

Progress in Geochemistry of Non-Traditional Stable Isotope-Iron Isotope

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Abstract

Fe, one of the most abundant and well studied non-traditional stable isotopes in the earth's crust, has a specific atomic number (26), atomic weight (55.845) and density (7.86g/cm³). At present, it is found that there are three valence states of Fe in minerals, rocks and fluids that have undergone various geochemical processes: metallic iron (Fe⁰), bivalent iron (Fe²⁺) and trivalent iron (Fe³⁺). The four stable isotopes were ⁵⁸Fe (0.33%), ⁵⁷Fe (2.25%), ⁵⁶Fe (91.52%) and ⁵⁴Fe (5.90%). In recent years, as for the cause of Fe isotope composition, migration, sorting, distribution, research development, and testing methods, the improvement of experimental equipment and complete, and gradually develop and use Fe isotopes, fluid out of the soluble and evolution process of magma, metallogenic material source and genesis, biological absorption and induction process, the fractionation mechanism, the mantle metasomatism, etc were studied. With the further development, the application of Fe isotopes will be an extremely important analytical means in the multidisciplinary research progress of geochemistry and even cosmology in the future.

Keywords

Iron isotope; Isotope fractionation; MC-ICP-MS; Non-traditional stable isotopes.

1. INTRODUCTION

Iron is the fourth most abundant element in the Earth's crust, with four naturally occurring stable isotopes: ⁵⁸Fe (0.33%), ⁵⁷Fe (2.25%), ⁵⁶Fe (91.52%), ⁵⁴Fe (5.90%). The isotopic abundances were ⁵⁴Fe=5.845 ±0.023(2σ), ⁵⁶Fe=91.754±0.024, ⁵⁷Fe=2.1192 ± 0.0065, ⁵⁸Fe=0.2818±0.0027(Nicolas Dauphas, 2006). In general, not much has been reported about δ⁵⁸Fe, due to the difficulty of accurately measuring the variation of low isotope abundances (0.282‰) with current techniques. In general, ⁵⁸Fe can be used to study primitive solar system materials to examine the non-mass dependent process of nucleosynthesis.

Iron is produced in massive stars, and the lives of stars end in high-energy explosions called supernovae because any fusion reaction on iron is endothermic, so iron cores are endothermic. It is estimated that about 30% of iron is produced in the SNIA galaxy, and this ratio applies to ⁵⁶Fe as it is the dominant isotope of iron (Nicolas Dauphas, 2006). Iron usually occurs in the form of reduced iron in oxygen-poor environments and in the form of iron oxide in oxygen-rich environments. Unless the pH is very low, the reduced material is soluble in oxygen-containing aqueous solutions.

During the Archean and early Proterozoic, the Earth may have been relatively anoxic, indicating that there may have been a large amount of Fe(0.9mmol) dissolved in the ocean in the form of Fe(II) aq. The extensive iron strata from Archean to early Proterozoic may have been deposited by iron-rich oceans. However, in modern oxygenated oceans, iron levels are very low. In the open ocean, iron levels are very low. 1 nmol. The behavioral differences between iron and

REDOX states and the significant isotope fractionation associated with REDOX conditions (1‰ or more in $^{56}\text{Fe}/^{54}\text{Fe}$) suggest that iron isotope studies will be extremely useful for tracing the iron geochemical cycle.

The greatest variation in iron isotopic composition is associated with chemical precipitates, such as the Pliocene to recent Fe-Mn crusts and the Archean and Proterozoic band-shaped iron formations. In addition, the iron isotopic composition of black shales has a similarly large range, resulting in petrogenesis under anoxic conditions. In contrast, the range of iron isotopic compositions of clastic sedimentary materials deposited in oxygen-rich environments, such as loess, turbidite, fluvial suspended sediments, and gray shales, is very small. However, variability in iron isotopic composition seen in nature is not limited to low-temperature depositional environments; for example, chondrites, especially single chondrules, have a diffusivity of 2.5‰ for the $\delta^{54}\text{Fe}$ ratio. In contrast, the range of iron isotopes in chondrite block analyses and terrestrial igneous rocks is relatively narrow. Indeed, the iron isotopic composition of terrestrial igneous rocks is very uniform; The composition of the igneous rocks is not uniform, and the ratio of $^{56}\text{Fe}/^{54}\text{Fe}$ in the peridotite is 0.05‰(1 σ).

