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# Iron Isotopes

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## Definition

Iron has four naturally occurring stable isotopes:  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$ , and  $^{58}\text{Fe}$  of respective abundances 5.80 %, 91.72 %, 2.20 %, and 0.28 %. They are increasingly used to determine the source of the iron present in geological or biological materials and/or to characterize the chemical reactions that may have lead to the form of iron under study. The isotopic signature of Fe is particularly sensitive to redox effects, including certain biological reactions such as bacterial dissimilatory iron reduction (DIR).

## Overview

Although less variable in abundances than carbon or oxygen stable isotopes, iron isotopes show analytically significant mass-dependent isotopic variations in nature. The geochemical community has investigated the range of Fe isotope compositions in both high- and low-temperature geological environments. Contrary to early expectations, there are no specific biological-type iron isotope

signatures. On the other hand, the largest isotopic fractionation was observed for low-temperature redox reactions, and biological dissimilatory iron reduction (DIR) is one of those biological reactions that affect significantly iron isotope compositions. Another requirement for inorganic or organic reactions to leave an isotopic imprint is that the reaction exchange is not complete, that is, not all of the original pool of iron has been consumed. Nature-based and experimentally-based astrobiology studies have shown that iron isotopes are particularly useful to study traces of life and/or their environment when used in conjunction with other mineralogical, biological, and chemical indicators.

## Basic Methodology

The isotopic composition of iron in natural samples has been measured since the 1940s by electron impact ionization and, more recently, by thermal ionization mass spectrometry (TIMS) after sample dissolution and chemical purification using anion exchange chromatography. The level of precision reached relative to natural variations rendered the study of Fe isotope signatures of little interest until the end of the twentieth century. The advent of the second generation of multiple collector inductively coupled plasma mass spectrometers (MC-ICP-MS) led to an order of magnitude improvement in analytical precision (Belshaw et al. [2000](#)). This opened the way to an exponential development of these “non-traditional isotopes,” such as iron isotopes. Although the purification chemistry is straightforward and has been known for some time (Strelow [1980](#)), MC-ICP-MS techniques vary among laboratories. Mass bias corrections range from the simple sample-standard bracketing approach to more sophisticated Cu- or Ni-doping methods. A few groups have also adopted the double spike technique, which remains the only way to determine precise Fe isotope composition by TIMS. Isotopic results are conventionally reported using the delta notation with reference to the IRMM 14 reference material (unfortunately no longer available from the European Institute for Reference Materials and Measurements, Geel, Belgium, but it may be conveniently replaced by the IRMM 524A reference material) that has a composition close to that of chondrites. For example:

$$\delta^{57}\text{Fe} (\text{‰}) = \left( \frac{{}^{57}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}}}{{}^{57}\text{Fe}/{}^{54}\text{Fe}_{\text{IRMM14}}} - 1 \right) \times 10^3$$

and this notation can be equally defined for  $\delta^{56}\text{Fe}$ . Some groups still report their Fe isotope compositions with reference to average of igneous rocks. Although being isotopically homogeneous, this convention should be abandoned since some igneous rocks depart significantly from this average value (e.g., some granites from the Earth’s continental crust; Poitrasson and Freydier [2005](#)), and therefore, this may generate some confusion among non-specialists.

## Key Research Findings

A first important finding is that the iron isotope compositions of igneous rocks that form the Earth’s crust vary very little. As a result, they make a baseline against which low-temperature, superficial biogeochemical processes that display larger isotope variations may be compared to (Beard et al. [2003](#); Poitrasson [2006](#)). Various field-based, experimental, and especially theoretical studies

conducted over the past two decades revealed that the main driving factors generating Fe isotope variations are redox and coordination chemistry changes. For example, the largest equilibrium Fe isotope fractionation among two coexisting iron reservoirs ( $\sim 4.5$  ‰ in  $\delta^{57}\text{Fe}$ ) was observed between aqueous  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species (Welch et al. [2003](#); Anbar et al. [2005](#)). The importance of the bonding environment on Fe isotope signatures is best illustrated by theoretical prediction of Fe isotope fractionation between mineral phases holding iron in the same redox state, but with different network-forming anions, such as in sulfide and carbonate minerals (Polyakov and Mineev [2000](#); Blanchard et al. [2009](#)). Ab initio computations also illustrate the importance of iron coordination chemistry and nature of aqueous ligands to interpret the Fe isotope composition of environmental samples (Fuji et al., 2014). The finding that mass-dependent Fe isotope variation occurs in nature is interesting in itself. Even more important however is the discovery that for the same rocks, the stable isotopes of iron show contrasted fractionation when compared to those of carbon (Matthews et al. [2004](#)). Although not unexpected given the contrasted interatomic bonding environments of Fe and C, this illustrates that the stable isotopes of different elements can trace different processes and/or different properties of the studied reservoirs. As such, combining different isotopic tracers is certainly a promising approach for future research, notably to detect biological activity (Johnson et al. [2008](#); Severmann and Anbar [2009](#)).

