Unraveling carbon isotope signals from glendonites using NanoSIMS

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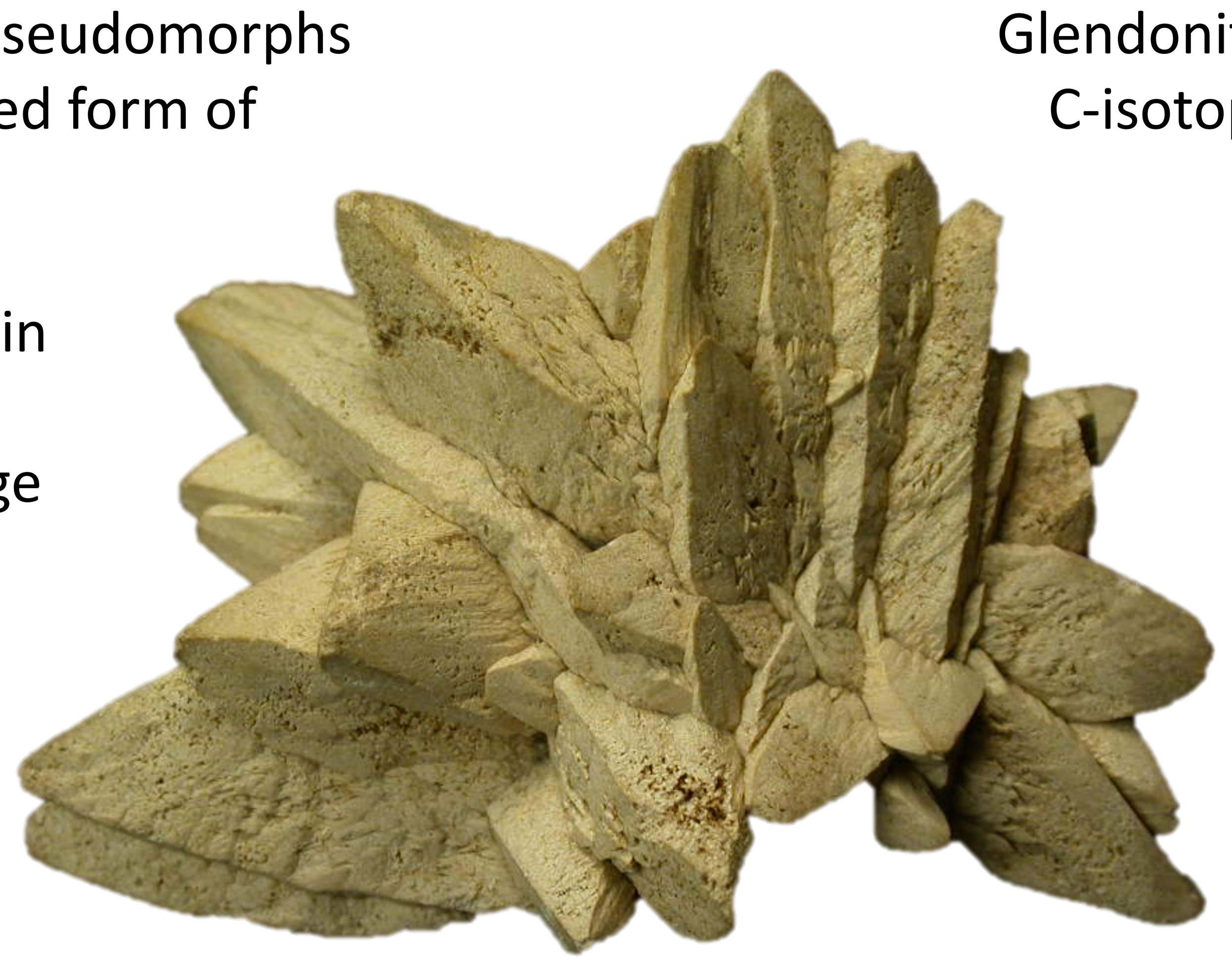
What are glendonites?

1. Glendonites are fossil pseudomorphs of Ikaite, a hexa-hydrated form of $CaCO_3$
2. Glendonites are abundant in high-latitude sedimentary successions of Mesozoic age
3. Glendonites are considered proxies for icehouse conditions during the Mesozoic greenhouse



4. Glendonites show extremely low C-isotope values (up to -50 per mille)
5. Glendonites are rich in methane gas
6. Glendonites likely form as a result of methane seepage

Research rationale

The large spread in C-isotope values (ranging from +20 to -50 per mille) in bulk glendonite records (Fig. 1C) suggests a complex diagenetic history. This is also reflected in different mineral phases, including the primordial rosette phase, and various infilling and overgrowth phases each with presumably distinct C-isotope signatures (Fig. 1B). Here we test whether the primordial rosette phase preserves a signature related to methane. Because of the chaotic distributions and the small sizes of the crystals we are using NanoSIMS to measure transects across minerals.