2. DETERMINATION METHOD, EXPRESSION MODE AND VARIATION RANGE OF FE ISOTOPE

At present, there are two different methods of Fe isotope representation: δ (thousandth deviation) and ϵ (thousandth deviation). The δ expression of Fe isotope is as follows:

$$\delta x\text{Fe} = \left[\frac{(^x\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^x\text{Fe}/^{54}\text{Fe})_{\text{standard}}} - 1 \right] \times 10^3 \quad (1)$$

Fe isotopic values vary in a wide range, up to ($\delta^{57}\text{Fe} = -8.8 \sim 9.3$). Different types of rocks show different values, as shown in Table (1):

Table 1. $\epsilon^{57}\text{Fe}$ values for different rock types

Rock types	$\delta^{57}\text{Fe}$ value
Carbonaceous chondrites	$\delta^{57}\text{Fe} = -8.8 \sim 9.3$
Common chondrites	$\delta^{57}\text{Fe} = -6.5 \sim 6$
No chondrites	$\delta^{57}\text{Fe} = -2.5 \sim 2.1$
Iron meteorites	$\delta^{57}\text{Fe} = 0.6 \sim 2.3$
Lunar igneous rock	$\delta^{57}\text{Fe} = 2.06$
Mars chondrites	$\delta^{57}\text{Fe} = 0.03$
The earth material	$\delta^{57}\text{Fe} = 1.05$
Magmatic rocks	$\epsilon^{57}\text{Fe} \approx 1.5$
Continental and oceanic crust materials	$\delta^{57}\text{Fe} \approx 0$
Hydrothermal deposit	$\epsilon^{57}\text{Fe} = -25.8 \sim 13.5$
Organic shale	$\epsilon^{57}\text{Fe} = -35.4 \sim 10.2$
Fe-Mn crusts on the ocean floor	$\epsilon^{57}\text{Fe} = -14.5 \sim 2$
Precambrian banded iron-bearing formation	$\epsilon^{57}\text{Fe} = -51.8 \sim 34.5$
North Atlantic Fe-Mn crust	$\epsilon^{57}\text{Fe} = -11.5 \sim 2$
There are 37 Fe-Mn compounds worldwide	$\epsilon^{57}\text{Fe} = -11.9 \sim -0.7$
Pacific Fe-Mn crust	$\epsilon^{57}\text{Fe} = -14.5 \sim -4.8$

(Data from: Zhu, 2000; Poitrasson, 2004; Beared, etc., 2003; Levasseur, 2004; Chu, 2006)

When the change of Fe isotope is small, it is expressed by ϵ 10000 deviation:

$$\epsilon_{\text{Fe}} = \left[\frac{(\text{}^x\text{Fe}/\text{}^{54}\text{Fe})_{\text{sample}}}{(\text{}^x\text{Fe}/\text{}^{54}\text{Fe})_{\text{standard}}} - 1 \right] \times 10^4 \quad (2)$$

Zhu (2000) through the study of the north Atlantic Fe - Mn crusts shows that during the period of 6~0 Ma, epsilon ⁵⁷ Fe = 11.5~2, confirmed by Fe isotope source area to the precipitation process is influenced by biological fractionation effect is not obvious, there is no isotopic fractionation. Levasseur etc. (2004) to the global scope of the 37 Fe - Mn crust sample Fe isotope research shows that epsilon ⁵⁷ Fe = 11.9 ~ 0.7, found that Fe isotope composition not only affected by the content source, and is affected by the surrounding environment. Chu et al. (2006) studied the Fe isotopes of Fe-Mn crusts in the Pacific Ocean, showing that ε⁵⁷Fe= -14.5 ~ -4.8, and pointed out that the isotopic compositions of Fe-Mn crusts in the range of 100 km are different, and believed that the material sources may be hydrothermal fluid, river or pore water in continental shelf precipitation.

