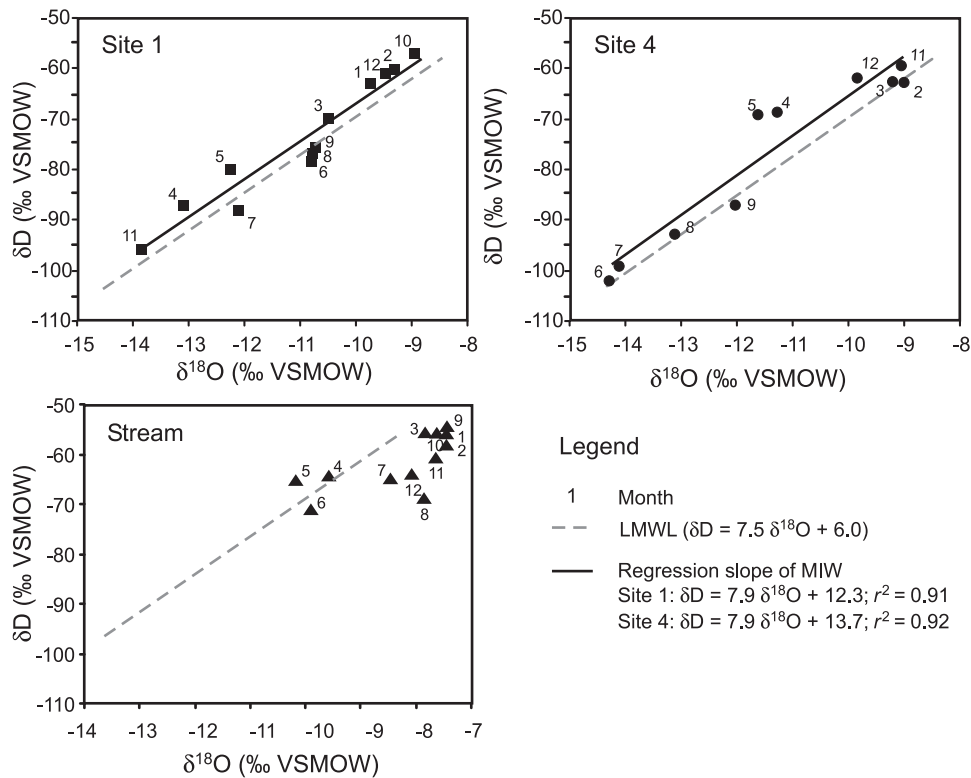
Interpretation

Origin of the water in moonmilk

Several important points emerge from a comparison of the isotopic composition of the MIW, the local precipitation, and the stream flowing inside the cave. First, the average MIW $\delta^{18}\text{O}$ value of -11‰ is equivalent to the average $\delta^{18}\text{O}$ value of $-11.4 \pm 3.6\text{‰}$ measured in the local precipitation (IAEA/WMO 2001) but is depleted by about 3‰ over the average $\delta^{18}\text{O}$ of the stream ($-8.3 \pm 1\text{‰}$). However, distinct monthly $\delta^{18}\text{O}$ time series exist between the MIW and the local precipitation (Fig. 5). The opposing trends argue against

the percolation of surface waters into the cave as the origin of MIW, as suggested by Yonge et al. (1985). The $\delta^{18}\text{O}$ time series of the stream in the cave displays a similar trend to the MIW and is consistently enriched by about 2‰ – 3‰ over the MIW $\delta^{18}\text{O}$ values. This suggests that the MIW is controlled by the condensation of seasonally varying water vapour originating from the stream pumping ^{18}O depleted vapour into the cave's atmosphere in winter and spring. The effect of condensation of water vapour in the cave is evident on a $\delta\text{D} - \delta^{18}\text{O}$ diagram (Fig. 6), where the MIW plot above the local meteoric water line (LMWL) in winter and spring (i.e., high d excess) along a slope very similar to the LMWL. Deuterium excess values $> \sim 10$ are generally found in water vapour generated by secondary evaporation under unsaturated humidity conditions (Clark and Fritz 1997). When such water vapour condenses, it plots above the LMWL along a condensation line with a slope very similar to the LMWL (Fig. 7). Assuming the evaporation of the stream's water under the relative humidity conditions encountered in the cave ($h = 85\text{‰}$ – 98‰), followed by condensation, the monthly $\delta^{18}\text{O}$ values of the condensate follow closely the monthly $\delta^{18}\text{O}$ values recorded in the MIW (Fig. 8). However, it is possible that the collected samples have experience

