Triple oxygen isotope variations in magnetite from iron-oxide deposits, central Iran, record magmatic fluid interaction with evaporite and carbonate host rocks

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ABSTRACT
Oxygen isotope ratios in magnetite can be used to study the origin of iron-oxide ore deposits. In previous studies, only 18O/16O ratios of magnetite were determined. Here, we report triple O isotope data (16O/18O and 17O/18O ratios) of magnetite from the iron-oxide–apatite (IOA) deposits of the Yazd and Sirjan areas in central Iran. In contrast to previous interpretations of magnetite from similar deposits, the triple O isotope data show that only a few of the magnetite samples potentially record isotopic equilibrium with magma or with pristine magmatic water (H2O). Instead, the data can be explained if magnetite had exchanged O isotopes with fluids that had a mass-independently fractionated O isotope composition (i.e., MIF-O), and with fluids that had exchanged O isotopes with marine sedimentary carbonate rocks. The MIF-O signature of the fluids was likely obtained by isotope exchange with evaporite rocks of early Cambrian age that are associated with the IOA deposits in central Iran. In order to explain the triple O isotope composition of the magnetite samples in conjunction with available iron isotope data for magnetite from the deposits, we propose that magnetite formed from magmatic fluids that had interacted with evaporite and carbonate rocks at high temperatures and at variable water/rock ratios; e.g., magmatic fluids that had been released into the country rocks of a magma reservoir. Additionally, the magnetite could have formed from magmatic fluids that had exchanged O isotopes with SO2 and CO2 that, in turn, had been derived by the magmatic assimilation and/or metamorphic breakdown of evaporite and carbonate rocks.

INTRODUCTION
The formation of iron-oxide–apatite (IOA) deposits is much debated. Studies on the origin of IOA deposits have often focused on the δ18O values of magnetite, which were suggested to reflect isotopic equilibrium with magmas or with magmatic water; i.e., H2O in equilibrium with magma (e.g., Jamel et al., 2007; Nyström et al., 2008; Knipping et al., 2015; Bilek et al., 2016; Johnson et al., 2016). In some cases, the δ18O of the magnetite was interpreted to also reflect isotopic equilibrium with water of a nonmagmatic origin (e.g., Rhodes and Oresk, 1999). Based on δ18O data, magnetite from IOA deposits was therefore suggested to have predominantly formed by magmatic and magmatic-hydrothermal processes, whereas a minor portion of the magnetite would have formed by late-stage hydrothermal processes that involved fluids of a nonmagmatic origin (Jonsson et al., 2013; Troll et al., 2019).

Additional constraints on the origin of IOA deposits may be obtained from determining not only δ18O, but also δ17O of magnetite. Mass-dependent isotope fractionation processes can result in variable δ17O/δ18O between different rocks and minerals, due to variations in the triple O isotope exponent theta (θ; e.g., Pack and Herwartz, 2014; Sharp et al., 2018). Studying the triple O isotope composition (i.e., δ18O, δ17O of magnetite from IOA deposits therefore potentially provides better constraints on the phases with which magnetite isotopically exchanged when it formed. A second motivation for studying the triple O isotope composition of magnetite is the fact that evaporite rocks were conjectured to play a role in the formation of iron-oxide deposits (e.g., Barton and Johnson, 1996; Hitzman, 2000; Torab and Lehmann, 2007; Li et al., 2015; Ghazi et al., 2019). Oxygen in evaporite sulfate can in part be derived from atmospheric O2 and, consequently, carry a mass-independent deficit in 18O relative to 16O and 17O (e.g., Crockford et al., 2019). Determining the triple O isotope composition of magnetite from IOA deposits therefore potentially allows us to test whether evaporite rocks were involved in the formation processes of these deposits.

We determined the triple O isotope compositions of 23 magnetite samples from IOA deposits in the Yazd and Sirjan areas in central Iran (Fig. 1). The mineral assemblages of these deposits are characteristic of “Kiruna-type” ore deposits. They are hosted within and close to early Cambrian felsic igneous rocks (Ramezani and Tucker, 2003). For comparison, a sample from a Cenozoic granite-related magnetite skarn deposit in the Sangan area in northeastern Iran was also analyzed. We studied the triple O isotope compositions of magnetite from the IOA deposits of the Yazd and Sirjan areas, in particular, because the country rocks of the felsic intrusions and their IOA deposits consist of limestone and evaporite rocks of late Ediacaran to early Cambrian age (Faramarzi et al., 2015). Evaporites from the Ediacaran and early Cambrian carry large 17O deficits compared to evaporites that formed later in the Phanerozoic (Bao et al., 2008; Crockford et al., 2019). The deposits from these areas are therefore well suited to investigating the potential role of evaporite rocks in the formation of iron-oxide deposits.

