Global Fe-O isotope correlation reveals magmatic origin of Kiruna-type apatite-iron-oxide ores

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Two sentence summary
The origin of giant Kiruna-type iron ores has been debated for nearly 100 years. This study employs extensive stable isotope data from Kiruna-type ores worldwide and magmatic and hydrothermal reference materials to show that iconic Kiruna-type ores originate primarily from ortho-magmatic processes.

Summary paragraph
Kiruna-type apatite-iron-oxide ores are key iron sources for modern industry, yet their origin remains controversial. Diverse ore-forming processes have been discussed, comprising low-temperature hydrothermal processes versus a high-temperature origin from magma or magmatic fluids. We present an extensive set of new and combined iron and oxygen isotope data from magnetite of Kiruna-type ores from Sweden, Chile and Iran, and compare them with new global reference data from layered intrusions, active volcanic provinces, and established low-temperature
and hydrothermal iron ores. We show that approximately 80 % of the magnetite from the investigated Kiruna-type ores exhibit $\delta^{56}$Fe and $\delta^{18}$O ratios that overlap with the volcanic and plutonic reference materials (> 800 °C), whereas ~20 %, mainly vein-hosted and disseminated magnetite, match the low-temperature reference samples (≤ 400 °C). Thus, Kiruna-type ores are dominantly magmatic in origin, but may contain late-stage hydrothermal magnetite populations that can locally overprint primary high-temperature magmatic signatures.

**Keywords:** Kiruna-type apatite-iron-oxide ores, magmatic vs. hydrothermal origin, magnetite. iron isotopes, oxygen isotopes

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Apatite-iron oxide ore is by far the biggest source of iron in Europe and one of the main iron sources worldwide. In Europe, these magnetite-dominated ores have traditionally been sourced from two principal regions, the Bergslagen ore province in south central Sweden and the Kiruna-Malmberget region in northern Sweden (Fig.1). The apatite-iron oxide ores from these localities are internationally renowned and similar ores elsewhere are usually referred to as being of Kiruna-type. While the Grängesberg and Kiruna deposits are Palaeoproterozoic in age, similar apatite-iron oxide deposits along the American Cordilleras are much younger and range in age from Jurassic to Neogene, like the Pliocene El Laco deposit in Chile. Together with the occurrences of
Paleozoic apatite-iron oxide ores in Turkey, Iran, and China, and Triassic examples from Korea\textsuperscript{10–13}, apatite-iron oxide ores have repeatedly formed across the globe and throughout geological time.

The origin of the Kiruna-type apatite-iron-oxide ores remains ambiguous, however, despite a long history of study and a concurrently intense scientific debate. Several fundamentally different modes of formation have been proposed. Today two broad schools of thought prevail, represented by either direct magmatic formation processes, such as segregation or crystallization, or by hydrothermal replacement processes, including hydrothermal precipitation in the sense of iron-oxide-copper-gold (IOCG) deposits\textsuperscript{3,4,14–31}. Specifically, the discussion revolves around a direct magmatic origin (ortho-magmatic) from volatile- and Fe-P-rich magmas or high-temperature magmatic fluids\textsuperscript{1,5,18,31}, versus a purely hydrothermal one, where circulating, metal-rich fluids replace original host rock mineralogy with apatite-iron-oxide mineralization at medium to low temperature\textsuperscript{4,19,28–30,32}. An ortho-magmatic origin is generally understood to be either formation by direct crystallization from a magma or from high-temperature magmatic fluids (e.g. $\geq 800 ^\circ$C), or via high-temperature liquid immiscibility and physical separation of an iron oxide-dominated melt from a silicate-dominated magma, where the former may subsequently crystallize as a separate body\textsuperscript{17,18,33–38}. Hydrothermal processes, in turn, encompass transport and precipitation, including replacement-type reactions, by means of aqueous fluids at more moderate to low temperatures (typically $\leq 400 ^\circ$C)\textsuperscript{27,29,30,32}. Both the magmatic and the hydrothermal hypotheses are supported in part by field observations, textural relationships, and mineral chemistry, however, petrological field evidence and chemical trends of major and trace elements have frequently been interpreted in different ways\textsuperscript{5,14,16–22,28–32}. Moreover, many of previous investigations have focused on one case study only and frequently present a range of various data, with individual data sets often being relatively restricted in respect to data volume. What has so far been missing is a broad and decisive geochemical approach to distinguish between these two rival formation hypotheses on an across-deposit scale. To date no systematic stable isotope study employing several distinct Kiruna-type apatite iron oxide ore deposits is available and, importantly, no systematic comparison with
accepted magmatic and hydrothermal rock and ore suites has previously been presented in the
literature.