Fig. 6. $\delta D - \delta^{18}O$ diagram showing the monthly distribution of D and ^{18}O recorded in the moonmilk interstitial water from sites 1 and 4 compared with the stream in Caverne de l'Ours.



a more heterogeneous evolution than this simple model. This would account for the deviations in the MIW values compared with the model. Nonetheless, the good match between model and measured MIW $\delta^{18}O$ time series supports seasonal stream – water vapour isotopic exchange, followed by condensation along the surface of the walls. Condensation of water vapour in thermally responsive caves is a natural process and is the main source of water for weathering of walls and roofs in caves found in all climatic regions whether it is seasonally, diurnally or aperiodically driven (Tarhule-Lips and Ford 1998; Zupan Hajna 2003). In addition, Caumartin (1964) and Klimchouk and Gudzenko (1996) noticed that moonmilk was often located in caves where condensation occurs.

The condensation of water vapour in Caverne de l'Ours is seasonally driven, as the water content in the moonmilk decreases in summer and fall to values < 55%. The dehydration of moonmilk implies a reduction in its water content by slow evaporation, as relative humidity in the cave remains fairly high (near 90%). Evaporation is attributed to the warming of the cave's air temperature, which leads to an increasing hygrometric capacity of the air, thereby reducing the relative humidity in the cave to values near 90% in summer (Fig. 2). The effect of slow evaporation is evident on a $\delta D - \delta^{18}O$ diagram, where the MIW plot below the MIW water line and on the LMWL (i.e., low d excess) during summer and fall. This is a consequence of the fairly high relative humidity in the cave in summer and fall, which attenuates the ^{18}O -enrichment (or d excess depletion) in the residual waters during evaporation.

Fig. 7. $\delta D - \delta^{18}O$ systematic during condensation of secondary evaporated water. When humidity conditions are near 100%, precipitation plots close to the local meteoric water line, however, under decreasing relative humidity conditions, the vapour becomes strongly depleted and precipitation formed by equilibrium condensation plots further above the LMWL along a condensation line with a slope very similar to the LMWL. The condensation of secondary evaporated water vapour originating from the stream was calculated using the following equilibrium ($\epsilon^{18}O_{w-v} = 10.85\%$; $\epsilon D_{w-v} = 95.90\%$; Majoube 1971) and kinetic fractionation factors ($\Delta^{18}O = 14.2(1 - h)$; $\Delta D = 12.5(1 - h)$, where h equals relative humidity; Gonfiantini 1986) at 8 °C.

