Analysis of sea ice and phytoplankton biomarkers in marine sediments from the Nordic Seas - a calibration study

ALBA NAVARRO RODRIGUEZ[1*], PATRICIA CABEDO SANZ[1], SIMON BELT[1], THOMAS BROWN[1], JOCHEN KNIES[2], KATRINE HUSUM[3], AND JACQUES GIRAUDEAU[4]

[1]Plymouth University, Plymouth, UK, alba.navarrorodriguez@plymouth.ac.uk (* presenting author)
[2]Geological Survey of Norway, Trondheim, Norway, Jochen.Knies@NGO.NO
[3]University of Tromsø, Tromsø, Norway, katrine.husum@uit.no
[4]Université Bordeaux, Bordeaux, France, J.Giraudeau@epoc.u-bordeaux.fr

Abstract

The work presented here is part of the Changing Arctic and Sub-Arctic Environment (CASE) program which is an Initial Training Network (ITN) that focuses on biological proxies and their use in reconstructing climate change and, in particular, the marine environment. One of these proxies is the sea ice diatom biomarker IP_{25} which is a highly branched isoprenoid (HBI) alkene synthesised by some Arctic sea-ice diatoms and has been shown previously to be a specific, stable and sensitive proxy measure of Arctic sea ice when detected in underlying sediments [1].

The current study focuses on three key elements: (1) An analytical calibration of IP_{25} isolated from marine sediments and purified using a range of chromatographic methods was conducted in order to improve the quantification of this biomarker in sediment extracts [2]. (2) Analysis of >30 near-surface sediments from the Nordic Seas was carried out to quantify biomarkers previously suggested as indicators of open-water phytoplankton (brassicasterol) [3] and sea-ice (IP_{25}) conditions [4]. The outcomes of the biomarker analyses were used to make comparisons between proxy data and known sea ice conditions in the study area derived from satellite record over the last 20 years. (3) A consideration of possible processes occurring within surface sediments and the implications of these on downcore analysis of biomarkers for palaeo-climate reconstructions.

[1] Belt et al. (2007) *Org. Geochem.* **38**, 16-27. [2] Belt et al. (2012) *Environ Chem Lett* DOI 10.1007/s10311-011-0344-0. [3] Müller et al. (2011) *EPSL* **306,** 137-148. [4] Belt et al. (2010) *Quaternary Science Reviews*, **29** 3489-3504.

Energetic Studies of Nanophase and Amorphous Carbonate Minerals

ALEXANDRA NAVROTSKY[1]*

[1]Peter A. Rock Thermochemistry Lab, University of California Davis, Davis, CA 95616 USA, anavrotsky@ucdavis.edu

13f. Physicochemical constraints of the marine carbonate system: recent insights into the reactivity of carbonate minerals in aqueous solutions

Solution calorimetric methodology has been applied to measuring the energetics of formation and transformation of amorphous and nanophase carbonates in the CaCO3 - MgCO3 - FeCO3 system. The data point to several general conclusions, summarized here. (1) Amorphous calcium carbonate (ACC) exists in two forms: a heavily hydrated material initially precipitated from strongly oversaturated aqueous solution and a less hydrated form, which is energetically similar whether formed by biomineralization or by thermal dehydration of the initially precipitated phase. Transformation in the sequence hydrated ACC – relatively anhydrous ACC – vaterite – aragonite – calcite is energetically downhill and thus ACC can be a precursor to any of these crystalline phases. (2) Amorphous magnesium carbonate (AMC), despite being energetically more metastable than ACC, is more persistent (can be kept for a year rather than a few days before crystallizing under ambient conditions). This is attributed to the kinetic difficulty of removing water of hydration from the environment of Mg2+. (3) Amorphous iron carbonate (AFC) is energetically similar to AMC but is very susceptible to crystallization and oxidation. The energetics of the amorphous versus crystalline carbonate phases may be controlled by the ionic radius of the cation. (4) The ACC – AMC system shows a striking change in energetic behavior near Ca/Mg = 1. More Mg-rich compositions, though amorphous, appear to be heterogeneous and consist of nanoscopic regions of dolomitic and magnesitic composition. The amorphous material with Ca/Mg = 1 may be a precursor to dolomite. (5) Measurement of the surface energies of calcite, aragonite, and vaterite is currently in progress. These general trends are discussed in the context of carbonate formation in biological, carbon sequestration, diagenetic, and fresh water and oceanic environments.