Results

Scientific rationale and sample selection

Here we use the isotopes of iron and oxygen, the two essential elements in magnetite (Fe₃O₄), on
magnetite samples from four major Kiruna-type ore provinces. Magnetite is the main iron-bearing
component in Kiruna-type deposits and our approach therefore utilizes highly reliable major
elements as petrogenetic tracers, as opposed to e.g., traditional minor element approaches that rely
on low-concentration constituents in these ores and their host rocks. We present an extensive set of
new Fe and O isotope data of magnetite from a suite of world-class Kiruna-type ores from three
continents, represented by Sweden, Chile, and Iran and complement these data by a large suite of
new comparative data on accepted magmatic and hydrothermal reference samples (54 new Fe-O
coupled isotope ratios and another 12 individual ratios, totaling 120 new individual isotope ratios).
In addition, the four different regions of Kiruna-type deposits investigated are separated in space
and time, as are the extensive suite of volcanic, plutonic and low-temperature reference materials
that we employ to define the endmember processes reflected in our ore deposit data (see Fig.1 and
Supplementary Table 1). We use these data to address whether Kiruna-type apatite-iron oxide ores
form primarily through direct magmatic processes (magma and magmatic fluids) at high
temperatures (≥ 800°C), or alternatively, through precipitation from hydrothermal fluids at
considerably lower temperatures (≤ 400°C). The comparative aspect of our work is a particular
strength and to the best of our knowledge, no other systematic study with such global coverage has
been performed to date. In addition, we offer the first substantial data sets for coupled Fe and O
isotopes for the world famous Kiruna, Grangesberg, and Bafq deposits, plus new comparative data
for El Laco that are consistent with published data for this deposit. The study’s global
extent, its systematic approach, its large data volume, and most crucially, the global Fe-O isotope
correlation permits a decisive conclusion, which allows us to advance our understanding of the
relationship between magmatic and hydrothermal processes in the genesis of Kiruna-type iron-
oxide ore deposits. The use of a broad set of Fe-O isotope data is especially useful as it establishes
not only genetic similarities between different deposits but also provides constrains on the
formation temperatures \(^{1,5,39}\) and allows us to identify a high- versus a low-temperature origin of
individual ore deposits.

To facilitate a widely applicable comparison of apatite-iron-oxide ores analyses of iron and
oxygen isotope ratios of magnetite from massive apatite-iron-oxide ores from the Kiruna Mining
District in northern Sweden (n=14), the Grängesberg Mining District and the nearby Blötberget ore
body in central Sweden (n=16), the El Laco district in Chile (n=6) and the Bafq Mining District in
central Iran (n=6) (Figs.1 & 2) were performed. These ore provinces and regions are briefly
introduced below, and full details are given in Supplementary Note 1.

The study of apatite-iron-oxide mineralizations began at the iconic deposits of the Kiruna
Mining District \(^3\). The present Kiruna mine at Kirunavaara, is the largest deposit of its type, and is
the main supplier of iron ore in Europe. This deposit alone represent a pre-mining reserve of ≥ 2
billion tons of high grade ore. The ores in Kiruna and similar Palaeoproterozoic deposits in the
district (Supplementary Table 1), are dominated by magnetite and contain between 50-70 % Fe
with a P content of, commonly, up to 2 wt. % that is mainly hosted by fluorapatite and subordinate
monazite-(Ce) \(^{25}\). Additional gangue minerals that can occur in small proportions are Mg-rich
actinolite, phlogopite, chlorite, titanite, talc, feldspar, quartz, carbonates, sulphides, sulphates and
clays \(^3,5,25\).

The apatite-iron-oxide ores of the Grängesberg and the nearby Blötberget deposits represent
the largest iron ore accumulation in the Bergslagen ore province, a classic mining region in central
Sweden considered to represent a Palaeoproterozoic continental rift or back arc basin \(^{40}\). A historic
production of 156 Mt of ore, averaging 60 % Fe and 0.81 % P, is documented from Grängesberg. In
addition to iron oxides (dominantly magnetite), the presence of phosphates such as fluorapatite, monazite-(Ce), and xenotime-(Y), together with REE-silicates constitute a potentially significant resource \(^1,41\).