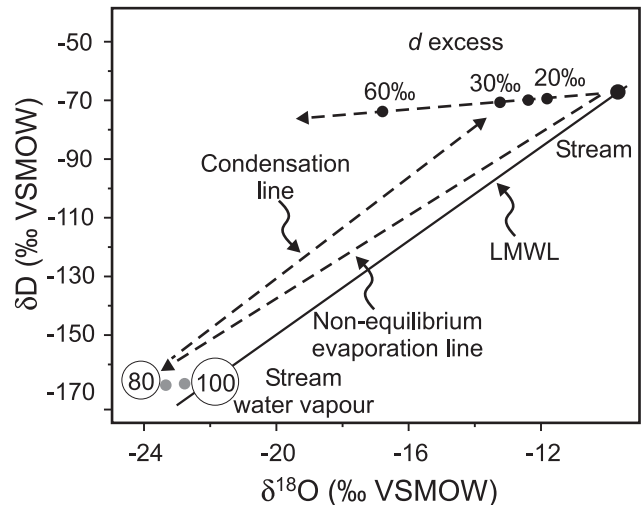
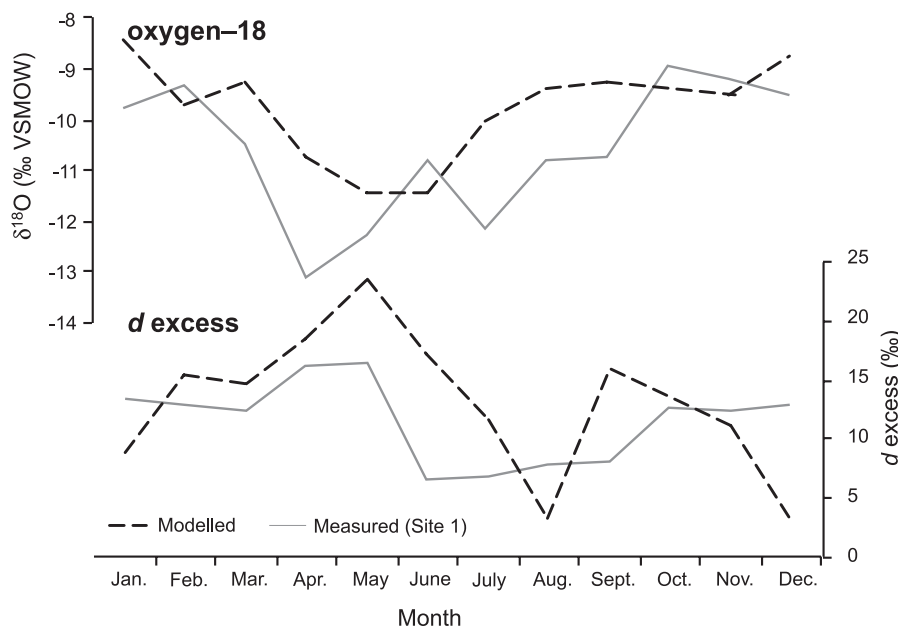


Fig. 8. Monthly $\delta^{18}\text{O}$ and d excess time series of moonmilk interstitial water from site 1 compared with the model calculation discussed in the text.



Origin of the calcite in moonmilk

Oxygen isotopes

Stable isotopes are useful in helping to understand the conditions under which moonmilk precipitated in Caverne de l'Ours. Calcite precipitating under equilibrium involves the preferential incorporation of ^{18}O from water into calcite with a known thermodynamic fractionation factor. The narrow range of the $\delta^{18}\text{O}$ values from the active moonmilk suggests isotope equilibrium deposition in the calcite–water system, as it is unlikely to have kinetically fractionated speleothems that exhibit a homogeneity in their $\delta^{18}\text{O}$ values. The equilibrium conditions during isotope exchange in the calcite–water system were examined by converting the $\delta^{18}\text{O}_{\text{VPDB}}$ values of moonmilk to the VSMOW scale using the following equation:

$$[1] \quad \delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \delta^{18}\text{O}_{\text{VPDB}} + 30.91\% \quad (\text{Coplen et al. 1983})$$

and then correcting for the temperature-dependent fractionation of ^{18}O between calcite and water for the air temperature range observed in the cave (5–14 °C). This fractionation factor decreases by 0.3‰ per °C increase (from 33.0‰ at 5 °C to 30.8‰ at 14 °C; O'Neil et al. 1969). Thus, the $\delta^{18}\text{O}$ composition of the water from which moonmilk precipitated ($\delta^{18}\text{O}_{\text{w}}$) can be calculated as

$$[2] \quad \delta^{18}\text{O}_{\text{w}} = \delta^{18}\text{O}_{\text{moonmilk(VSMOW)}} - \epsilon^{18}\text{O}_{\text{calcite-water}}(\%) \quad (\text{O'Neil et al. 1969})$$

