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Precise measurement of Fe isotopes in marine samples by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS)

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Abstract

A novel analytical technique for isotopic analysis of dissolved and particulate iron (Fe) from various marine environments is presented in this paper. It combines coprecipitation of dissolved Fe (DFe) samples with $Mg(OH)_2$, and acid digestion of particulate Fe (PFe) samples with double pass chromatographic separation. Isotopic data were obtained using a Nu Plasma MC-ICP-MS in dry plasma mode, applying a combination of standard-sample bracketing and external normalization by Cu doping. Argon interferences were determined prior to each analysis and automatically subtracted during analysis. Sample size can be varied between 200 and 600 ng of Fe per measurement and total procedural blanks are better than 10 ng of Fe. Typical external precision of replicate analyses (1S.D.) is ±0.07‰ on δ^{56}Fe and ±0.09‰ on δ^{57}Fe while typical internal precision of a measurement (1S.E.) is ±0.03‰ on δ^{56}Fe and ±0.04‰ on δ^{57}Fe. Accuracy and precision were assured by the analysis of reference material IRMM-014, an in-house pure Fe standard, an in-house rock standard, as well as by inter-laboratory comparison using a hematite standard from ETH (Zürich). The lowest amount of Fe (200 ng) at which a reliable isotopic measurement could still be performed corresponds to a DFe or PFe concentration of ∼2 nmol L^{-1} for a 2 L sample size. To show the versatility of the method, results are presented from contrasting environments characterized by a wide range of Fe concentrations as well as varying salt content: the Scheldt estuary, the North Sea, and Antarctic pack ice. The range of DFe and PFe concentrations encountered in this investigation falls between 2 and 2000 nmol L^{-1} Fe. The distinct isotopic compositions detected in these environments cover the whole range reported in previous studies of natural Fe isotopic fractionation in the marine environment, i.e. δ^{56}Fe varies between −3.5‰ and +1.5‰. The largest fractionations were observed in environments characterized by redox changes and/or strong Fe cycling. This demonstrates the potential use of Fe isotopes as a tool to trace marine biogeochemical processes involving Fe.

Keywords: Fe isotopes; MC-ICP-MS; Seawater; Sea ice; Scheldt estuary; North Sea; Antarctica

1. Introduction

Iron (Fe) is the fourth most abundant element in the Earth's crust with a mean content of ∼4.3% Fe [1]. It is of great interest to biogeochemists, because as a redox-sensitive element and potentially limiting plant nutrient, Fe is strongly involved in global biogeochemical cycling. For example, Fe fluxes to the oceans via atmospheric, fluvial, benthic and hydrothermal pathways have an important impact on marine primary productivity, and hence on the global oceanic carbon cycle and the global climate [2]. Iron isotopic studies of these fluxes could help in clarifying the biogeochemical cycling of this element in the marine environment [3]. Until now, the elucidation of the marine biogeochemistry of Fe has been quite elusive due to analytical difficulties and undersampling of the oceans [4]. The complex biogeochemical behavior of Fe in the marine environment is controlled by redox changes, organic/inorganic speciation, solubilizing processes, particle sorption/desorption, and uptake and metabolic processing by marine biota [4,and references therein], each phase change being accompanied by isotopic fractionation factors that need to be identified [5]. Iron isotopic data have already been useful in palaeo-

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reconstructions of ancient anoxic and early oxygenated marine environments [6,7].

Iron has four isotopes with masses 58 (0.282%), 57 (2.119%), 56 (91.754%) and 54 (5.845%) [8], which can be fractionated by biotic and abiotic processes [9]. These naturally occurring fractionations range generally from $\delta^{56}Fe = -3‰$ to +1‰ [9]. The investigation of natural mass-dependent isotopic fractionation of Fe was bolstered by the recent development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). When compared with thermal ionization mass spectrometry (TIMS) the advantages of MC-ICP-MS are its high ionization efficiency minimizing drastically the required sample size, better precision and higher sample throughput. In recent years, many new applications emerged in such diverse fields as cosmochemistry [e.g. 10–12], earth and ocean sciences [e.g. 7, 13–17] and life sciences [e.g. 18,19].