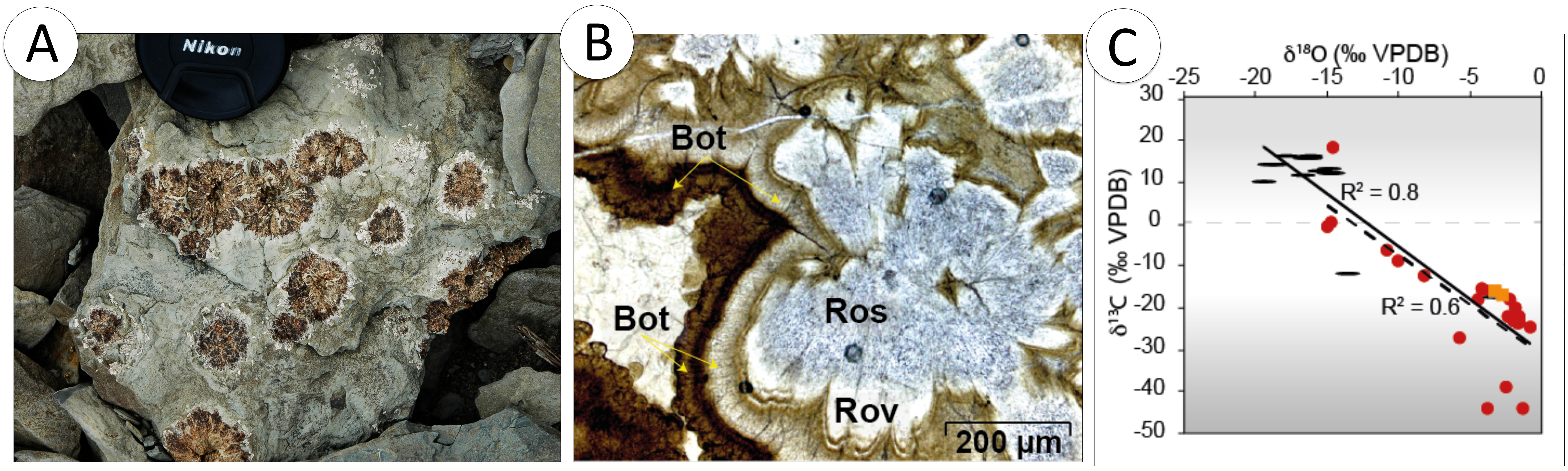
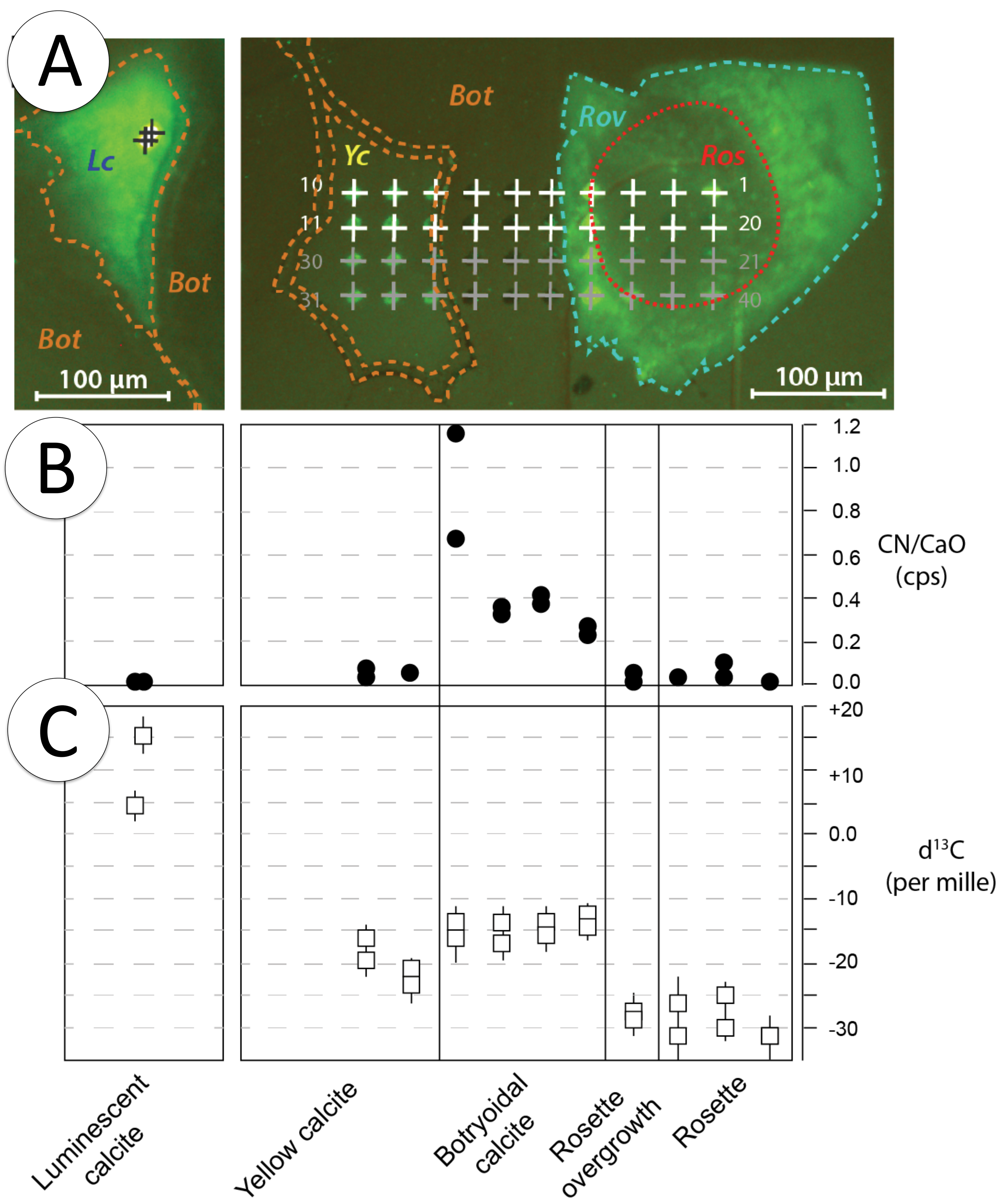


