



Application of flow-through time-resolved analysis (FT-TRA) to isolate the elemental composition in ostracod calcite



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ABSTRACT

Trace element concentrations in ostracod shells are a vital tool for paleoenvironmental reconstructions. The most common approach used to measure trace element concentrations in ostracod shells is batch dissolution followed by analysis of the resulting solution. However, oxide coatings, secondary carbonate crusts, or adhering clay minerals can contaminate their surface with significant quantities of the trace elements of interest, which requires thorough cleaning to prevent biasing the results. Cleaning ostracod shells is time consuming and, more importantly, it is difficult to verify whether the cleaning procedure used has effectively removed all contamination. There is also the possibility that chemical cleaning procedures affect the elemental composition of the biogenic calcite, so that manual removal of contaminant phases is often the method of choice.

To address this cleaning conundrum, it would be beneficial to develop a method which could identify and correct for contamination, instead of attempting to remove contaminants as has been done so far. In this study, we explore the applicability of flow-through time-resolved analysis (FT-TRA) to determine the contamination-free trace element composition of biogenic carbonate in ostracod shells. In this system, for shells with a relatively simple surface geometry, such as most ostracods, dissolution proceeds gradually from their outer to inner layers. Time-resolved eluate composition thus documents the initial dissolution of the surface layers, often contaminated with Mn-carbonates and Fe-Mn oxides coatings, followed by the dissolution of the inner layers of uncontaminated biogenic carbonate, whose elemental composition can thus be retrieved from the time series data. Partial dissolution of adhering clays can also be corrected using elemental ratios measured after total dissolution of the carbonates. As a result, unbiased elemental data can be obtained even when the shells have not been sufficiently cleaned, and the cleaning step could even be omitted. The method is sensitive enough to allow single shell measurements for many elements of interest (Mg, Sr, Ba, Mn), although elements with lower concentration (U) or higher background (Fe) require multiple shell measurements.

Comparing FT-TRA and laser ablation measurements of manually cleaned ostracod shells indicate that Mg, Ba, Mn, Fe and U surface contamination can still remain despite prior manual cleaning and bias the laser ablation data. FT-TRA demonstrates that, while thorough manual cleaning can remove adhering clay minerals, it cannot effectively remove Fe-Mn oxides or Mn-carbonates incrustations. FT-TRA is thus preferable to LA-ICP-MS because it does not rely on questionable cleaning procedures.

1. Introduction

Ostracods are bivalved microcrustaceans commonly found in continental, estuarine and marine waters (Holmes, 1992). Their shells have been used as source material for geochemical analysis in paleoenvironmental reconstruction. Their low-Mg calcite shells are calcified within a few hours to several days after molting (Turpen and Angell, 1971; Okada, 1982; Roca and Wansard, 1997). Prior to molting, calcium phosphate is stored within granules in the outer epidermis

together with sodium, chloride, potassium, and sulphur, but neither strontium nor magnesium (Keyser and Walter, 2004). Thus, Mg and Sr, as well as other trace elements are incorporated from ambient waters during calcification, recording composition of the ambient water at the time of shell secretion (Chivas et al., 1986; Smith, 1993; Mischke and Holmes, 2008), from which environmental conditions (e.g., temperature, salinity, dissolved ion composition, hydrology) can be deduced (Lister, 1988; Chivas et al., 1993; Haskell et al., 1996; Bridgwater et al., 1999; Yu and Ito, 1999; Gouramanis and De Deckker, 2010; Börner

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et al., 2013). Most commonly used are Mg/Ca and Sr/Ca in ostracod shells from lake environments to infer changes in temperature and salinity and reconstruct lake level. Other trace elements have only been used in a few preliminary studies. For instance, Ba/Ca has been used to assess changes in temperature (Chivas et al., 1983) or salinity (Yang et al., 2014), while Mn/Ca, Fe/Ca and U/Ca have been tested as proxies for redox and oxygenation cycles (Gasse et al., 1987; Holmes, 1997; Ricketts et al., 2001; Yang et al., 2014).

The most commonly used method to determine the chemical composition of ostracod shells is batch dissolution. The ostracod shells are dissolved in HCl or HNO₃ and the solution is analyzed by ICP-AES, AAS or ICP-MS (McCulloch et al., 1989; Holmes, 2008; Hu et al., 2008). Single shell measurements are possible with shells weighing at least 20 µg each (De Deckker, 1988; De Deckker et al., 1999) but multiple shells are often combined (e.g. Engstrom and Nelson, 1991; Anadón et al., 2002, 2006; Janz and Vennemann, 2005) either to reach measurable concentrations or to account for bioturbation, which mixes shells of different ages in the same sediment horizon. To reach necessary sample sizes, often thicker sediment horizons are sampled, decreasing the time resolution of the paleolimnological data.

Not all trace elements are distributed homogeneously within the ostracod shell. As reported in previous studies, especially the outside and inside periphery of the shell are potentially enriched in Mg, Ba or Mn, depending on the taxa analyzed (Cadot et al., 1972; Cadot and Kaesler, 1977; Ito et al., 2003). In contrast, Sr seems to be homogeneously distributed throughout the shell (De Deckker et al., 1999). Elemental heterogeneity has been attributed to changes in physiological activity (calcification rate) rather than changes in environmental conditions (Ito et al., 2003; Morishita et al., 2007). Batch dissolution cannot document elemental heterogeneity within shells. To overcome this limitation, another method has gained popularity in recent years: laser ablation coupled to ICP-MS analysis (LA-ICP-MS) (Ito et al., 2003; Yang et al., 2014).