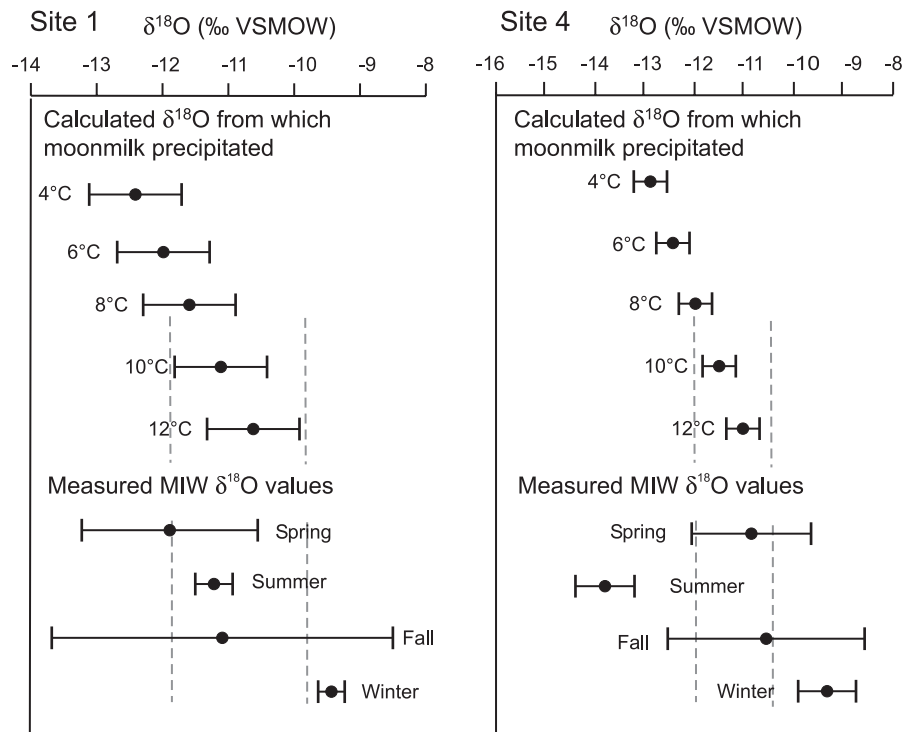
The calculated $\delta^{18}\text{O}_{\text{w}}$ values can be compared directly with the measured monthly MIW $\delta^{18}\text{O}$ values to determine if calcite precipitates under equilibrium conditions and possibly determine during which season moonmilk precipitates. At site 1, the calculated $\delta^{18}\text{O}_{\text{w}}$ values are in the same range of the MIW $\delta^{18}\text{O}$ values recorded during the summer and fall (Fig. 9). While at site 4, the calculated $\delta^{18}\text{O}$ composition of the water

from which moonmilk precipitated is in the same range of the MIW $\delta^{18}\text{O}$ values recorded during the spring and fall (Fig. 9). This suggests that the $\delta^{18}\text{O}$ values of the calcite in moonmilk might preserve a valuable climatic signal regarding summer–fall temperatures.