Figure 1. (A) Large slab of Bajocian calcareous sandstone from Cape Kystatym (Siberia, Russia) showing with numerous glendonites. (B) Thin-section of a Bajocian glendonite showing complex internal structure and various carbonate mineral phases. Ros = Rosette phase; Rov = Rosette overgrowth phase; Bot = Botryoidal phase. Rosette phase is considered primary phase after Ikaite. (C) Cross-plot of carbon and oxygen isotope data from glendonites from Cape Kystatym (Bajocian). Bulk glendonite isotope values show large variations ranging from -50 per mille to +20 per mille (Morales et al., 2017).



Results & Conclusions

- NanoSIMS analyses were performed on a Bajocian glendonite from Siberia. The CN over CaO ratio highlights the presence of organic matter in the botryoidal phase, but not in the other phases. Hence, these isotope values were not influenced by impurities
- NanoSIMS analyses (i.e. Ros and Rov phases) are associated with the lightest $\delta^{13}C$ values (-25 to -32 ± 2.8 ‰), indicating that the carbon source were hydrocarbons. In the succeeding carbonate phases, $\delta^{13}C$ values gradually increase, indicating a mixing with other carbon sources.
- The latest carbonate phase exhibits extremely high $\delta^{13}C$ values (of up to +15 ‰), which are poorly understood.
- Together, the isotope measurements confirm the lowest C-isotope values in the most primordial phase.

Figure 2. NanoSIMS analyses performed on a Bajocian glendonite from Siberia. (A) Photograph of the various carbonate phases identified in the sample (UV-light microscopy) and sampling positions (white crosses). By paragenetic order: Ros: rosette crystals; Rov: Rosette overgrowths; Bot: botryoidal carbonates; Yc: Yellow anhedral calcite; Lc: late carbonate blocky infillings. (B) The CN over CaO ratio (in cps) highlights the presence of organic impurities in the botryoidal phase. (C) Carbon stable isotope data show depleted values in the first phases precipitated, pointing to a carbon source derived from the anaerobic oxidation of hydrocarbons.

Glendonites track methane seepage in Mesozoic polar seas Chloé Morales, Mikhail Rogov, Hubert Wierzbowski, Victoria Ershova, Guillaume Suan, Thierry Adatte, Karl B. Föllmi Erik Tegelaar, Gert-Jan Reichart, Gert J. de Lange, Jack J. Middelburg, Bas van de Schootbrugge. **Geology** (2017) 45 (6): 503-506.