Both batch dissolution and LA-ICP-MS require adequate sample cleaning prior to analysis, because surface coatings, added after the deposition of biogenic carbonate, often contain significant quantities of the trace elements of interest (Holmes, 1996; Ito, 2002; Keatings et al., 2006). Additional contamination may arise from adhering aluminosilicates, detrital carbonate minerals, and organic matter (Keatings et al., 2006). Cleaning procedures include manual cleaning, sonic baths, or chemical treatment. Chemical pre-treatment methods have the potential to alter the elemental composition of the ostracod shells (Holmes, 1996), thus manual cleaning with a fine brush, needle and deionized water is often recommended (Jin et al., 2006; Keatings et al., 2006; Li et al., 2007; Mischke et al., 2008). Manual cleaning of ostracod shells, however, is time-consuming and does not guarantee complete removal of all contaminants, particularly secondary mineral precipitates. In order to overcome this limitation, this study explores the potential of flow-through time-resolved analysis (FT-TRA) (De Baere et al., 2015, 2016) to identify and correct for contamination by surface coatings and adhering silicate minerals.

2. Materials and methods

2.1. Ostracod samples

This study utilizes ostracod samples originating from a fluvio-lacustrine outcrop on the northwestern shore of lake Tangra Yumco (31°16'N, 86°38'E, central Tibetan Plateau), 11 to 15 m above present day lake level. The sampled section represents a limestone bank consisting of soft micritic carbonate of white to beige color interbedded with whitish-gray laminae with variable thickness (1 mm to a few centimeters). Small and irregularly shaped carbonate concretions (< 1 cm) were randomly scattered throughout the bank. ¹⁴C dating of lacustrine carbonates revealed an age of approximately 8000 a BP. Burial of shells took place in a low energy, possibly deep lacustrine

environment with little or no terrestrial input. Ostracod shells were subject to shallow burial diagenesis resulting in recrystallization (opaque shells) and cavity filling cement. The outcrop yielded abundant adult shells of one species, *Leucocytherella sinensis* (Huang, 1982), from the same sediment layer, facilitating method development and allowing for the comparison between shells of different preservation states and contamination. *L. sinensis* is a small and lightweight ostracod species (ca. 700 µm long, shell weight ~7 µg) and is the most abundant species in lakes on the central Tibetan Plateau.

The sediment samples were sieved using 63 and 200 µm mesh size sieves and rinsed with deionized water. Adult *L. sinensis* shells were picked with a fine brush under a low magnification stereoscopic microscope from the > 200 µm size fraction. A subset of the sample was manually cleaned with a fine brush using deionized water and ethanol to remove all visible surface contamination. Both male and female shells were used, as there is no chemical difference between sexes or between right and left shells (Dwyer et al., 2002; Morishita et al., 2007; Marco-Barba et al., 2012).

In addition, we analyzed ostracod shells from a subset of samples of a study conducted by Yang et al. (2014), who analyzed ostracod shells from a long core of lake Nam Co (NC08/01, Tibetan Plateau) using LA-ICP-MS. FT-TRA was done on ostracod shells originating from the same sediment horizons as Yang et al. (2014), but without prior cleaning. Ostracods from core NC08/01 were sampled at 35 cm, 123.5 cm, 186 cm, 221 cm, 236 cm, 301 cm and 356 cm core depth (NC1 to NC7).

2.2. Flow-through time-resolved analysis (FT-TRA)

FT-TRA was originally developed by Haley and Klinkhammer (2002) to analyze elemental ratios in foraminifera tests. FT-TRA uses automated chromatographic equipment to gradually dissolve a sample in a continuous flow of solvent, and an on-line ICP-MS to monitor the time-resolved composition of the eluate. For ostracod shells, which have a relatively simple geometry, carbonate dissolution in dilute acids starts from the initially exposed surfaces of the shells and progresses gradually into the sub-surface layers until the carbonate shell is fully dissolved. Time-resolved analysis of the eluate can thus reveal the presence of outer layers contaminated by secondary carbonate or oxide precipitation, and differentiate the elemental composition of the underlying uncontaminated biogenic carbonate. In addition, aluminosilicate minerals adhering to the samples dissolve at much slower rates and their contribution to the eluate composition can be estimated by extending the flow-through analysis after total carbonate dissolution to measure the elemental ratios needed to correct for their partial dissolution.

During a typical flow-through experiment, a single ostracod shell is loaded in a 13 mm Millex syringe filter with a 0.2 µm Millipore membrane. The incoming eluent, whose composition is controlled by an Ion Chromatography grade gradient pump, flows through the sample holder at a well-constrained rate (0.70 ± 0.04 mL min⁻¹; 95% confidence interval). The eluate is directly introduced into the plasma of an ICP-MS (Agilent 7700x Quadrupole ICP-MS) to acquire concentration data in time-resolved mode. A detailed description of the FT-TRA module is provided in De Baere et al. (2015) and De Baere (2015).

The leaching sequence used in this study starts with deionized water (DIW) for 10 min, followed by nitric acid (Seastar Chemicals Inc.) at concentration gradually increasing to 5 mM (for samples S1–S8) over a period of 2 min, and maintained for 8 min (Fig. 1). At this time, a second gradual increase in nitric acid concentration occurs over 2 min to 10 mM, after which the concentration remains constant until the final concentration increase to 155 mM HNO₃. In order to reduce the overall dissolution time, molarity of the nitric acid solutions during the procedure was increased for samples S9–S11 to 25 mM and 50 mM, respectively (Fig. 1). The moment in time when the acidity is increased to 155 mM HNO₃ is based on when the Ca peak, which is associated with the dissolving ostracod shell, returns to baseline. This is

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