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METHODS AND DEFINITIONS

Magnetite samples were taken from high-grade magnetite ore from run-of-the-mine material in open pits and drill cores. Individual, millimeter-sized magnetite crystals were handpicked for triple O isotope analysis. Oxygen was extracted from the samples as O$_2$ by laser fluorination, using BrF$_5$ as the fluorinating agent, at the University of Göttingen, Germany (Pack et al., 2016). The extracted O$_2$ was cleaned from contaminant gases using freeze-thaw techniques in combination with liquid nitrogen, a 5 Å mesh molecular sieve, and a gas chromatograph. The cleaned sample gas was released at 65 °C from a molecular sieve into the sample bellows of a dual-inlet system of a MAT253 gas-source mass spectrometer. The O isotope composition of the sample gas was then measured as m/z = 32, 33, and 34 relative to a reference gas that had been calibrated against the Vienna standard mean ocean water 2 (VSMOW2) standard. The samples were analyzed together with UWG2 garnet standard as an external reference material (Valley et al., 1995). In order to test the reproducibility of the laser fluorination method for iron oxides, we also performed replicate extractions of a hematite fluorination method for iron oxides, we also performed replicate extractions of a hematite fluorination method for iron oxides, we also performed replicate extractions of a hematite fluorination method for iron oxides, we also performed replicate extractions of a hematite fluorination method for iron oxides, we also performed replicate extractions of a hematite fluorination method for iron oxides.

RESULTS

The δ$^{18}$O values of magnetite samples from the Yazd and Sirjan areas are similar to orthomagmatic magnetite and orthomagmatic water. orthomagmatic magnetite and orthomagmatic water can have δ$^{18}$O values in the range of −4‰ to 1‰, whereas the δ$^{18}$O values of orthomagmatic water can range from −6‰ to 4‰. These values are typical for magnetite that is in equilibrium with magma or with magmatic water.

DISCUSSION

The δ$^{18}$O values of some of the magnetite samples from the Yazd and Sirjan areas are close to −40 ppm; i.e., the δ$^{18}$O values of these samples are similar to those of igneous rocks and minerals (Fig. 2). The δ$^{18}$O values of these samples are typical for magnetite that is in equilibrium with magma and with magmatic water; i.e., typical for “orthomagmatic magnetite” (δ$^{18}$O = 1‰–4‰; Taylor, 1968). These particular samples were therefore potentially in equilibrium with magma or with pristine magmatic water when they formed. The samples were not in equilibrium with fluids derived from seawater or from meteoric water either, because magnetite that is in equilibrium with such fluids has δ$^{18}$O ≥ 40 ppm (Fig. 2).

Three End-Member Mixing Model for Magnetite Triple O Isotope Variations

In triple O isotope space, the magnetite samples from central Iran define trends with higher δ$^{17}$O/δ$^{18}$O slopes than predicted for mass-dependent O isotope variations (Fig. 2). The variations in magnetite triple O isotope compositions may therefore reflect mixing of isotopically distinct magnetite end-member components in different proportions. At least three magnetite end-member components are apparent reflected in the triple O isotope compositions of the samples (Fig. 3). One magnetite end-member component (Mgt A) has δ$^{18}$O and δ$^{17}$O similar to orthomagmatic magnetite; i.e., δ$^{18}$O = 1‰–4‰ and δ$^{17}$O = −4‰. The second magnetite end-member component (Mgt B) has δ$^{18}$O similar to orthomagmatic magnetite, but it has a significantly lower δ$^{17}$O than orthomagmatic magnetite; i.e., δ$^{17}$O = −4‰. The third magnetite end-member component (Mgt C) has a higher δ$^{18}$O than orthomagmatic magnetite (δ$^{18}$O > 4‰), and it has δ$^{17}$O in between the two other end-member components.
Mgt B: Influence of MIF-O from Evaporitic Sulfate

The lowest $\Delta^{17}$O$_{528}$ values in the data set, at the corresponding $\delta^{18}$O of the samples, plot significantly below the array of mass-dependent O isotope variations (Fig. 2). It is therefore conceivable that the magnetite end-member component with $\Delta^{17}$O$_{528}$ ∼−200 ppm (Mgt B) contains oxygen with a relative deficit in $^{18}$O, i.e., oxygen with a mass-independently fractionated isotope composition (MIF-O). Terrestrial rocky materials that carry MIF-O have gained oxygen from atmospheric $^{16}$O. Rocky materials that are known to have incorporated atmospheric $^{18}$O are biotite (Gehler et al., 2011), cosmic spherules (Pack et al., 2017), some tektites (Magna et al., 2017), possibly ocean-floor manganese nodules (Sharp et al., 2019), carbonate-associated sulfate (CAS), and sulfate in marine barite and in evaporite rocks (Bao et al., 2008; Crockford et al., 2018, 2019). It is therefore probable that the magnetite end-member component that is recorded in the data set with $\Delta^{17}$O$_{528}$ ∼−200 ppm (Mgt B) formed from fluids that had exchanged O isotopes with the early Cambrian evaporite rocks that are associated with the IOA deposits in central Iran. The $\Delta^{17}$O$_{528}$ of these evaporite rocks was likely similar to that of the evaporite rocks from the Hormuz Formation in south Iran, which is stratigraphically equivalent to the evaporite horizons in the Yazd and Sirjan areas. Gypsum samples from the Hormuz Formation have an average $\Delta^{17}$O$_{528}$ of ∼−200 ppm (Crockford et al., 2019).

