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Ikaite precipitation in a lacustrine environment – implications for palaeoclimatic studies using carbonates from Laguna Potrok Aike (Patagonia, Argentina)

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ABSTRACT

The monoclinic mineral ikaite ($CaCO_3 \cdot 6H_2O$) and its pseudomorphs are potentially important archives for palaeoenvironmental reconstructions. Natural ikaite occurs in a small temperature range near freezing point and is reported mainly from marine and only rarely from continental aquatic environments. Ikaite transforms to more stable anhydrous forms of $CaCO_3$ after an increase in temperature or when exposed to atmospheric conditions. The knowledge about conditions for natural ikaite formation, its stable isotope fractionation factors and isotopic changes during transformation to calcite is very restricted. Here, for the first time, primary precipitation of idiomorphic ikaite and its calcite pseudomorphs are reported from a subsaline lake, Laguna Potrok Aike, in southern Argentina. The calculated stable oxygen isotope fractionation factor between lake water and ikaite-derived calcite ($\alpha_{PAI} = 1.0324$ at a temperature of 4.1 °C) is close to but differs from that of primarily inorganically precipitated calcite. Pseudomorphs after ikaite rapidly disintegrate into calcite powder that is indistinguishable from µm-sized calcite crystals in the sediment record of Laguna Potrok Aike suggesting an ikaite origin of sedimentary calcites. Therefore, the Holocene carbonates of Laguna Potrok Aike have the potential to serve as a recorder of past hydrological variation.

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1. Introduction and site description

Modern ikaite is a mineral frequently observed in certain marine anoxic sediments (e.g. Suess et al., 1982; Shearman and Smith, 1985; Stein and Smith, 1986; Jansen et al., 1987; Hacke et al., 1994; Schubert et al., 1997; Zabel and Schulz, 2001) and more currently also in Antarctic and Arctic sea ice (Dieckmann et al., 2008, 2010). To our knowledge, however, only four locations of modern occurrences of ikaite in fresh and brackish water systems have been reported. At all these locations ikaite occurred during spring and winter. Two findings were from cold-water springs: Shiowakka, Japan (Ito, 1996) and Expedition Fiord, Canadian High Arctic (Omelon et al., 2001). The other two were from subaquatic springs where two different types of water mix: Ikka Fjord, Southwest Greenland (Pauly, 1963; Buchardt et al., 1997, 2001) and Mono Lake, California (Council and Bennett, 1993; Bischoff et al., 1993b). When temperature rises above ca 4 °C at atmospheric conditions (Larsen, 1994; Rickaby et al., 2006) ikaite transforms within minutes to hours into calcite with a 68.6% volume loss described by the equation: $CaCO_3 \cdot 6H_2O \rightarrow CaCO_3 + 6H_2O$ (Larsen, 1994). The result of this transformation is a loose mesh of calcite crystals or very fragile and porous pseudomorphs (Bischoff et al., 1993b; Ito, 1998; Koenigsberger et al., 1999; Selleck et al., 2007). Calcite pseudomorphs after ikaite are at times preserved in the sediment record (Larsen, 1994) and are commonly known as glendonites (e.g., Shearman and Smith, 1985; Greinert and Derkachev, 2004; Huggett et al., 2005; Pueyo et al., 2011).

Here we report the first direct evidence of ikaite precipitation in the water body of a lake, the subsaline maar lake Laguna Potrok Aike (51°57′S, 70°23′W). This bowl-shaped lake is located in the

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Patagonian steppe of Argentina and has a maximum diameter of 3.5 km and a maximum water depth of 100 m. It is mainly ground and rainwater fed (Mayr et al., 2007) and exhibits a year-round holomixis of the water body with a pH between 8.7 and 9.0 and high evaporation rates due to the everlasting and strong westerly winds in these latitudes (Zolitschka et al., 2006). Calcite saturation indices of the lake water document oversaturation during austral summer ($\Omega = 22–79$, Haberzettl et al., 2005), but precipitation of $CaCO_3$ was never observed in the summer seasons during various field campaigns between 2002 and 2008. The high phosphorus and Mg concentration of the lake water (up to 3.609 mg L^{-1} and 73 mg L^{-1}, respectively, Zolitschka et al., 2006) most likely inhibits calcite formation (Bischoff, 1968; Reddy and Nancollas, 1973; House, 1987; Raidt and Koschel, 1988; Bischoff et al., 1993a; Lin and Singer, 2006). In the framework of the International Continental Scientific Drilling Program (ICDP) campaign 5022 (project PASADO) in austral winter 2008, mm-large carbonate crystals were collected at Laguna Potrok Aike with the typical morphology of ikaite. The aims of this study were to confirm that these crystals are indeed ikaite, to calculate the oxygen isotope fractionation factor directly from lacustrine ikaite, and to elucidate the origin of sedimentary carbonates from Laguna Potrok Aike.