3. FE ISOTOPE FRACTIONATION MECHANISM

Isotope fractionation is a phenomenon in which isotopes of elements are distributed among different substances in different proportions during physical, chemical and biological reactions. Isotope fractionation between minerals or molecules in equilibrium state can be used to indicate some information about the temperature and process of material formation. Fe of stable isotopes in the earth's surface and interior of the earth's chemical and physical transport process has experienced depends on the quality related isotope fractionation, Fe isotope fractionation mechanism caused by many factors, such as the nature of chemical reaction and irreversible reaction, evaporation, diffusion, adsorption and biochemical reaction process. The segmentation effect factors can be crystal fractionation, the mantle magmatic or hot liquids, temperature gradient or dynamic effect, molten rock interaction mutual diffusion, and so on one or more elements caused by common action of valence, further lead to the change of coordination number between atoms in the lattice bond energy change.

In many studies, fractionation is considered as an equilibrium process, but in fact isotopic fractionation is divided into thermodynamic equilibrium fractionation and kinetic non-equilibrium fractionation. Isotope equilibrium fractionation includes many physical and chemical processes with different mechanisms, but the end of the process is in the equilibrium distribution state of isotopes. Once the isotopic equilibrium is established, the distribution of isotopes in different minerals or phases will remain unchanged as long as the physical and chemical conditions of the system remain unchanged. The fractionation of isotopes between two minerals or phases is called equilibrium fractionation. According to the size of isotope fractionation between coexisting phases in geological system, the isotopic "equilibrium" temperature between phases can be calculated by using the known isotope fractionation coefficient. If isotope fractionation does not reach equilibrium, it cannot be used to determine geological temperatures. In other words, the precondition for isotopic geological temperature recording is that the isotopic composition of the symbiotic mineral pairs should be in equilibrium with each other. The difference in stable isotopic composition, i.e. isotopic fractionation coefficient, is a function of temperature among co-occurring minerals in the geological body. The relationship is as follows:

$$10^3 \ln \alpha_{1-2} = A(10^6 T^{-2} + B) \quad (3)$$

And

$$10^3 \ln \alpha_{1-2} = \delta_1 - \delta_2 = \Delta_{1-2} = A(10^6 T^{-2}) + B \quad (4)$$

α : The fractionation coefficient of isotopes (1 and 2 represent the fractionation coefficient of two minerals)

T : Absolute temperature

A, B: Constants, which vary with the type of mineral pair and are generally obtained experimentally.

Isotope kinetic nonequilibrium fractionation refers to the time dependent fractionation that deviates from isotopic equilibrium, that is, the distribution of isotopes among phases varies with time and the reaction process. Many isotopic fractionations in nature have chemical kinetic properties, such as unidirectional chemical reactions, evaporation, diffusion, and biological processes (photosynthesis, root respiration, bacterial reduction). In one case, there is no isotopic balance between the formed minerals and the system at the time of mineral formation. For example, the isotopic homogenization rate of the crystalline minerals themselves is too slow to keep up with the growth rate of the crystals, resulting in different isotopic compositions of the first and second crystalline parts. In the other case, during mineralization, the formed minerals and the system reach isotopic equilibrium, but after mineralization, the external conditions change, such as temperature change, the addition of new components or the escape of the original components. Under new conditions, isotopic exchange and rebalance occur to the generated minerals, which often fail to reach the new equilibrium state, and are often accompanied by other reaction processes, which also have the property of isotopic dynamic fractionation (Liu Geng, 2015; Liu Qi, 2009; Huang Fang, 2011; Lu Shuangfang, 2006).

J.G. Konter (2016) believed that the preference for iron isotopes in different parts depends on the oxidation state of iron, and crystal fractionation is generally considered to be the main mechanism to control the fractionation of Fe isotopes in eruptive rocks. For example, the value of heavy iron isotope $\delta^{56}\text{Fe}$ in high silicon igneous rocks (≥ 70 wt% SiO_2) varies significantly from $0.05 \pm 0.05\text{‰}$ to $0.55 \pm 0.05\text{‰}$, which was confirmed by De-Hong Du (2017). Most of the variation of ^{56}Fe in the fractionation of iron isotopes in the hydrothermal system and in the hydrothermal rich iron deposits may also reflect the fractionation of hydrothermal systems, Sharma (2001). However, the fractionation system between minerals of extrusive rocks is smaller than that of intrusive rocks, and the fractionation system between minerals and melt is generally smaller. Extrusive rocks may record the equilibrium of magma temperature, while intrusive rocks record the equilibrium of lower co-crystallization and even after crystallization. The fractionation size of stable isotopic rocks is inversely proportional to the square of temperature. However, the influence of chemical diffusion on fractionation in each phase of extrusive rocks cannot be excluded. Chen Chen (2015) pointed out that iron isotopes can be fractionated during the process of mantle magma. Ronny Schoenberg (2006) believed that continental basalts seemed to be slightly heavier than mantle xenoliths, so partial mantle melting preferred to transfer heavy iron to the melt.