Carbon isotopes

The carbon sources in Caverne de l'Ours are threefold; carbon derived from the dissolution of the bedrock, biogenic CO_2 , and atmospheric CO_2 , and can be constrained by the $\delta^{13}\text{C}$ and ^{14}C measurements. The ^{14}C activities obtained from active moonmilk, even though they represent minimum values, provide valuable information regarding the source of carbon, as the carbon derived from the bedrock (Grenville marble) is ^{14}C free. The ^{14}C activities measured in the moonmilk vary between 58 pMC, near the contact with the bedrock (Grenville marble), and 87 pMC at the surface. Such a trend in ^{14}C activities is consistent with the dissolution of the Grenville marble followed by partial reequilibration with ambient CO_2 . Bernasconi (1961) suggested that moonmilk forms when its water content is between 45% and 65%. These conditions are reached during the summer and fall when the water content of the moonmilk decreases to < 55%. It was also demonstrated earlier in the text from the $\delta^{18}\text{O}$ systematic of the MIW that moonmilk tends to precipitate during these seasons. Calculation using the $\delta^{13}\text{C}$ of biogenically depleted CO_2 in the cave (–19‰) under open system conditions at 12 °C ($\epsilon^{13}\text{C} \text{ CaCO}_3 - \text{CO}_2 = 12.3\%$; Bottinga 1968) yields a $\delta^{13}\text{C}$ for calcite of –6.7‰ and up to –6‰ at 8 °C ($\epsilon^{13}\text{C} \text{ CaCO}_3 - \text{CO}_2 = 13.0\%$; Bottinga 1968). These $\delta^{13}\text{C}$ values for calcite produced under open system conditions during the summer and fall are within the range of the measured $\delta^{13}\text{C}$ values from the moonmilk (–7.7‰ to –4.4‰; average $-6.0 \pm 1.3\%$), with the slight enrichment that can be attributed to carbon contribution from the bedrock ($\delta^{13}\text{C} = 2.3\%$). This is consistent with the ^{14}C activities measured at the surface of the moon-

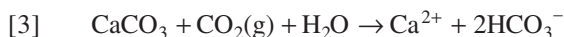
Fig. 9. Calculated $\delta^{18}\text{O}$ of water from which moonmilk precipitated based on the ^{18}O of calcite compared with the measured $\delta^{18}\text{O}$ moonmilk interstitial water.



milk, as they are not fully reequilibrated with ambient CO_2 (^{14}C activities < 100 pMC; Table 3).

Proposed growth mechanism

Based on the data and discussion presented in the preceding text, the formation of moonmilk in Caverne de l'Ours is attributed to a two-step process controlled by the changing seasonal climatic conditions in the cave. When examined in cut section, non-calcitic mineral inclusions protrude from the Grenville marble into the moonmilk, while other minerals are entirely enclosed within the moonmilk (Fig. 4). This observation strongly suggests a mechanism of wall rock dissolution and reprecipitation for the formation of moonmilk. In winter, the cave's atmosphere is near saturation with water vapour and has a PCO_2 value near $10^{-2.8}$. Therefore, the first process involves the condensation of corrosive water vapour along the walls, which causes the dissolution of the Grenville marble. This solution becomes quickly saturated with calcium and bicarbonate ions necessary for the moonmilk growth as they are released given this dissolution reaction:



This equation implies that under ideal and stoichiometric conditions, half the carbon will be derived from the bedrock (Grenville marble) and the other half will be derived from ambient CO_2 . However, following dissolution of the Grenville marble, the dissolved HCO_3^- partially reequilibrates with the ambient CO_2 in the cave by isotopic exchange, as indicated by the ^{14}C activities of active moonmilk that are greater than 58 pMC, since the carbon equilibration also applies to ^{14}C . The second process occurs in summer and fall when the relative humidity in the cave decreases to values near 90%.

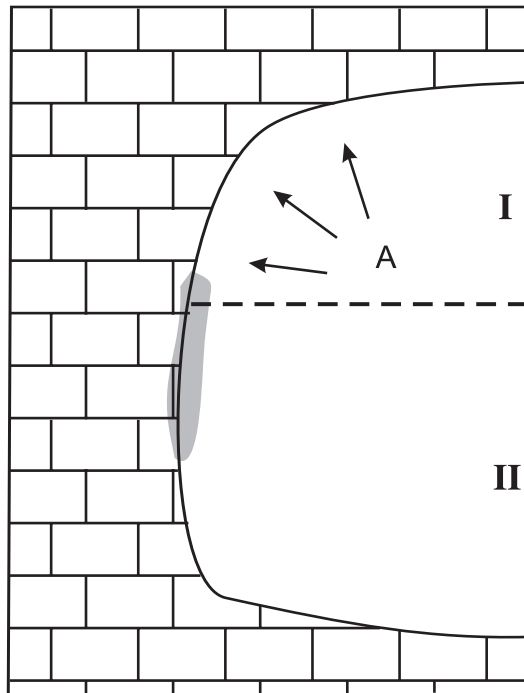
This allows for evaporation from the calcite-rich solution, which takes place under near-equilibrium conditions with little to no modification of the $\delta^{18}\text{O}$ signature in the MIW and calcite being formed. This cycle of condensation and near-equilibrium water evaporation produces the soft microcrystalline deposits of moonmilk. Therefore, the organic matter observed in the moonmilk could result from the deposition of aerosol-borne material during the condensation of water vapour.

