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# SPELEOTHEM DEPOSITS IN A PROTEROZOIC PALEOKARST, MESOPROTEROZOIC DISMAL LAKES GROUP, ARCTIC CANADA

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## SPELEOTHEM DEPOSITS IN A PROTEROZOIC PALEOKARST, MESOPROTEROZOIC DISMAL LAKES GROUP, ARCTIC CANADA

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### Abstract

A well-preserved paleokarst within the Mesoproterozoic Dismal Lakes Group, Arctic Canada, is marked by an extensive grike system, spectacular cave-collapse breccias, and the oldest known speleothem deposits. Karst development is interpreted to have occurred during an abrupt fall in relative sea level resulting from tectonic uplift during emplacement of the ~1.27 Ga Muskox igneous intrusion. Sedimentary deposits within the grike network include flowstone, pisoids, carbonate microspar, and detrital quartz sand/silt. Here we use petrographic, cathodoluminescence, and  $\delta^{13}$ C and  $\delta^{18}$ O isotope analysis to determine the depositional history and origin of these speleothem deposits.

Primary speleothem fabrics include micritic carbonate coating all host rock surfaces, flowstone which precipitated as void-filling and vadose drip cements, at least two generations of detrital quartz, micritic pisoids, and a matrix of carbonate microspar. Adhesion and alignment of quartz grains along pisoid margins suggest a combination of carbonate precipitation in standing pools, transport of both carbonate and siliciclastic elements, and ultimate deposition in fluid and gas-filled grikes. Flowstone crystal fabrics are similar to herringbone carbonate and probably denote precipitation from anoxic waters or oxic waters with fluctuating levels of HCO<sub>3</sub><sup>-</sup>. Isotopic analysis indicates that the speleothem possesses significantly lighter  $\delta^{13}$ C and  $\delta^{18}$ O values as compared to the host dolostone, implying alteration of host rock and eventual carbonate precipitation by terrestrial fluids rich in decomposing organic material. Such observations suggest that the Dismal Lakes Group karst system represents carbonate dissolution, buffering of terrestrial fluid pH, and eventual precipitation of speleothem from these modified fluids.  $\delta^{13}$ C data suggest geochemical evidence for an active terrestrial biomass in the Precambrian.

#### Introduction

The purpose of this paper is to characterize the primary features of the Dismal Lakes Group paleokarst system and to interpret the origin and depositional history of associated speleothem deposits via petrographic, cathodoluminescence, and geochemical techniques. These deposits are significant not only because they represent the oldest known speleothem material, but also because they preserve a unique record of Precambrian paleoclimatic and terrestrial conditions. In the Dismal Lakes Group, the speleothem occurs within a paleokarst horizon separating the lower and upper members of the Greenhorn Formation. Samples used for analysis were collected from the paleokarst horizon at a locality west of the September Lakes (SL) region (Fig. 1). Petrographic observations were made of thin sections using transmitted light, and the depositional sequence of the speleothem deposits were deduced from these observations. Cathodoluminescence analysis was performed on polished thick sections, while geochemical analyses ( $\delta^{13}$ C and  $\delta^{18}$ O) were made on distinct phases identified and drilled from the polished thick sections. The resulting isotopic signature of speleothem material was then compared to the isotopic signatures of the host Greenhorn formation provided by Frank et al., (2003). These comparisons revealed a truly distinct isotopic signature for the speleothem material and made possible the characterization of the precipitating fluid composition.

#### **Geologic Setting**

The Dismal Lakes Group is a 1500+ m succession of siliciclastic and carbonate formations extending in a sinuous exposure from Great Bear Lake to Coronation Gulf in Northwest Territories and Nunavut, Arctic Canada (Fig. 1). The age of the Dismal Lakes Group is constrained by the underlying Narakay Volcanic Complex (1662  $\pm$  8 Ma) and the overlying Coppermine Flood basalts (1270  $\pm$  4 Ma). Various regional and tectonic constraints have been interpreted to suggest that Dismal Lakes Group deposition began after 1370 Ma (Kerans et al. 1981).

