

## Development and application of LA-ICP-MS in the geosciences: past, present and future

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The rapid advances in *in situ* laser ablation (LA) inductively coupled plasma-mass spectrometry (ICP-MS) and multicollector (MC)-ICPMS have provided datasets in geochronology and geochemistry that have revolutionised our understanding of the geodynamic Earth at all scales. The development and application of LA-ICP-MS continues to grow at a dramatic rate and *in situ* analyses for elements and isotopic ratios are now performed routinely in numerous laboratories worldwide. Like other microbeam techniques LA-ICP-MS provides the benefit of high spatial resolution and produces data that can be interpreted in a microstructural context.

The development of new LA-ICP-MS methodologies has been enabled by advances in instrumentation in conjunction with studies of the fundamental processes involved in ablation and in the ICP (e.g. laser-induced elemental and isotopic fractionation, plasma loading, mass bias). The emergence of the multi-collector ICP-MS for high-precision *in situ* measurement of radiogenic (e.g. Hf in zircon [1]) and 'non-traditional' stable isotopes (e.g. Cu and Fe in sulfides) has revolutionised analytical geochemistry. On the laser front, Nd:YAG (266, 213 or 193 nm) or ArF excimer (193 nm) remain the most commonly used laser sources. In comparison with these nanosecond pulse-width systems, ablation using femtosecond lasers has been shown to approach stoichiometric sampling and reduce laser-induced fractionation effects. However the high cost of the commercial femtosecond systems has restricted their uptake.

Despite the significant advances of the last decade, the continued rapid spread and acceptance of the technology may be jeopardized while any significant analytical issues remain unsolved. The accuracy and precision of *in situ* isotope ratio measurements are inherently lower than solution measurements because of the complexity of matrix effects and corrections for mass bias and isobaric interferences. Optimising precision of elemental and isotope ratio measurements while maintaining spatial resolution brings challenges, and emphasises the need for improved understanding of measurement uncertainties and error budgets. Well characterized and readily available reference materials combined with more inter-laboratory comparison exercises are essential.

Future goals for LA-ICP-MS include a quantum increase in sensitivity, fine-scale compositional mapping of geological samples, and overcoming effects of elemental and isotopic fractionation. Elimination of elemental fractionation will accelerate development of procedures to measure major, minor and trace-element abundances without depending on matrix-matched calibration materials and independently determined internal standard concentrations.

[1] Griffin *et al.* (2000) *Geoch. Cosm. Acta* **64**, 133-147.

## First record of Ediacaran iron formations: Origin and paleoenvironmental significance

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It is widely believed that the Earth's oceans became increasingly oxygenated during the late Neoproterozoic, most notably after the end of the Marinoan glaciation approximately ~635 million years ago. However, recent geochemical data for Ediacaran sediments suggest that some deep ocean basins were instead anoxic and ferruginous [Fe(II)-enriched] throughout the Ediacaran and possibly into the Cambrian, suggesting a more complex global redox structure than previously envisioned. An apparent absence of Ediacaran iron formations (IF) presented a challenge to this emerging paradigm; these chemical sediments were common under Fe-rich conditions in the Archean and Paleoproterozoic oceans.

Here, we report detailed sedimentological, stratigraphic, petrographic and geochemical data from an Ediacaran IF and associated rocks, including 'iron-rich' black shales, siltstones and cherts of the Arroyo del Soldado Group in Uruguay [1]. The IF and cherts occur at the top of two siliciclastic units characterized by retrogradational stacking patterns with fining-upward cycles deposited during transgressive system tracts and represent two major episodes of basin flooding and sediment starvation. Geochemically, the IF and cherts have coherent rare earth element and yttrium (REY) patterns and display the essential shale-normalized characteristics of marine precipitates. REY signatures and mixing calculations show that they differ from Archean and Paleoproterozoic IF as far as high-temperature hydrothermal input did not influence their chemistry. Instead, we suggest that low-temperature hydrothermal input may account for the geochemical signatures displayed. By analyzing the REY signature of chemical precipitates (cherts and IF) and evaluating the redox chemistry of the marine water column within a sedimentological and sequence stratigraphic framework, our results confirm that ferruginous conditions dominated the pre-Gaskiers but also the post-glaciation deep-water chemistry. Therefore, global ocean oxygenation may not have occurred until well into the upper Ediacaran or even during the Cambrian as was recently proposed [2].

[1] Pecoits *et al.* (2011) *Precambrian Research* **in press**. [2] Canfield *et al.* (2008) *Science* **321**, 92-95.