Nicolas Languh in 1708 (in Bernasconi 1976) first proposed a similar model, suggesting that the condensation of acidic water vapour could dissolve the limestone in a cave. More recently, Krivacsy and Molnar (1998) suggested that aerosols, which would be preferentially deposited in areas of condensation in the cave, are more acidic in winter than in summer, favoring dissolution of the limestone during winter. In a recent study of cave wall weathering, Zupan Hajna (2003) suggested that the action of condensation in caves is a major component of wall rock dissolution and that it could result in the formation of moonmilk (Fig. 10).

Climatic reconstruction

Speleothems can archive climate information, providing that the waters from which they precipitated have not experienced significant evaporation and that they reflect the mean annual air temperature of the region above the cave. The $\delta^{18}\text{O}$ record from speleothems (i.e., stalactites and stalagmites) has been widely used to reconstruct past climatic and environmental changes (Schwarcz 1986; Genty et al. 2002; Clark et al. 2004; McDermott 2004). However, the $\delta^{18}\text{O}$ record of moonmilk was never examined as a proxy for paleoclimatic reconstructions. The $\delta^{18}\text{O}$ record of moonmilk from

Fig. 10. Schematic representation of an ideal setting for moonmilk precipitation in Caverne de l'Ours (modified from Zupan Hajna 2003). Condensation in the cave occurs mostly in winter and moonmilk grows during summer, as some of the interstitial water is lost through the process of evaporation.

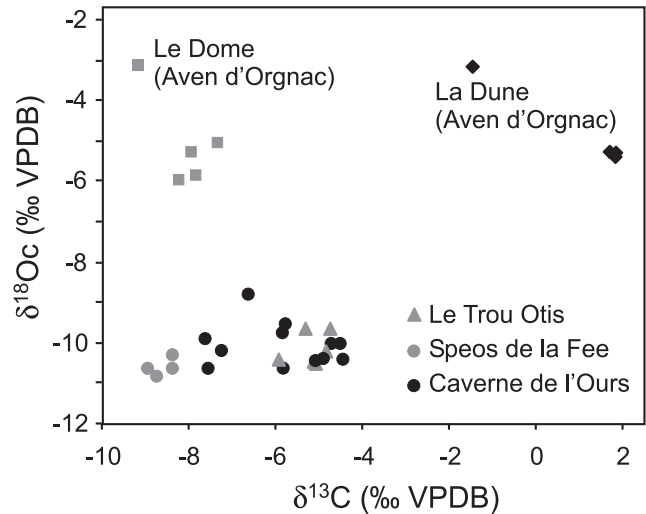


- I Warm and saturated air
- II Cool / warming air
- A Condensation, weathering of cave's roof and walls and running water-film.
- Moonmilk

Caverne de l'Ours (Ottawa Valley region, Canada) was presented earlier in the text. Here, the $\delta^{18}\text{O}$ records of active moonmilk from Spéos de la Fée and Trou Otis (Gaspésie, Canada) and Aven d'Orgnac (Ardèche, France) are presented to evaluate the use of the $\delta^{18}\text{O}$ record of moonmilk as a possible paleothermometer.

