

In-situ Carbonate Micro-Sampling Informed by Laser ICP-MS Trace Element Maps

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Diagenetic overprint of carbonates is one of the most significant impediments to reading the geochemical and isotopic record of seawater and other carbonate forming fluids. Much progress has been made in terms of minimising sample volume and using micro-drilling devices to target specific areas in a sample, for example from plaquettes adjacent to thin sections.

Mapping with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is also an effective tool to visualise the distribution of elements (e.g. Mg/Ca, Ba, Sr) in carbonates and maps help to identify areas to be avoided for micro-drilling. However, drilling still extracts material from well below the imaged surface.

Here we present trace element data for components extracted from Carboniferous limestones. The samples were extracted by using the LA unit as a milling device. Ahead of extracting the micro-samples, potential sampling targets (distinguishable bioclasts such as brachiopods, crinoids and corals vs. micrite) were mapped by LA-ICP-MS for trace element distribution. The maps revealed internal features within the targets and allowed us to identify areas of constant chemistry, devoid of diagenetic features or extraneous matter. The processed maps were re-coordinated with the LA stage and using the flexibility of the LA software, we then programmed area patterns for milling, performed with high repetition rate ablation. To facilitate sample collection, the aerosol transfer tube was disconnected from the ICP-MS and instead, the sample aerosol was transported with He directly into centrifuge tubes containing ultra-clean H₂O. The sampled areas were retrospectively inspected with white light interferometry.

The samples were then digested by acidifying the water in which they were collected. A small aliquot of the sample was next analysed by solution ICP-MS for a much greater number of elements than would be possible in LA mode. The bulk of the solution remains for elemental separation and eventual analysis of isotope ratios (e.g. Sr) in aid of chemostratigraphy. Because LA milling enables shallow sampling with a beam resolution of down to 2x2 µm the risk of contaminating bioclasts with enclosing matrix or diagenetic artefacts is drastically reduced.