2. Material and methods

Lake water temperatures between March 2006 and October 2008 were recorded every 6 h by Minilog thermistors (M-08TR, Vemco ltd., Canada) in 0 and 90 m water depth attached to a mooring in the centre of the lake. Two sediment traps were also installed in 90 m water depth which had an active area of 55 cm^2 (Ohlendorf et al., 2013 for more details). pH, electric conductivity (EC), salinity, and the alkalinity were measured with an Universal Pocket Meter (Multi 340i, WTW). The water chemistry (anions, cations) were analysed via ion chromatographic method and ICP-MS method, respectively (Zolitschka et al., 2006). Euhedral carbonate crystals were discovered on aquatic macrophytes (*Myriophyllum* sp., *Drepanocladus* sp.) and on the rope of a mooring in the centre of the lake (Fig. 1 a, b) during the ICDP-field campaign at Laguna Potrok Aike in September 2008. The untypical crystal morphology for common carbonates (calcite,

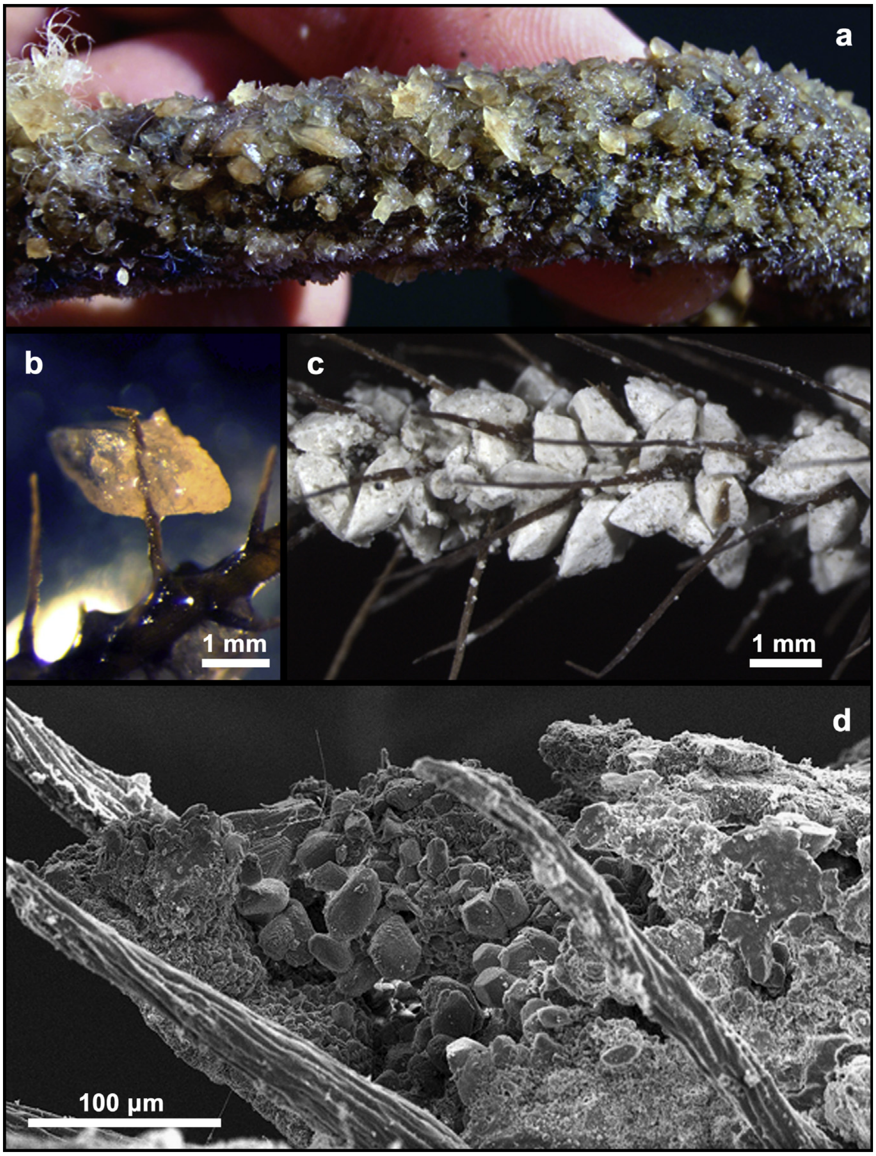

Fig. 1. (a) Ikaite crystals precipitated on a rope and (b) an idiomorphic ikaite crystal precipitated on aquatic moss; (c) Transformed ikaite crystals on aquatic moss collected at the lake shore and (d) SEM image of a transformed ikaite crystal showing the high porosity of the weakly bound calcite crystals.

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