Spéos de la Fée and Trou Otis are located in Silurian limestone, west of Lake Matapédia, in Gaspésie, Quebec (Canada). The mean annual air temperature in the region is 4 °C and precipitation reaches a total of 1200 mm annually (Environment Canada 2003). The overlying ground surface is covered with conifers (*Picea* and *Abies*) and a few deciduous trees (e.g., birches). The $\delta^{18}\text{O}$ values of moonmilk from Spéos de la Fée range from -11.2‰ to -10.8‰ , while in Trou Otis, the $\delta^{18}\text{O}$ values of moonmilk are in the -10.5‰ to -9.6‰ range. These $\delta^{18}\text{O}$ are similar, albeit slightly more depleted than those obtained in moonmilk in Caverne de l'Ours (Fig. 11). In addition, Ek et al. (1981) proposed that the moonmilk in Spéos de la Fée was the result of condensation of water vapour in a biogenic-rich CO_2 atmosphere, which could dissolve the limestone on the wall, followed by precipitation of moonmilk driven by progressive evaporation

Fig. 11. $\delta^{13}\text{C} - \delta^{18}\text{O}$ diagram of moonmilk from Caverne de l'Ours, "Le Dome" and "La Dune" Aven d'Orgnac, and from Le Trou Otis and Spéos de la Fée, Gaspésie.

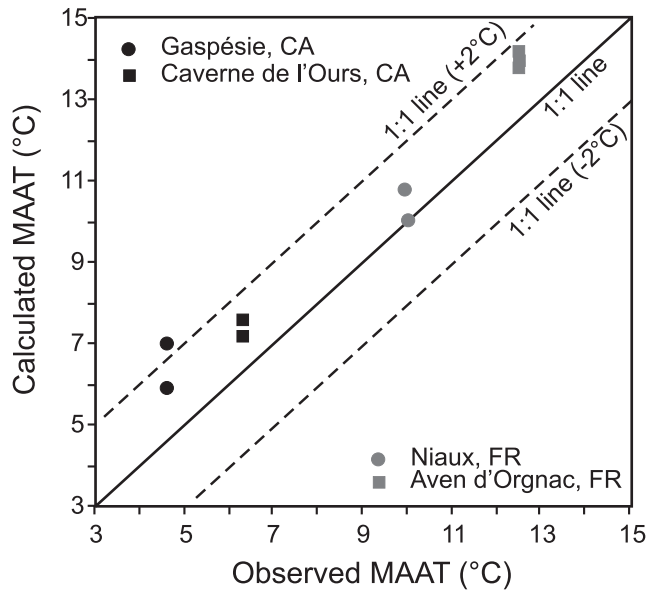


or evasion of CO_2 , a process comparable to the one currently observed in Caverne de l'Ours.

The Aven d'Orgnac karstic system is located in Cretaceous limestone, 40 km northwest of Avignon, in southern France. The mean annual air temperature in the region is 13 °C, while precipitation reaches a total of 600 mm. The overlying ground surface is covered with a dense deciduous forest dominated by oak (*Quercus ilex* and *Quercus humilis*) and common box (*Buxus sempervirens*). Moonmilk was collected from two sites in Aven d'Orgnac, at "La Dune" and "Le Dome" (Fig. 11). The $\delta^{18}\text{O}$ values of moonmilk from La Dune average $-5.4 \pm 0.1\text{‰}$ ($n = 4$), while at Le Dome, the $\delta^{18}\text{O}$ values of moonmilk average $-5.1 \pm 0.6\text{‰}$ ($n = 6$). These $\delta^{18}\text{O}$ values are similar to $\delta^{18}\text{O}$ values of modern speleothems that formed under equilibrium conditions in that region (Duplessis et al. 1969).