The El Laco apatite-iron-oxide ore deposit at the Pico Laco volcanic complex in northern Chile consists of seven individual ore bodies which together comprise \(~500\) Mt of mainly magnetite-dominated ore with an average grade of \(60\%\) Fe \(^5,18,26,30\). The Plio- to Pleistocene El Laco deposit is part of the young apatite-iron-oxide mineralizations that characterize the eastern high Andes and is separate from the Cretaceous apatite-iron-oxide ores of the so-called Chilean Iron Belt \(^7,14,17,18\).

The Bafq Mining District in Central Iran comprises 34 documented iron ore mineralizations with a total reserve of \(~2\) billion tons of iron ore with grades between 53 and 65\% \(^11,42\). The apatite-iron oxide ores of the Bafq region are coeval with their early Cambrian andesitic and rhyolitic host rocks that formed in a volcanic arc setting \(^43\). Samples from the Bafq Mining District were collected from the Sechahun, Lakkeh Siah, Chadormalu and Esfordi deposits \(^42\).

Analyzed plutonic reference samples (Fig. 1) include magnetite from the layered igneous intrusion of Panzhihua in China (n=2), the Bushveld igneous complex in South Africa (n=1), and the layered intrusions of Taberg (n=1), Ulvön (n=1), and Ruoutevare (n=1) in Sweden and an iron-rich gabbro nodule from Iceland (n=1). Samples representative of magmatic magnetites of volcanic derivation were chosen from basalts and dolerite from the Canary Islands (n=3), recent basaltic andesites from Indonesia (n=6), dacites from New Zealand (n=2) and a hypabyssal dolerite from Cyprus (n=1) (Supplementary Table 1). Reference samples for low-temperature or hydrothermal iron ore deposits include magnetite from the polymetallic magnetite-skarn deposit at Dannemora (n=4), the banded iron formation at Striberg (n=1) and the marble-hosted iron oxide deposit at Björnberget (n=1), all situated in Bergslagen, Central Sweden (Supplementary Table 1, Supplementary Note 1).
Our interpretations are based on the combination of new iron (n=63) and oxygen (n=57) isotope ratios combined with literature data for magnetite from apatite-iron-oxide ores and available volcanic, plutonic and the low-temperature or hydrothermal reference materials.\(^1,5,14,31,32,44-48\)

Notably, the literature data for low-temperature or hydrothermal magnetite include a sample from the north-American Mineville apatite-iron-oxide deposit, which has been extensively overprinted by later hydrothermal processes.\(^14,49\)

**Iron and oxygen isotope results.**

Magnetite from massive apatite-iron-oxide ores from Kiruna have a relatively restricted $\delta^{56}$Fe range of +0.12 to +0.41 ‰ (n=11) (Supplementary Table 1, Fig. 3). The Grängesberg and Blötberget magnetite samples show $\delta^{56}$Fe-values mainly between +0.11 and +0.40 ‰ (n=16).

However, one sample from Grängesberg shows an exceptionally high value of +1.0 ‰. Apatite-iron-oxide ores from El Laco yield $\delta^{56}$Fe-values between +0.24 and +0.36 ‰ (n=6). Magnetite from Bafq have a range in the +0.20 to +0.32 ‰ interval (n=6).

Magnetite samples from the plutonic and volcanic reference suites show $\delta^{56}$Fe-values from +0.11 to +0.61 ‰ (n=5) and from +0.06 to +0.46 ‰ (n=13), respectively, consistent with iron isotope values for magmatic rock suites elsewhere (e.g. Fig. 3)\(^39,46\).

The low-temperature deposit group, i.e. the Dannemora iron oxide skarn samples and the Björnerberget and the Striberg samples, on the other side, show relatively low $\delta^{56}$Fe-values that range from -0.57 to +0.01 ‰. The magnetite compositions in the low-temperature group form a separate group (Fig. 3) that does not overlap with the reported range of igneous magnetites (+0.06 to +0.49 ‰)\(^39,46\), but with low-temperature hydrothermal samples from elsewhere (e.g., Mineville, USA and Xinqiao, China)\(^14,45,49\).
Magnetite separates from the Kiruna Mining District range in $\delta^{18}$O value from $-1.0 \%$ to $+4.1 \%$ (n=14), and those from Grängesberg and Blötberget are between $-1.1$ to $+2.8 \%$ (n=16). (Supplementary Table 1, Fig. 4). Magnetite from El Laco shows a large range in $\delta^{18}$O values from $-4.3$ to $+4.4 \%$ (n=6), whereas magnetite samples from Bafq give a smaller range of $+0.6$ to $+3.4 \%$ (n=6).