There is also obvious Fe isotopic fractionation in the sediments. Paul R. Claddock (2011) obtained $\delta^{56}\text{Fe} = \pm 0.03$ and $\delta^{57}\text{Fe} = 0.05$ by analysis, and concluded that the Fe isotopic composition of the iron-rich chemical sediments has obvious fractionation of $\delta^{56}\text{Fe} = +0.639 \pm 0.013$. The precipitation and the early Precambrian banded iron formation (BIF) by micro quartz, iron oxides and iron rich silicate (such as silicate), as a kind of special chemical sedimentary rocks, Kejun Hou (2017), the experimental analysis shows that the Fe^{2+} in solution by biological or non-biological oxidation of Fe^{3+} , can cause considerable Fe isotope fractionation, lead to Fe^{3+} in ChongTie enrichment, Fe^{2+} , on the other hand, the LRT isotope enrichment. The temperature gradient also acts as a controlling factor controlling the

fractionation mechanism, which shows a strong correlation between the isotopic composition and the sampling depth. In fact, the isotopic composition follows a temperature gradient in which heavy isotopes are systematically enriched in the cold zone. This fractionation can entirely be attributed to a thermal transfer process in which the distribution of isotopes essentially follows a vertical temperature gradient Thomas Zambardi (2014). Skulan et al. (2002) argue that fractional distillation is the result of dynamic effect, $^{56}\text{Fe}/^{54}\text{Fe}$ between precipitation and solution of isotope fractionation is $\alpha_{\text{Fe(III)}-\text{hematite}} = 1.00132$. Found that the sedimentation rate, the greater the isotope fractionation, the greater the dynamic fractionation decreases with the decrease of the precipitation rate, if the case to the sedimentation rate of 0, can draw $\Delta^{56}\text{Fe(III)}_{\text{aq-hematite}} = 0.15\text{‰}$. Bullen et al. pointed out that the fractionation of Fe isotopes in their experiments was influenced by the species of experimental subjects. Johnson, et al. Based on the room temperature (22 plus or minus 2°C) extremely dilute solution ($\cong 22$ tendency for Cl-L) Fe(III), Fe(II) CaCO₃ precipitation separation, determination to $\delta^{56}\text{Fe(III)}-\text{Fe(II)} = +2.75 + 0.15\text{‰}$ (^{56}Fe) δ , this deviation may be caused by the interaction between different Fe complex.

Should not be neglected and Fe(III) hydrolysis, hydrolysis is a common process of supergene environment, to some extent control of the Fe in the migration of water and redistribution. Zhu Xiangkun et al. (2012) conducted the hydrolysis experiment of ferric iron and believed that when Fe isotope fractionation occurred in the hydrolysis process, it was mainly Rayleigh fractionation, and the Fe isotope exchange occurred in the dissolving and reprecipitation process was ignored. When combined with other elements, such as stable isotopes of iron and vanadium, which work together in the magmatic mantle of closed system differentiation, silicates, oxides and sulfides fractionation systems can be formed. However, the stable isotopic characteristics of transition metals in magmatic rocks cannot be used as a direct REDOX proxy without limiting magmatic division and partial melting (H.M. Williams, 2018). Another example is the dynamic isotope fractionation caused by the diffusion of Fe and Mg during the interaction of molten rock. These processes play an important role in the formation of Fe and Mg isotopic imbalance between minerals and local Fe and Mg isotopic heterogeneity in the mantle of the subcontinent. Even in the Ca-Fe isotopic characteristics of some Fe-rich peridotites, the time scale of dynamic isotopic fractionation in melt-peridotite reactions ranges from several years to several hundred years, and inter-mineral calcium isotopic fractionation between coexisting plagiopyroxene and orthopyroxene pairs may have compositional effects (Xinmiao Zhao, 2017). However, Paul R. Craddock (2013) believes that Fe isotopic fractionation is mainly the action of melt, rather than the residue from the formation of oceanic and continental crust. Different iron isotopic compositions in deep-sea peridotites and debris provide more and more evidence for Fe isotopic fractal. Deep sea peridotite average $\delta^{56}\text{Fe} = +0.010 \pm 0.007\text{‰}$.