## Applications

Since astrobiology aims at looking for traces of life on the early Earth and on planets other than the Earth, one would ideally do precise Fe isotope measurements of extraterrestrial samples to determine signatures that could be tracking life or at least environmental conditions suitable for life. However, the need for high-precision mass spectrometry methods that were established in terrestrial laboratories over the past decade makes such delicate measurements on robotic missions on other planets impossible at present. Aside for the Moon that has never been prone to the development of life since the beginning of its history given its extreme temperatures, lack of liquid water, and lack of atmosphere, we should wait for sample return missions from other planetary bodies. In the meantime, we have to rely on meteorites thought to come from planets where life may have existed, such as Mars. However, Martian meteorites that belong to the Shergotty, Nakhla, and Chassigny (SNC) class are essentially igneous rocks. Hence, looking for traces of life on those rocks using iron isotopes was unsuccessful (Anand et al. [2006](#)). This was not unexpected given that even if traces of life were searched on bulk terrestrial fresh igneous rocks, the igneous rock Fe isotope signature would have likely overwhelmed the biologically processed Fe. Another limitation is that despite initial expectation (Beard and Johnson [1999](#)), there are, like for carbon isotopes, no unique Fe isotope biological signatures (Anbar et al. [2000](#)). Indeed, inorganic processes may also produce strong Fe isotope fractionation leading to light products, notably when kinetic effects are involved. Hence, the use of Fe isotopes to search for traces of biological activity should necessarily be conducted in conjunction with other mineralogical, chemical, and isotopic indicators.

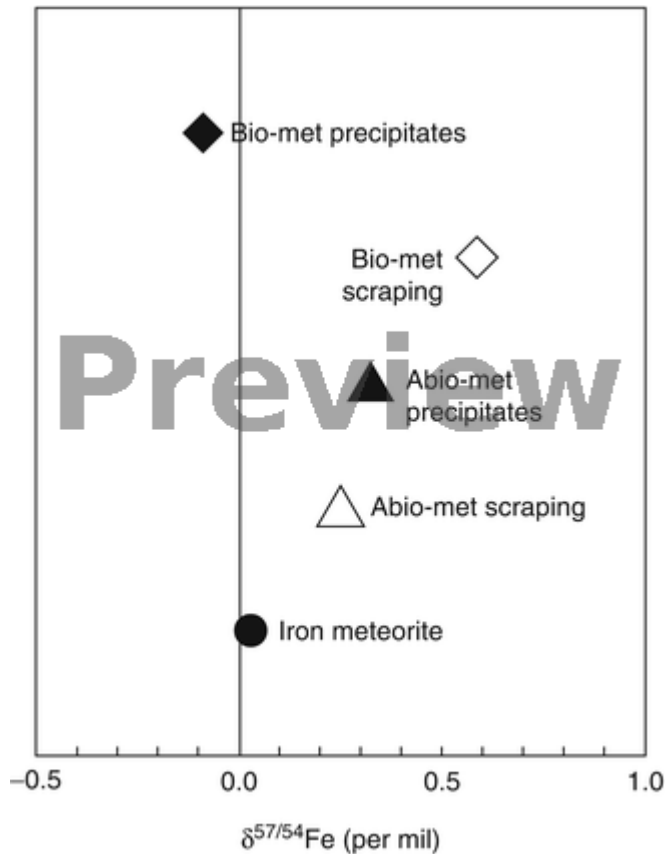
Astrobiology also looks at extreme terrestrial environments where life may occur despite hostile conditions. This is the case of acid mine drainage waters from the [Rio-Tinto-Odiel](#) sulfide deposit basin, southern Spain, that is characterized by anomalously acidic waters ( $1.5 < \text{pH} < 3.9$ ) containing elevated concentrations of dissolved Fe ( $> 20\,000$  ppm). Despite these conditions, bacterial activity occurs. This geological setting is of interest to astrobiologists because it forms specific minerals including [jarosite](#) that also occur at the Martian *Meridiani Planum* site. Iron isotopes were used by

Egal et al. ( [2008](#)) to study this Spanish site. Although the biological activity imprint could not be detected through Fe isotope compositions, this study combined mineralogical, aqueous geochemistry, and iron isotope determinations to put constraints on the mechanisms that led to the formation of such an extreme geochemical environment on Earth.

