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Comparison of iron isotope variations in modern and Ordovician siliceous Fe oxyhydroxide deposits

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Abstract

Formation pathways of ancient siliceous iron formations and related Fe isotopic fractionation are still not completely understood. Investigating these processes, however, is difficult as good modern analogues to ancient iron formations are scarce. Modern siliceous Fe oxyhydroxide deposits are found at marine hydrothermal vent sites, where they precipitate from diffuse, low temperature fluids along faults and fissures on the seafloor. These deposits exhibit textural and chemical features that are similar to some Phanerozoic iron formations, raising the question as to whether the latter could have precipitated from diffuse hydrothermal fluids rather than from hydrothermal plumes.

In this study, we present the first data on modern Fe oxyhydroxide deposits from the Jan Mayen hydrothermal vent fields, Norwegian-Greenland Sea. The samples we investigated exhibited very low δ^{56}Fe values between −2.09‰ and −0.66‰. Due to various degrees of partial oxidation, the Fe oxyhydroxides are with one exception either indistinguishable from low-temperature hydrothermal fluids from which they precipitated (−1.84‰ and −1.53‰ in δ^{56}Fe) or are enriched in the heavy Fe isotopes. In addition, we investigated Fe isotope variations in Ordovician jasper beds from the Løkken ophiolite complex, Norway, which have been interpreted to represent diagenetic products of siliceous ferrihydrite precursors that precipitated in a hydrothermal plume, in order to compare different formation pathways of Fe oxyhydroxide deposits. Iron isotopes in the jasper samples have higher δ^{56}Fe values (−0.38‰ to +0.89‰) relative to modern, high-temperature hydrothermal vent fluids (ca. −0.40‰ on average), supporting the fallout model. However, formation of the Ordovician jaspers by diffuse venting cannot be excluded, due to lithological differences of the subsurface of the two investigated vent systems.

Our study shows that reliable interpretation of Fe isotope variations in modern and ancient marine Fe oxyhydroxide deposits depends on comprehensive knowledge of the geological context. Furthermore, we demonstrate that very negative δ^{56}Fe values in such samples might not be the result of microbial dissimilatory iron reduction, but could be caused instead by inorganic reactions.

1. INTRODUCTION

Deciphering the environmental conditions that led to the formation of ancient iron formations has been the focus of numerous studies over the past decades (e.g., Beukes, 2004; Klein, 2005; Beukes and Gutzmer, 2008). The occurrence of massive banded iron formations (BIF), which requires large amounts of aqueous Fe(II), has been interpreted as evidence for a reduced state of the oceans during the time of their deposition (e.g., Cloud, 1973). In an Archaean anoxic ocean, oxidation of Fe(II) might have occurred inorganically by UV photo-oxidation (Braterman and Cairns-Smith, 1987) or might have been related to

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microbial activity, either indirectly by free oxygen produced by cyanobacteria or their predecessors in the photic zone (Cloud, 1968) or directly by anaerobic phototrophic Fe-oxidising bacteria (Widdel et al., 1993; Konhauser et al., 2002; Kappler et al., 2005).

It is assumed that the isotopic composition of the iron source of iron formations, i.e., hydrothermal $Fe(II)_{aq}$, did not vary significantly throughout Earth's history and was similar to modern hydrothermal vent systems with $\delta^{56}Fe$ values of about −0.5‰ to 0.0‰ (Johnson et al., 2003, 2008). Most ferric minerals in iron formations are enriched in the heavy Fe isotopes relative to hydrothermal $Fe(II)_{aq}$ by up to ca. 1‰ (Johnson et al., 2003; Rouxel et al., 2005; Planavsky et al., 2012). Fractionation of Fe isotopes is caused by oxidation of hydrothermal $Fe(II)_{aq}$ to $Fe(III)_{aq}$ (Welch et al., 2003) and subsequent precipitation of Fe oxyhydroxides (Bullen et al., 2001; Beard and Johnson, 2004; Beard et al., 2010; Wu et al., 2011). In contrast, in Archaean iron formations $\delta^{56}Fe$ values as low as −2‰ have been observed in ferrous and mixed-valence minerals, such as siderite and magnetite, which is attributed to dissimilatory iron reduction (DIR) (Johnson et al., 2005, 2008; Yamaguchi et al., 2005). This interpretation is strengthened by combined Fe and C isotope studies (Czaja et al., 2010; Heimann et al., 2010; Craddock and Dauphas, 2011). Overall, the measured Fe isotope variations in iron formations span a very large range of about 3‰ in $\delta^{56}Fe$. These variations, however, are not necessarily exclusively related to redox reactions. Other reactions that potentially fractionated Fe isotopes in iron formations include, for instance, adsorption of aqueous iron and isotopic exchange with minerals (Icopini et al., 2004; Crosby et al., 2005, 2007; Jang et al., 2008; Mikutta et al., 2009) or diagenetic and metamorphic overprint (Dauphas et al., 2004; Frost et al., 2007). Furthermore, changes in the Fe isotopic composition of the $Fe(II)_{aq}$ source have been discussed (Rouxel et al., 2005; Yamaguchi et al., 2005). Estimation of the impact of certain reactions on Fe isotopic fractionation during and after precipitation of ancient iron formations, however, is challenging, mainly because modern analogues are scarce.