The uppermost formation in the Dismal Lakes Group is the mixed siliciclasticcarbonate Greenhorn Formation, and it is overlain by the Coppermine River Group flood basalts (Kerans et al. 1981). The Greenhorn Formation is divided into upper and lower members, where the sequence boundary is denoted by a paleokarst horizon. This horizon represents abrupt subaerial exposure of lower Greenhorn strata and contains an extensive network of grikes, cave-collapse breccias, significant speleothem formation, and terrigenous sediments (Kerans and Donaldson, 1988). Exposure of this platform resulted from a combination of a eustatic fall in sea level and an abrupt, more localized fall in sea level related to tectonic uplift of the September Lakes region (SL) associated with emplacement of the ~1.27 Ga Muskox igneous intrusion. The Muskox intrusion has been interpreted as the primary feeder chamber for the extrusion of the Coppermine flood basalts, which were later extruded following deposition of the upper member of the Greenhorn Formation (Kerans, 1983).

### **Petrographic Observations**

Transmitted light petrography was performed on twenty thin sections made from samples collected at the paleokarst horizon. Speleothem material is restricted to grikes

and cavities, 10-20 cm wide, which extend up to 12 m into the lower Greenhorn strata (Fig 2A). At outcrop scale, this material is characterized by 4 cm-thick crystalline flowstone, pisoids, and quartz-bearing carbonate (Fig 2B). Through comparative analysis of these samples, six primary fabrics have been interpreted as being characteristic of the Dismal Lakes Group paleokarst-speleothem system. Host dolostone of the lower Greenhorn member forms the walls of the grikes and cavities and shows varying degrees of diagenetic recrystallization and alteration. Also, several smaller, broken fragments (1-5 mm) of the host dolostone are found throughout the matrix. Laminated micrite forms the first generation speleothem and coats all host rock surfaces (Fig. 3). Another primary fabric is a matrix of fine to coarse-grained carbonate (Fig. 3). Pisoids occur throughout the samples and are sometimes found in discrete layers, with diameters up to 1 cm. These pisoids are dominantly micritic and concentrically laminated, while a few have nucleation centers made of quartz grains and are composed of sparry to crystalline carbonate (Figs. 4A, 4B). At least two generations of detrital quartz are present and include large, rounded, moncrystalline quartz grains in addition to small, angular, monopolycrystalline quartz grains (Fig. 5). Minor feldspar also occurs with the angular quartz fragments. Flowstone exhibits crystalline micro-fabrics and ranges from simple acicular crystals showing competitive growth and orientation of long axes perpendicular to the substrate, to unusual curved crystals (Fig 6).

Several relationships among these primary fabrics are essential to understanding the depositional history of the speleothem deposits. The micritic carbonate coating host rock surfaces contain small (< 100 $\mu$ m in length) quartz grains with their long axes parallel to the vertical and bottom edges of host rock surfaces (Fig. 3B). Likewise, larger

quartz grains appear to be adhered to the underside of host rock surfaces and around the margins of pisoids (Fig. 4A). Isopachous carbonate microspar also envelopes certain other quartz grains and overall, the quartz grains appear to "float" in the carbonate matrix material so that the individual grains rarely occur in point-to-point contact (Figs 3B, 4A). Many of the speleothem deposits in the grikes and cavities are complexly layered, containing interbeds of silt, quartz, pisoids, and flowstone, often chaotic in appearance, while much of the matrix fill is dominated by clotted microspar carbonate (Figs. 4B, 5).

### **Cathodoluminescence and Geochemical Data**

Polished thick sections of the Dismal Lakes Group speleothem were examined via cathodoluminescence. All phases showed moderate luminescence, with the exception of earliest micritic phases, which were non- to dully luminescent, and crystalline flowstone fabrics, which showed bright luminescence. Discrete phases were microdrilled and 35 powder samples were collected and analyzed for isotopic composition. These samples were divided into three broad petrographic categories (host rock, speleothem, and cross-cutting Fe-rich dolostone), and isotopic compositions were compared to those measured from depositional and diagenetic phases in the host Greenhorn Formation (Frank et al. 2003). The resulting data was then plotted for graphical analysis (Fig. 7).

The data revealed that the isotopic compositions of the host dolostone are broadly similar to those observed elsewhere in the lower Greenhorn Formation below the karst horizon, but are distinct from compositions typical of the upper Greenhorn Formation directly overlying the karst horizon. The host dolostones show a trend toward isotopically lighter values of both  $\delta^{13}$ C and  $\delta^{18}$ O. However, the speleothem fabrics reveal  $\delta^{13}$ C and  $\delta^{18}$ O compositions distinct from the surrounding host dolostone.  $\delta^{18}$ O are lighter than the host dolostone by ~2.5‰ and  $\delta^{13}$ C are lighter by up to 2.5‰. The late stage cross-cutting Fe-rich dolostones bear  $\delta^{13}$ C signatures of the host speleothem material, but have lighter  $\delta^{18}$ O signatures (Fig. 7).