Archean [apex cherts](#) from Marble Bar, Western Australia, is another interesting geological case study for astrobiologists since it has been claimed to contain the oldest fossils of microbes found yet on Earth, ca. 3.5 Ga years ago, although this finding generated a lot of debate. Pinti et al. ( [2007](#)) used iron isotopes to study Fe-Mn-oxyhydroxides containing C and N with a biological-like isotopic signature that occur in these cherts. They found  $\delta^{57}\text{Fe}$  values compatible with oceanic hydrothermal precipitation, thereby strengthening the inference that C and N isotope compositions mark 3.5 Ga old biological activity.

Archean banded iron formations (BIFs) are also obvious geological records to look for ancient traces of life. Combining a detailed petrographic study with C, O, and Fe isotope investigations of carbonates from these sedimentary formations led Heimann et al. ( [2010](#)) to highlight the importance of bacterial dissimilatory iron reduction back to ca. 2.5 Ga ago. Studying again Fe and C isotopes in magnetites and carbonates from BIFs of ca. 2.5 and 3.8 Ga, Craddock and Dauphas ( [2011](#)) concluded that this bacterial process is in fact recorded in the oldest available sedimentary rocks we have on Earth.

Experimental investigations may also help to study processes that may have occurred on the early Earth. For example, Gronstal et al. ( [2009](#)) examined experimentally how the first living organisms on Earth, that is, prokaryotes, could have extracted energy by oxidizing metallic iron from meteoritic material. Such a form of Fe, which is nearly nonexistent on the present Earth's surface, was supposedly abundant at that time corresponding to the end of the [Late Heavy Bombardment](#) and there was an anoxic atmosphere. Interestingly, these authors found that whereas metal weathering occurred regardless of the presence of iron-oxidizing bacteria, the weathering products clearly showed isotopically contrasted iron pathways during oxidation with and without bacteria. This suggests that the biological action in meteorite weathering could be highlighted with Fe isotopes (Fig. [1](#)).



**Fig. 1:** Products of iron meteorite weathering in aqueous solutions with (Biomet) and without (Abiomet) iron-oxidizing bacteria. Both the weathered layers at the surface of the meteorites (scraping) and precipitates elsewhere in the experimental cell (precipitate) were sampled. Iron isotope composition relative to the starting meteorite shows contrasted Fe isotope signatures for these weathering products with and without bacteria, suggesting contrasted reaction pathways (Error bars within symbols; From Gronstal et al. [2009](#))

Among subsequent experimental studies, Amor et al. (2016) investigated the Fe isotope fractionation during the growth of magnetotactic bacteria and found a unique mass independent iron isotope fractionation between the culture medium and the bacterially-produced magnetites. The next challenge is to find geological formations where this effect can be recorded despite obvious risks of dilution of this isotopic signature in the rock matrix (Amor et al., 2020).

## Future Directions

Iron isotopes have not yet been applied frequently to astrobiology problems. More case studies therefore need to be investigated, either experimentally, and from natural examples of extreme terrestrial environments, or of the oldest remains of the early Earth. There are however more fundamental issues that need to be addressed first to be able to fully exploit the potential of iron isotope signatures in this endeavor. In a number of studies, equilibrium isotopic fractionation between phases is taken as a reference against which the observed natural variations may be interpreted. This is especially important in low-temperature environments where kinetic isotope fractionations are more likely to be observed given the sluggishness of chemical reactions under such conditions and therefore the large amount of time required to reach equilibrium. For this, more experimental and numerical determinations of the fractionation factors are required. It is important to

conduct both approaches simultaneously since cross-validation of experimental, theoretical, and natural determinations is clearly needed (Hill et al., 2010). Another important development is the need for in situ data. Meteorites and very old terrestrial samples have had a protracted history that generated chemical and isotopic heterogeneity. Producing bulk sample data unveils only a portion of the message. Doing precise and accurate in situ Fe isotope determinations (Horn et al. [2006](#); Steinhoefel et al. [2010](#); [Czaja et al., 2013](#)) is more likely to fully unfold the history that iron isotopes can tell.

## See Also

- . [Archean Traces of Life](#)
- . [Banded Iron Formation](#)
- . [Biomarkers](#)
- . [Isotope](#)
- . [Isotopic Fractionation \(Interstellar Medium\)](#)
- . [Jarosite](#)
- . [Late Heavy Bombardment](#)
- . [Rio Tinto](#)

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