Ancient iron formations are thought to have formed as fall-out deposits on the seafloor (e.g., Beukes and Gutzmer, 2008). However, some of the more recent iron formations exhibit geochemical and textural features that are similar to modern siliceous Fe oxyhydroxide deposits that precipitate from diffuse hydrothermal fluids (e.g., Little et al., 2004), such as filamentous structures of Fe-oxidising bacteria (Alt, 1988; Juniper and Fouquet, 1988; Iizasa et al., 1998; Boyd and Scott, 2001). Therefore, the question is raised whether these ancient iron formations could have also formed from diffuse hydrothermal fluids and whether the modern Fe oxyhydroxide deposits could therefore be seen as analogues to ancient iron formations.

In this study, we investigated the Fe isotopic composition of both modern hydrothermal Fe oxyhydroxides and Phanerozoic jasper beds. Siliceous Fe oxyhydroxide deposits related to hydrothermal activity are widely found in modern marine environments (e.g., Alt, 1988; Juniper and Fouquet, 1988; Iizasa et al., 1998; Boyd and Scott, 2001; Emerson and Moyer, 2002; Toner et al., 2009; Dekov et al., 2010). Fe oxyhydroxides precipitate from diffuse, low-temperature hydrothermal fluids that emanate from faults and fissures at the seafloor distal to high-temperature venting sites. We present the first data of Fe isotopes in modern hydrothermal siliceous Fe oxyhydroxide deposits, sampled at the Jan Mayen vent fields, which are located at the Arctic-Ocean Ridge System, Norwegian-Greenland Sea. Hydrothermal $Fe(II)_{aq}$ emanates with low-temperature fluids along faults at the seafloor on top of hyaloclastites and basaltic debris at around 600 m water depth. Microbial mats of Fe-oxidising bacteria mediate the precipitation of distinct layers of siliceous ferrihydrite. The investigated jasper beds are derived from the ~490 Ma old Løkken ophiolite complex, Norway. They consist of fine-grained haematite in a quartz matrix and have been interpreted as siliceous ferrihydrite fallout deposits from a hydrothermal plume at intervals of oxic or suboxic conditions during a time when widespread ocean anoxia was common (Grenne and Slack, 2003b, 2005). We will show that the modern Jan Mayen Fe oxyhydroxides exhibit distinct Fe isotopic compositions that are inherited from the diffuse hydrothermal fluids. This observation will be further used to address the question whether the Løkken jaspers could have formed from diffuse hydrothermal fluids and to demonstrate the importance of the Fe isotopic composition of the $Fe(II)_{aq}$ source for interpreting Fe isotope variations in ancient iron formations.

2. GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

2.1. Jan Mayen vent fields

The Jan Mayen vent fields consist of two distinct vent areas, Troll Wall and Soria Moria, which lie approximately 5 km apart. Both vent areas are located at the southernmost segment of the ultra-slow spreading Mohns Ridge at approximately 71°N and 6°W (Pedersen et al., 2010; Fig. 1a). The two vent areas are situated at rather shallow depths of about 550–700 m below sea level. The southern vent field, Soria Moria, lies at the top of a volcanic ridge formed by lava flows (Fig. 1b), that are overlain by hydrothermal sulphide. The Troll Wall vent field is located along the eastern flank of a rift valley (Fig. 1b). Here, high-temperature hydrothermal fluids are channelled along a normal fault, forming several vent sites with white smoker type chimneys, composed of anhydrite, barite, sphalerite and pyrite over a distance of ~1 km. Maximum temperatures of ~270 °C were measured for the emanating fluids at both vent sites. Northwest of Troll Wall at the bottom of the rift valley, diffuse venting with fluid temperatures of ~7 °C occurs along faults and fissures on top of hyaloclastites and basaltic debris that fill the rift valley. Yellow–brown deposits of siliceous Fe oxyhydroxides, varying in appearance from thin mats to several-metres-high mounds, follow these faults and fissures (Pedersen et al., 2010). The mounds are made of stratified, millimetre- to centimetre-thick layers of siliceous ferrihydrite, separated by fluid-filled voids (Fig. 2a). Scanning electron microscopy studies revealed