### **Interpretation of Petrographic Observations**

Many of the speleothem features of the Dismal Lakes Group are analogous to those of modern day karst/speleothem systems and probably formed via the same processes. Interpretations of the petrographic features point to both phreatic and vadose speleothem precipitation, accompanied by in-filling terrigenous sediments. The first generation speleothem micritic laminations probably precipitated from a thin film of water as it seeped over the cavity walls in the host dolostone (Fig. 3). The quartz grains aligned with their long axes parallel to the vertical and subhorizontal surfaces of the host rock and pisoids (Figs. 3B, 4A) suggest transport into an open grike system and adherence via a thin fluid film (Chafetz and Butler, 1980). In addition, the adhesion of grains along pisoid margins and the presence of isopachous microspar rims around quartz grains indicate deposition in both open and fluid-filled grikes (Peryt, 1983).

The simple, acicular flowstone fabrics of the Dismal Lakes karst display competitive growth fabrics (Fig. 6) typical of carbonate flowstones and probably formed as void-filling or vadose drip cements (Broughton, 1983; Self et al. 2003). The more complex, curved crystals exhibit increasing degrees of curvature as distance from the substrate increases (Fig. 6). These fabrics are similar to herringbone carbonate, which is believed to represent precipitation either from anoxic waters containing Fe<sup>2+</sup> (Sumner and Grotzinger 1996), or from oxic waters with fluctuating levels of HCO<sub>3</sub><sup>-</sup>. Even at the relatively low oxygenation levels of the Proterozoic biosphere, terrestrial waters should have been oxic, but changing levels of dissolved carbon could have resulted from either decomposing organic matter or degassing of waters during transport through the grike system. Furthermore, de Wet et al. (2004) has shown that organic decay from microbial matter can rapidly hasten anoxic conditions in restricted cavities, leading to the formation of herringbone carbonate. Thus, the presence of herringbone-like fabrics could be indirect evidence for a terrestrial biomass.

The appearance of floating quartz grains in a carbonate matrix (Figs. 3B, 4A) occurs when more carbonate precipitates than can be accommodated by the original void spaces. Such a texture is typical of calcrete and caliche horizons (Goudie, 1983), and has been described from other paleokarst horizons (Mustard and Donaldson, 1990). Likewise, the nearly ubiquitous micritic pisoids are typical of caliche horizons and suggest precipitation in standing pools and eventual transport through the grike network (Chafetz and Butler, 1980). The complex, layered sediment deposits within the karst horizon (Fig. 5) contain layers of speleothem, terrigenous sediment, pisoids, and clotted microspar. These layered relationships are found in modern cave systems charged by seasonal streams, where an episodic flow of surface waters deposits sediments and initiates precipitation of flowstone (White, 1988).

#### **Interpretation of Geochemical Data**

Analysis of Fig. 7 shows the trend of the host dolostone toward lighter isotope values, suggesting an alteration of the host rock by speleothem precipitating fluids (orange arrow). This trend is noticeably away from the composition of the upper Greenhorn Formation, which was deposited by marine fluids. This trend suggests that the same fluid that precipitated speleothem also moved through the host rock and altered its signature slightly. The light  $\delta^{18}$ O values of the speleothem and altered host rock are characteristic of  $\delta^{18}$ O values for meteoric fluids (Fairchild et al. 2006), not marine fluids. In addition, the significantly lighter  $\delta^{13}$ C values for the speleothem suggest the presence

of isotopically light C in the terrestrial fluids, likely originating from decomposing organic material in soils or from microbial activity in the cave system. Furthermore, the late stage Fe-rich dolostone bears  $\delta^{13}$ C values similar to those of the speleothem, but the  $\delta^{18}$ O values are clearly different, indicating the Fe-rich dolostone was altered by hydrothermal fluids. Ultimately, the geochemical data suggests that speleothem precipitated from meteoric fluids that had acquired a significant light C component, possibly from decomposing organic material, as the fluid moved through the karst system.

### **Interpretation of Karst and Speleothem Development**

The Dismal Lakes Group karst profile has been interpreted to have occurred in three stages: subaerial exposure and phreatic dissolution, vadose fill by clastic sediments and flowstone precipitation, and eventual cave collapse; all reflecting a gradual lowering of the water table (James and Choquette 1988). The  $\delta^{13}$ C and  $\delta^{18}$ O data, coupled with the petrographic observations, suggest a developmental sequence for this karst horizon. Following exposure of the lower Greenhorn Formation platform, carbonate dissolution and karst development were almost certainly hastened by acidic meteoric fluids resulting from elevated pCO<sub>2</sub> levels in the Precambrian atmosphere (Fairchild et al. 2006). Increased pCO<sub>2</sub> in the atmosphere lowers the pH of rain waters, such that a small increase in pCO<sub>2</sub> can produce acidic terrestrial waters capable of extensively dissolving carbonate exposed to the atmosphere (White, 1988).