Mgt C: Influence of Oxygen from Marine Sedimentary Carbonates

The magnetite end-member component with $\delta^{18}$O > 4‰ that is recorded in the data set (Mgt C) exchanged O isotopes with a phase that had higher $\delta^{16}$O than most magmas and magmatic H$_2$O ($\delta^{18}$O = 5.5‰–10‰, excluding S-type granitoids; Bindeman, 2008; Eiler, 2001), and that had a higher $\Delta^{17}$O$_{528}$ than evaporite rocks. Such a triple O isotope composition is predicted for fluids that have interacted with marine sedimentary carbonate rocks ($\delta^{18}$O = ~−20‰–30‰; Hoefs, 2009). The third magnetite end-member component (Mgt C) therefore possibly records magnetite that formed from fluids that had exchanged O isotopes with the marine sedimentary carbonate rocks that are associated with the iron-oxide deposits in central Iran, and/or with CO$_2$ that was derived from those carbonate rocks. The possible relevance of fluid interaction with carbonate rocks in the formation of the IOA deposits is also demonstrated by the presence of abundant secondary carbonate minerals in most of the deposits in central Iran (Jami et al., 2007; Daliran et al., 2010; Heidarian et al., 2017; Deymar et al., 2018).

Geological Mechanisms of Isotope Exchange

In order to explain the triple O isotope compositions of the magnetite samples, we propose that magnetite from the IOA deposits in the Yazd and Sirjan areas formed from magmatic fluids that had exchanged O isotopes with evaporite and carbonate rocks at variable water/rock ratios (Fig. 3). The available iron isotope data for magnetite from the deposits in the Yazd and Sirjan areas ($\delta^{56}$Fe = 0.2‰–0.5‰) indicate a high-temperature magmatic (e.g., >800 °C) rather than a low-temperature hydrothermal origin for the magnetite (Troll et al., 2019; Alibaai et al., 2019, personal commun.). We therefore propose two geological mechanisms by which O isotopes could have been exchanged at high temperatures between magmatic fluids and evaporite and carbonate rocks. First, magmatic fluids could have reacted with evaporite and carbonate rocks, e.g., as would be the case for magmatic fluids that were injected into the country rocks of a magma reservoir. A second
possible scenario is that magmatic fluids exchanged O isotopes with SO\(_2\) and CO\(_2\) that, in turn, had been derived by the magmatic assimilation and/or metamorphic breakdown of evaporite and carbonate rocks, respectively (cf. Rye et al., 1984; Sharp et al., 2003; Troll et al., 2012; see the Data Repository). The latter suggestion is supported by, e.g., the occurrence of dolomite xenoliths in the volcanic sequences that host some of the deposits, which attest to the magmatic assimilation of carbonate rocks (Moore and Modabberi, 2003).

The conclusion that magnetite from the iron-oxide deposits in central Iran formed from magmatic fluids that had interacted with evaporite and carbonate rocks is in good agreement with the continuum that is found between, respectively, magmatic and crustal δ\(^{34}\)S in sulfide minerals from the deposits, and also with the continuum between magmatic and crustal δ\(^{18}\)O and δ\(^{17}\)O in carbonate minerals from the deposits (Jami et al., 2007; Heidarian et al., 2017). Whereas magnetite likely formed from fluids at magmatic temperatures, sulfide and carbonate minerals in the deposits, and also apatite, likely formed when temperatures of the magmatic fluids had dropped below about <600 °C (Heidarian et al., 2017). Whereas the triple O isotopes of magnetite from the deposits in the Yazd area apparently predominantly record the interaction between magmatic fluids and evaporite rocks, magnetite from the deposits in the Sirjan area, in contrast, apparently predominantly records the interaction between magmatic fluids and carbonate rocks (Fig. 3). This conclusion demonstrates that the triple O isotope composition of magnetite, in general, may help us to better understand the geological and lithological contexts within which iron-oxide deposits formed.

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