Magnetites from the plutonic reference samples (Panzhihua, Bushveld, Taberg, Ulvön, Ruoutevare, Iceland gabbro bomb; n=7), and from recent volcanic provinces (New Zealand, Indonesia and Tenerife, n=3) show exclusively positive $\delta^{18}$O-values between $+1.8$ and $+4.8 \%$ and $+3.7$ to $+3.9 \%$ respectively, which is within or near the commonly accepted range of igneous magnetites ($\delta^{18}$O = $+1.0$ to $+4.0 \%$) \(^{50}\). The low-temperature and hydrothermal reference ore samples (e.g. Dannemora, Björnberget, Striberg), have low $\delta^{18}$O values (-1.2 to -0.4 \%; n=5) with one exception; a skarn sample from Dannemora that has a $\delta^{18}$O-value of $+2.1 \%$ (Supplementary Table 1). This particular sample, however, comes from a part of the deposit (Konstång) which itself is reported to be geochemically anomalous with respect to the deposit as a whole (see Supplementary Note 1).

Comparing the oxygen and iron isotope data of magnetite samples from Kiruna, Grängesberg, El Laco and Bafq, we find that they overlap with the magnetite data from the plutonic and recent volcanic reference samples. Recognized low-temperature or hydrothermal deposits, such as Striberg, Björnberget, and Dannemora record magnetite isotope values that, in turn, differ distinctly in their Fe and O isotope signatures from magmatic values (Figs. 3 & 4). We note that the oxygen isotope data from two vein and disseminated (Ve-Di) magnetite samples from Grängesberg, three samples from Kiruna, as well as magnetite from two samples from El Laco overlap with the low-temperature and hydrothermal reference group. However, these samples still show Fe isotope signatures that are similar to our magmatic reference suite and are hence assumed to reflect originally igneous sources.
The compositional overlap between Kiruna-type magnetite and the plutonic and volcanic reference suite for Fe and O isotopes is consistent with an ortho-magmatic (magma or highest-temperature magmatic-fluids) origin for the Kiruna-type apatite-iron-oxide samples in this study. Low-temperature processes are reflected in a small number of the Kiruna-type ore samples (n=7) represented by vein- and disseminated-type magnetite samples. The exceptionally high Fe-value for one Grängesberg sample, in turn, is in agreement with the “ultra-magmatic” Fe isotope composition recorded in magnetite from the Bushveld complex (Fig. 3)\(^51\). In contrast, the lower \(δ^{56}\text{Fe}\)- and \(δ^{18}\text{O}\)-values in Figs. 3 and 4 then either reflect the lower end of the magmatic temperature range, or secondary effects, such as alteration, as well as leaching and subsequent re-precipitation at temperatures below 400 °C which postdates an initial high-temperature (magmatic) stage of formation (Fig. 5). Therefore, the oxygen and iron isotope data for the massive apatite-iron oxide magnetites indicate an originally high-temperature magmatic signature that, most clearly for oxygen isotopes, transitions to lower temperature values indicating a gradual cooling trend. One critical issue, especially for the Palaeoproterozoic Swedish deposits, which have gone through variable grades of metamorphism, is that post-depositional processes (e.g., fluid overprint, re-heating) might have affected the primary isotope composition of the ore and cannot be entirely excluded. Yet, since the same trends in isotope signatures are observed for both the older and younger, less geologically overprinted deposits, we argue that post-depositional changes in isotope composition was negligible in respect to the Fe-O isotope chemistry of our magnetite samples. This is particularly the case for the massive magnetite ores, where this overall chemically inert and refractory mineral would provide local buffering with regards to post-depositional re-equilibration\(^1\).

**Discussion**

Based on fluid and melt inclusion studies and isotope compositions of mineral pairs, high temperatures of ore formation have been proposed for various apatite-iron oxide ores. For instance,
temperature determinations for equilibrium magnetite–quartz pairs and magnetite–pyroxene pairs from Kiruna, El Laco and Grängesberg yield temperatures that consistently exceed 600 °C \cite{1,5}. Such crystallization temperatures are further supported by e.g. the occurrence of high-temperature actinolite in e.g. the Los Colorados and Kiruna deposits \cite{14,34,52} by Ti exsolution textures in magnetite from Kiruna \cite{52}, and by Zr in titanite studies at Kiruna that suggest 750-800°C \cite{53}. These temperature determinations provide independent support for a high-temperature (ortho-magmatic) origin of these ore assemblages. Using these temperatures as a reference point and employing appropriate equilibrium fractionation factors, we modeled the isotope compositions of respective equilibrium source to test the mineralization conditions of our sample suite (Supplementary Table 2 and Supplementary Fig. 2). We applied available fractionation factors between magnetite and andesite/dacite magma (T ~1000 °C) as well as between an equilibrium aqueous magmatic fluid phase at temperatures between 600 and 800 °C for both iron and oxygen isotopes (see Supplementary Tables 2, 3, 4, 5).