The $\delta^{18}\text{O}$ values of moonmilk from Aven d'Orgnac are enriched over the $\delta^{18}\text{O}$ values of moonmilk in the Ottawa Valley and Gaspésie region, suggesting that a $\delta^{18}\text{O}$ -temperature relation possibly exists among the moonmilk collected from the three distinct geographical regions. To examine the possible temperature signal recorded in moonmilk, the $\delta^{18}\text{O}_{\text{VPDB}}$ values were converted to $\delta^{18}\text{O}_{\text{VSMOW}}$ using eq. [1] and then correcting for the temperature-dependant fractionation of ^{18}O between calcite and water using eq. [2] with the associated mean annual air temperature at the respective sites. Accordingly, temperatures can be retrieved through Dansgaard global $\delta^{18}\text{O} - T$ (°C) relation ($\delta^{18}\text{O} = 0.69 T$ (°C) - 13.6‰; Dansgaard 1964). A comparison of the measured cave temperatures with the temperatures retrieved from Dansgaard $\delta^{18}\text{O} - T$ (°C) relation is shown in Fig. 12. Of the seven sites from which $\delta^{18}\text{O}$ values of active moonmilk could be obtained, all of the data plot on or above the observed vs. predicted mean annual air temperature (MAAT) line except one site that has a temperature difference > 2 °C. This suggests that the $\delta^{18}\text{O}$ values recorded in moonmilk could potentially be used as a paleothermometer of summer-fall temperatures.

Fig. 12. Observed mean annual air temperatures in caves versus calculated mean annual air temperatures (derived from the $\delta^{18}\text{O}$ values of moonmilk).



Conclusions

Based on the results from active moonmilk in Caverne de l'Ours, four main conclusions can be drawn.

- (1) In Caverne de l'Ours, the moonmilk interstitial water originates mainly from the condensation of water vapour with the stream that flows inside the cave acting as its source. This is indicated by the $\delta\text{D} - \delta^{18}\text{O}$ systematic, where the MIW plots above the local meteoric water line (i.e., high d excess). Condensation occurs mainly during winter. Cold dry air from outside is drawn into the cave, where it warms up as it flows over the stream and acquires humidity. As the warm humid air rises, it condenses along the roof and walls in the cave. Thus the MIW is derived from water vapour evaporated under near-equilibrium conditions from the stream and advected through the cave's atmosphere.
- (2) During the summer and fall, the relative humidity in the cave remains fairly high, with values near 90%. The stable isotopes of the MIW indicate that slow evaporation is the main process that diminishes the water content of moonmilk. In the $\delta\text{D} - \delta^{18}\text{O}$ diagram, the MIW plots slightly below the MIW water line and on the LMWL. This indicates that water loss takes place under near-equilibrium conditions, with little to no modifications in the isotopic composition of the MIW.
- (3) Moonmilk growth is attributed a bedrock dissolution and reprecipitation mechanism controlled by the changing seasonal climatic conditions in the cave. The condensation of corrosive water vapour in winter in the cave causes the dissolution of the bedrock (Grenville marble) and releases the ions necessary for precipitation of moonmilk in summer. As water is lost in summer by near-equilibrium evaporation, moonmilk precipitates from this calcite-saturated solution. The growth of moonmilk during summer and fall is supported by the $\delta^{18}\text{O}$ values

of calcite, which are in equilibrium with the MIW during these seasons, and the $\delta^{13}\text{C}$ values, which are in equilibrium with biogenically produced CO_2 .

- (4) Based on $\delta^{18}\text{O} - T$ (°C) relation for moonmilk in various geographical locations, moonmilk retains temperature information valuable for paleoclimatic reconstruction as little to no modification of the $\delta^{18}\text{O}$ signature in the MIW and the calcite was observed.

Acknowledgments

This project was supported by Natural Sciences and Engineering Research Council of Canada (NSERC) grants to B. Lauriol and I.D. Clark. We would like to thank W. Abdy, P. Middlestead, and G. St-Jean (G.G. Hatch Laboratory, University of Ottawa, Ontario) and L. Ling (SEM Laboratory, Carleton University, Ottawa, Ontario) for their technical assistance in the laboratory. Moonmilk samples from Trou Otis and Spéos de la Fée (Gaspésie, Quebec, Canada) were made possible by D. Caron and the Société Québécoise de Spéléologie. J. Teyssier and the municipality of Orgnac granted permission to sample moonmilk in Aven d'Orgnac, France. This manuscript benefited from suggestions by J. Bjornson and from constructive comments provided by the two reviewers D.C. Ford and C. Hillaire-Marcel and the Associate Editor D. Lavoie.

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