4. APPLICATION OF FE IN MANTLE GEOCHEMISTRY

The mantle of the modern Earth is oxidized and chemically out of equilibrium with the core, relative to the reduction conditions initially assumed for core formation. The reasons for this phenomenon and the oxidation status of the mantle relative to that of other terrestrial planets are not clear, and the timing of mantle oxidation is not completely established, but it has important implications for the development of the hydrosphere and atmosphere. E.J. Hibbert (2012) Looking for the timing of mantle oxidation from Fe isotopes in ancient and modern comatite, the oxidation state or oxygen fugidity (FO_2) of the modern mantle is defined by the chemical equilibrium between Fe^{3+} and Fe^{2+} bearing minerals, and controlling when the mantle reached its present FO_2 level is fundamental to understanding the development of the hydrosphere and atmosphere. It is difficult to determine the long-term variation of mantle FO_2 from igneous rock analysis, and the precise control of iron isotope variation in igneous rock is still unknown. However, stable isotopes in igneous rock can be used as a potential tracer of

mantle FO_2 variation. Fe can be used as a tracer because its three oxidation states, FeO, Fe^{2+} , and Fe^{3+} , are located differently in the core, mantle, and crust, raising the possibility of tracking Earth's REDOX processes using stable iso-surface changes in Fe.

The modern mid-ocean ridge and oceanic island basalts (MORB and OIB) have a ratio of $(\pm 0.06\text{‰})^{56}\text{Fe}/^{54}\text{Fe}$, but the ratio is significantly higher than that of modern and Eocene Archean bogu andesites and many island arc basalts, which may be explained as a depleted mantle source. According to the ratio of $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$, the ratio of $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ in the glass composed of basalt, andesite, dacite and rhyolite is estimated. The stable Fe isotopes are helpful to reveal planetary REDOX conditions and igneous rock processes. When basalt and olivine crystals show higher than normal $\delta^{56}\text{Fe}$ values, this phenomenon cannot be fully explained by the common partial melting process from the mean mantle and subsequent differentiation and melting. It can be considered whether the fractionation process in the molten state is caused by the effect of oxygen fugacity, or whether the $\delta^{56}\text{Fe}$ value increases due to the combined effect of other metasomatism and other elements with high field strength, or whether it is related to the upwelling mantle plume or the previously metasomized upper mantle melting by establishing a relevant model. Mantle metasomatism or molten rock interaction can significantly change Fe isotopes and play an important role in the formation of lithospheric mantle Fe isotopic heterogeneity. Therefore, Fe isotopes can provide important information about the interaction and evolution of lithospheric mantle molten rock. Since mantle xenoliths provide direct information about lithospheric evolution and asthenospheric lithospheric interactions, it is important to accurately determine the age of host basalts carrying xenoliths. The variation of Fe isotopes in different minerals and peridotites may be the result of the interaction of mantle endmembers, so there are obvious allogenic Fe isotopic variations in the lithospheric mantle at xenolith scale. The Fe isotopic characteristics of the lithospheric mantle in the North China Craton indicate that mantle metasomatism is the most likely reason for the Fe isotopic variation of mantle peridotite (Xinmiao Zhao, 2010; Xinmiao Zhao, 2012; Xinmiao Zhao, 2013; Xinmiao Zhao, 2015; Dauphas (2009).

Partial melting of Fe isotopes occurs during fractionation, even at very high levels. Therefore, it is still a difficult problem to estimate the Fe isotopic composition of the primitive mantle. Helen M. Williams (2012) compared and analyzed the similar Fe isotopic composition and equilibrium model of the original terrestrial basalts and low-titanium lunar basalts, and concluded that the heavy iron isotopic composition of the Earth's mantle was formed before or during the giant impact. A.J. McCoy - West (2018) using the isotope 3D spatial modeling, olivine found negative isotopic composition of the Fe ($\delta^{56}\text{Fe} = 0.8\text{‰}$), which is unbalanced diffusion process from the results of the kinetic isotopic fractionation, he believed that for elements like Fe through the mantle rising process, the ultimate isotopic compositions of magma completely fused column of the weighted average process will continue to happen. However, in some iron-rich tholeiite basalts, unbalanced isotope fractionation has occurred, which may be due to the dynamic nature of isotope exchange between the mantle and the percolation melt. This process is the result of heterogeneous isotopic composition of the lower mantle in the central belt of the North China Craton.