Mass spectrometers produce instrumental mass bias, which is much higher for MC-ICP-MS (30–50‰ amu^{-1}) than for TIMS (3–5‰ amu^{-1}). It remains relatively unchanged over time with MC-ICP-MS, which is not the case for TIMS [7]. This makes mass bias corrections easier to perform. When instrumental mass bias drift occurs during and between analyses, it can be corrected for by standard-sample bracketing, or a combination of standard-sample bracketing with external normalization using a dopant in the same mass region as the element of interest, e.g. Cu [20] or Ni [18] for Fe. External normalization will not yield absolute, 'true' Fe ratios as instrumental mass bias behavior for Fe and Cu is not entirely similar, as was shown also for Cu and Zn [21]. It may nevertheless correct for matrix induced mass bias drift during the measurement and thus give a better internal precision. The fact that mass bias corrected Fe ratios are not equal to the 'true' ratios, explains why to date all measured Fe fractionations have been reported in delta notation relative to the international Fe standard IRMM-014 [22] or average terrestrial igneous rock [7]. It may be possible to obtain high precision absolute ratios using a double spike approach [23,24]. This technique has its drawbacks as it is mathematically complex and the resulting exotic isotopic ratios create a potential for memory effects, especially in dry plasma applications.

A caveat of Fe isotopic measurements by MC-ICP-MS is the formation of interfering argon isobars in the argon plasma, notably $^{40}Ar^{14}N^+$ on mass 54, $^{40}Ar^{16}O^+$ on mass 56 and $^{40}Ar^{16}O^1H^+$ on mass 57 [25]. To overcome these interferences, investigators have been using high amounts of Fe to overwhelm the isobaric interferences [25], dry plasma by sample desolvation to minimize oxide and nitride formation [20,25], collision cell technology to break down the argon interferences inside the mass spectrometer before arrival in the detector [7], cold plasma to prevent the formation of argon interferences in the plasma [11], and high mass resolution HR-MC-ICP-MS to enable full separation of the Fe masses from argon based interference masses [18,26,27]. The disadvantage of cold plasma and HR-MC-ICP-MS is the great loss of sensitivity that can be compensated by using a high amount of Fe, which is not always available in the sample. The techniques that offer the highest sensitivity (dry plasma, collision cell) are not capable to remove completely the argon interferences so that careful background evaluation is still necessary.

From its continental sources (~4.3% Fe) to its oceanic dissolved form (<1 nmol L^{-1} Fe), Fe decreases in concentration by more than six orders of magnitude and undergoes different phase transformations. This enormous range of natural Fe concentrations in very different natural matrices poses major analytical challenges, in terms of controlling sample contamination, matrix effects, isobaric interference, mass fractionation artifacts, analyte recoveries and blanks. This largely explains the paucity to date of Fe isotopic data from the marine environment. This paper describes a methodology for the precise determination in marine materials of Fe isotopic fractionations relative to the international Fe standard IRMM-014, by a combination of standard-sample bracketing and external normalization using Cu. The instrument used in this investigation is a Nu Plasma MC-ICP-MS operating in dry plasma mode by the use of a Cetac Aridus desolvating sample introduction system. The methodology centers on $Mg(OH)_2$ coprecipitation/preconcentration of dissolved Fe (DFe), acid digestion of particulate Fe (PFe), matrix separation/purification of Fe by double pass anionic exchange chromatography using Bio-Rad AG-MP1 resin. To demonstrate the versatility of the analytical technique, preliminary results are presented from contrasting marine environments characterized by varying Fe concentrations and salt content: North Sea and Scheldt estuary (DFe, PFe in suspended matter, and PFe in surface sediment), as well as Antarctic pack ice (DFe and PFe).

2. Experimental

2.1. Reagents

The following reagents were used or prepared: Liquinox detergent from Alconox (White Plains, NY, USA), 25% ammonia (NH_4OH, Merck suprapur), 30% hydrogen peroxide (H_2O_2, Merck suprapur), triple subboiled 6 M hydrochloric acid (HCl), triple subboiled 14 M nitric acid (HNO_3) and single subboiled 24 M hydrofluoric acid (HF). As starting materials for the subboiling distillations 1:1 diluted 12 M HCl (Merck reagent grade), 14 M HNO_3 (Merck reagent grade), and 24 M HF (Merck suprapur) were used. Subboiling distillation stills were either from Teflon PTFE (BSP929, Berghof, Eningen, FRG) for HCl and HNO_3, or from Teflon PFA (Savillex, Minnetonka, MN, USA) with infrared lamps for HF. Ultrahigh purity (UHP) water for rinsing and dilutions was drawn from a Millipore Element (18.2 MΩ cm) water purification apparatus, fed with water from a Millipore Elix reverse osmosis device. Iron in samples was separated from sample matrix constituents (e.g. Cu, Mg) using Bio-Rad AG-MP1 (100–200 mesh) strong anionic exchange resin.

2.2. Cleaning procedures

All cleaning and sample manipulations were carried out in a class 100 clean air laboratory, with personnel wearing Tyvek clean room coveralls, plastic clogs and Nitrile gloves. All plastic lab-ware was first cleaned by overnight soaking in a detergent