However, such acidic fluids would have inhibited speleothem precipitation in the near-subsurface. Two possibilities then exist to explain speleothem formation: 1) Speleothem precipitated from marine or modified marine waters associated with a rise in sea level initiating deposition of upper Greenhorn strata or 2) Speleothem precipitated in grikes and cavities from modified fresh waters following extensive carbonate dissolution and buffering of the fluid pH. Although petrographic and cathodoluminescence data hint at a terrestrial origin for the precipitating fluids, it is the  $\delta^{13}$ C and  $\delta^{18}$ O values of the speleothem material that clearly point to a distinct, organic-rich, meteoric origin for the precipitating fluids.

#### Conclusions

The above interpretations of the petrographic and geochemical data lead to several conclusions.

1) In the Precambrian, elevated  $pCO_2$  would have resulted in a greater acidity of terrestrial waters. Dismal Lakes Group karst system represents extensive carbonate dissolution, buffering of fluid pH, and eventual precipitation of speleothem upon either evaporative concentration or degassing of these fluids.

2) Petrographic analysis of Dismal Lakes Group speleothem reveals a complex series of depositional events, including influx of siliciclastic sediment from at least two distinct sources, and carbonate deposition in fluid pools, and in both vadose and phreatic environments. Clotted microtextures and herringbone carbonate-like fabrics may reveal a microbial influence during speleothem formation.

3) Isotopic compositions of speleothem material are distinct from that of surrounding host dolostone. Light  $\delta^{18}$ O values support deposition from terrestrial fluids, and light  $\delta^{13}$ C values suggest an organic influence on fluid compositions. If true, this data would represent geochemical evidence for an active terrestrial biomass in the Precambrian.

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**Figure 1.** Geologic map showing location and outcrop extent of the Dismal Lakes Group and basement features as well as the September Lakes locality, modified from Frank et al. (2003).



**Figure 2A.** Speleothem material (S) occurs in a system of grikes, 10-20 cm wide, that extend up to 12 m into underlying Greenhorn strata (G).



**Figure 2B.** Speleothem material is characterized in outcrop by crystalline flowstone up to 4 cm thick (F), sandy, micritic carbonate, and pisoids (P). Speleothem pisoids, up to 1 cm in diameter, occur in restricted deposits within the grike system, and as isolated occurrences within grike fill.



**Figures 3A and 3B.** Photomicrographs showing primary speleothem fabrics of Dismal Lakes Group paleokarst; host dolostone (H), micritic carbonate (M), flowstone (F), quartz (Q), micritic pisoids (P), carbonate microspar (MS).





**Figure 4A.** Quartz grains aligned with long axes parallel to host rock and pisoid (P) surfaces as well as isopachous rims around quartz grains suggest adherence to surfaces via a thin fluid film and deposition in fluid and gas-filled grikes.



**Figure 4B.** This photomicrograph shows a layered sequence of concentrically laminated micritic pisoids (P), quartz fill (Q), and microspar (MS)



**Figure 5.** In this photomicrograph, grike fill is dominated by clotted, microspar carbonate (MS), and several layers of quartz-bearing microspar. The central cavity is lined by flowstone (F), contains detrital quartz sand, and is cemented by micritic carbonate (M). Layered relationships suggest an episodic flow of surface waters that deposited sediments and initiated the precipitation of flowstone, filling the cavity from the top and bottom.



**Figure 6.** Flowstone fabrics range from simple, acicular crystals (A) to unusual curved crystals (C). A similar microfabric, herringbone carbonate, is believed to represent precipitation from anoxic waters containing  $Fe^{2+}$  (Sumner and Grotzinger 1996), or from oxic waters where changing levels of  $HCO_3^{-}$  alter crystal growth rates. Even at the low oxygenation levels of the Proterozoic biosphere, surface waters should have been oxic, but decomposing organic matter or degassing of these waters during transport could have altered the levels of inorganic carbon.



**Figure 7.** Isotopic compositions of speleothem, host rock, and late diagenetic Fe-rich dolostones compared to isotopic compositions of upper and lower Greenhorn strata provided by (Frank et al. 2003).