Enhanced ikaite precipitation by bentonite fertilisation in the Fur formation, northern Denmark

Jeroen Carmiggelt1, Helen E. King1, Mariette Wolthers1, Bo Pagh Schulz2, Bas van de Schootbrugge1
1Utrecht University, Department of Earth Sciences, Princetonlaan 8A, 3584 CB Utrecht, The Netherlands.

1. Background

Glendonites are calcite pseudomorphs after the mineral ikaite. Because ikaite in nature typically forms at low temperature (<7 °C), glendonite occurrences in deep time have been interpreted as indication for cold environmental conditions, even when found in sediments associated with greenhouse climates [1]. However, ikaite nucleation experiments have shown that the temperature stability range of ikaite can be extended under the influence of certain chemical compounds (e.g. Mg2+, PO43−) and foreign minerals [2][3].

The largest glendonites recorded are found in the early Eocene diatomite of the Danish Fur formation, a deposit associated with hothouse conditions. Numerous bentonites interbed this diatomite and are often found in close association with the glendonites. Therefore, this research sets out to investigate the ways in which bentonites affect ikaite crystallisation.

Figure 1: A) Transforming synthesised ikaite crystal under the SEM and; B) Replicative calcite pseudomorphs in the Fur glendonites, interpreted to be a result of ikaite transformation.

2. Methods

a) Collect Fur bentonites and glendonites and investigate their spatial relation in the sediments;
b) Perform ikaite synthesis with ‘standard’ (unmodified) and bentonite-modified artificial seawater;
c) Investigate the solutions involved during synthesis (with ICP-OES), bentonites (with XRD) and precipitates (with ATR-FTIR, Raman spectroscopy, optical microscopy and SEM).

3. Results

3A Proof for ikaite formation

3B Bentonites release Ca and P

3C The synthesized crystals

3A: ATR-FTIR and Raman spectra show characteristic vibrations motions of ikaite and coprecipitating nesquehonite; 3B: Bentonites nearby glendonites (e.g. +62, +14) release significantly more Ca and P to the solution compared to a bentonite where no glendonites were found (e.g +19); 3C: Solutions modified by bentonites precipitate more ikaite and less or no nesquehonite.

4. Discussion and Conclusion

1) Ca and P release from bentonites enhance ikaite precipitation and suppress co-precipitation of nesquehonite; 2) Ca and P are likely derived from the interlamellar space of montmorillonite, which is a clay mineral that often occurs in bentonites; 3) The Fur glendonites are likely a result of an unique combination of geochemical, geological and diagenetic controls rather than only climatic conditions.

Figure 2: A) Direct contact between bentonite and a Fur glendonite and; B) Schematic log of the Fur formation indicating the glendonite-bearing intervals (after [1]).

Figure 3: The setup that was used to synthesize ikaite. In red the effect that bentonite +62 found nearby glendonites, but on the solution chemistry. In both ‘standard’ and bentonite-modified experiments, a blood of white precipitates formed within the first few minutes of mixing. When pumping ceased after 3 hours, it was still present.

Figure 4: Schematic diagram of cation exchange of montmorillonite. Important cations for ikaite precipitation which are present in the interlayer space of montmorillonite are exchanged with other cations from the ambient solution (after [4]).