The concept that REDOX conditions may influence the fractionation of iron isotopes during melting provides a new way to understand the REDOX conditions of magma formation on early Earth and Mars. The establishment of Fe isotope fractionation can be used to estimate the oxygen from mantle melting, but it needs to carry out related experimental operation and theoretical work.

5. PROSPECT OF FE ISOTOPES

Fe is the only polyvalent major element that controls a range of geological processes on Earth and in space, from mineral to planetary scales, and reductive oxidation (REDOX) reactions in reservoirs. Fractionation of Fe is often accompanied by changes in the bonding environment, which means that changes in bonding strength in crystals, liquids, and gases lead to stable isotope fractionation, even at high temperatures. Thus, explaining these interactions between the past geosphere and biosphere, the outer space side can trace the movement and transport of iron in water systems in the past Martian environment (Nicolas Dauphas, 2006). Fe isotopes are powerful tools for studying the processes involved in mass transfer, REDOX reactions and bonding environment changes in planetary systems. At the same time, the variation of mantle Fe isotopic composition provides an independent means to monitor the long-term variation of mantle FO_2 and complements the information from other tracers.

The heavy iron isotopic composition of the crust relative to chondrites can be explained by vaporization during lunar formation and collision, metal-silicate equilibrium partitioning in core mantle margin conditions, partial melting and magmatic differentiation. However, the precise control of the variation of Fe isotopes in igneous rocks remains unknown. Studies have shown that stable isotopes of iron can help reveal planetary REDOX conditions and igneous rock processes (Dauphas, 2014). Other heterogeneous elements, such as Ti, V, Eu, Cr, Ce, or U, may exhibit similar isotopic variations in block rocks and individual minerals, which can be used to determine past and present REDOX conditions in the crust of Earth and other planets. In recent years, as for the cause of Fe isotope composition, migration, sorting, distribution, research development, and testing methods, the improvement of experimental equipment and complete, and gradually develop and use Fe isotopes, fluid out of the soluble and evolution process of magma, metallogenic material source and genesis, biological absorption and induction process, the fractionation mechanism, the mantle metasomatism, etc were studied.

As a member of the transition metal element, Fe is very active in organisms. Therefore, Fe isotope can be used to trace the interaction between the biosphere and the geosphere, as well as the pathways of its entry into organisms and biological activities under ancient and modern environmental conditions. Since Fe is strongly affected by human activities, it can even be used in agriculture. For example, the soil chronology of rice ($\delta^{56}\text{Fe} = -0.01\text{‰} \sim 0.18\text{‰}$) showed a strong negative correlation with the logarithm of total Fe concentration, indicating that lighter Fe isotopes were preferentially removed during the long-term evolution of paddy soil under major reductive conditions, leading to mass dependent Fe isotopic fractionation. Comparison of iron isotopic compositions in soils across the globe suggests that iron isotopes can be used as evidence for iron migration and can accurately identify factors and processes controlling iron migration and redistribution, especially in soils with changing water status and REDOX conditions.

The combination analysis of Fe and other isotopes can trace the formation of the ore deposit, which is helpful to the exploration of Fe isotope fractionation process. Such as Fe and S, O combination, etc. It can also be used to study the magma differentiation of high siliceous magma. Using $\delta^{56}\text{Fe}$ as a tracer for iron mobility, ophiolites have been found to represent remnants of Marine lithosphere that underwent subduction-related metamorphism (Severmann, 2004; Debret, 2016).

Therefore, Fe isotopes can be used as tracers for plate fluids. With the further development, the application of Fe isotopes will be a very important analytical means in the future research progress of geochemistry and even cosmic chemistry. At the same time, the importance of Marine hydrothermal iron input is very great, and the isotopic composition of Fe may be a valuable tracer to distinguish different sources of iron in the deep sea, and provide strong evidence support for submarine hydrothermal and global change.

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