

Reference materials for *in situ* microanalysis: Successes and needs

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Currently, about 50 homogeneous reference materials (RMs) are in use for *in situ* elemental and isotope analysis (GeoReM database; <http://georem.mpch-mainz.gwdg.de>), and can be divided into the following groups:

Synthetic reference glasses – Many geoanalysts use the NIST SRM 610 and 612 glasses, which have the advantage that the concentrations of all trace elements are similar and high enough for a precise calibration. Major drawbacks are: first, most trace element compositions are not yet sufficiently well established to match ISO guidelines; second, they are not certified at the microbeam scale; and third, the major element concentrations are very different from those of any geological matrix. Other synthetic RMs are the GS reference glasses from the USGS, which have a basaltic major element composition along with many elements in similar abundances at different concentration levels.

Geological reference glasses – The USGS (e.g. BCR-2G, BHVO-2G), the MPI-DING (e.g. KL2-G, ATHO-G) and, recently, NRCG in China have prepared large amounts of homogeneous glasses of natural composition. These RMs cover the entire spectrum from ultramafic to highly siliceous compositions.

RMs for mineral analysis – There are only a few well-characterized RMs available. Notable exceptions are zircon (e.g. 91500), carbonate (e.g. MACS-1), as well as some other (e.g. titanite, sulfide, phosphate, rutile) RMs, which are under development or recently produced.

RMs for *in situ* isotope analysis – Some comprehensive studies have determined radiogenic and stable isotope data for the MPI-DING and GSD-1G glasses. Currently, isotope ratios for H, Li, B, O, Si, Ca, Sr, Nd, Hf, Pb, Th and U are available.

The demand for suitable RMs for microanalysis has increased considerably in the past few years. An important step has been the development of the USGS GS glasses. For *in situ* isotope analysis an increasing need exists for well-characterized RMs. There is also a great lack of RMs suitable for mineral investigations. Unfortunately, most RMs are not yet certified. To overcome this, the IAG has undertaken to serve as a certifying body and to develop a protocol. The certification procedure of the MPI-DING glasses followed these guidelines.

Aerosol iron chemical processing by marine biologically derived carboxylic acids; Results from field observations over the equatorial Pacific Ocean

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Iron is a limiting nutrient in many parts of the open ocean where a main delivery pathway is through the deposition of iron containing aerosol particles. Despite the significant effect that a modification in atmospheric iron supply and bioavailability has on primary productivity and related biogeochemical cycles, the detailed mechanisms that control iron speciation both in the atmosphere and ocean are not fully understood.

In the present study we elucidate the relevance of photochemically mediated mechanisms between iron and marine derived carboxylic acids that lead to enhanced reductive dissolution of iron in atmospheric particles before deposition into the ocean. Laboratory simulation data are backed by field observations collected over the iron-limited Equatorial Pacific Ocean. Of particular novelty is the role of malonate, a dicarboxylic acid which concentrations were relatively enriched over those expected from continental sources and is likely marine derived. The specific role of malonate in increasing iron photochemical reduction stems from the ligand-to-metal-charge-transfer reaction between Fe (III) and carboxylic acids [1].

Results from this study further support the hypothesis that marine biogenic emissions, e.g. by phytoplankton, may play an active role in boosting the bioavailable component of iron in atmospheric aerosol particles [2].

[1] Wang *et al.* (2009) *Environmental Science & Technology* **44**, 263–268. [2] Johansen & Key (2006) *Geophys. Res. Lett.* **33**.