For oxygen isotopes, the calculations indicate that magnetite samples from apatite-iron oxide ores with $\delta^{18}$O $\geq$ 0, corresponding to over 80 % of our sample set, reflect equilibrium with either an intermediate magma ($\delta^{18}$O of +5.7 to +8.7 ‰) or a high-temperature magmatic fluid ($\delta^{18}$O of +5.2 to +9.6 ‰) (Supplementary Tables 2, 3, 4, 5, Supplementary Fig. 2). Although equilibrium with ortho-magmatic, high-temperature sources are found for most of our samples, it naturally remains difficult to distinguish between a magma or a very high-temperature, magmatically-derived aqueous fluid as the initial magnetite source. This realization is highlighted by the fact that our oxygen isotope values from Kiruna-type magnetite samples overlap with oxygen isotopes from the Granisle porphyry copper deposit presented in Bilenker et al. \cite{14}, which is proposed to have formed entirely from expelled ortho-magmatic fluids. For the same samples, iron isotope equilibrium source calculations yield values that correspond to magmas and modelled magmatic fluids with $\delta^{56}$Fe values from +0.08 to +0.38 ‰, and -0.13 to +0.17 ‰, respectively, which plot partly above the reported array of intermediate magmas and magmatic waters.
This suggests that the metal sources of the samples that exceed the range were likely enriched in the heavy iron isotope ($^{56}$Fe) already at the time of magnetite formation $^{39,46}$, which we refer to as ultra-magmatic. Such $^{56}$Fe enrichment may be caused by magmatic degassing, which is common in many volcanic systems $^{39}$, or more likely represents the result of iron oxide-enriched melts acting as an iron sink $^{55}$. Notably, this enrichment is also seen in some samples of our magmatic (plutonic and volcanic) reference suite (Supplementary Table 4, Supplementary Fig. 2), as well as in several Kiruna-type apatite-iron-oxide derived magnetite samples in other studies (Supplementary Table 5, Supplementary Fig. 2) $^{14,48}$. Magma degassing may preferentially remove the lighter Fe isotopes $^{39}$, increasing the $\delta^{56}$Fe in the melt. Alternatively, the iron-sink scenario is possibly caused by the tendency for magnetite to incorporate the heavy Fe isotopes over the lighter ones either during crystallization or during silicate-metal immiscibility.

This could lead to ultra-magmatic signals following prolonged crystallization of silicate phases from a basaltic magma. Specifically, the heavier iron isotope that partitions into the melt due to removal of early Fe-fractionating minerals, such as olivine and pyroxene, will deplete the melt in the isotopically lighter Fe$^{2+}$ and will leave Fe$^{3+}$ preferentially in the residual magma $^{46}$. When magnetite becomes the dominant iron-bearing phase later in the crystallization sequence it will consequently reflect the isotopically heavy melt signature $^{46}$. Finally, the high Fe$^{3+}$/Fe$_{tot}$ and the strong bonding in the tetrahedral site for Fe$^{3+}$ in magnetite make it a highly suitable host for the heavier iron isotope $^{46}$. The combined effects of magma degassing, prolonged fractional crystallization leading to more andesitic to dacitic melts, and the preference of magnetite for the heavy iron isotope are the likely reasons for the ultra-magmatic signature in several magnetite samples from the plutonic-volcanic reference suite as well as from some apatite-iron-oxide ore samples.

The key concepts proposed by the magmatic school of thought are formation of Kiruna-type ores by either liquid immiscibility or separation of magnetite cumulates (by sinking or flotation/frothing) from a silicate melt $^{5,17,18,31,38,48}$. To evaluate which magmatic process is dominantly responsible for
the formation of the massive magnetite bodies has proven difficult and while some petrological and experimental studies favour the concept of liquid immiscibility \( ^{18,38} \), other workers suggest cumulate-type processes \(^{14,31} \). Unfortunately, the currently available experiments that support liquid immiscibility are not truly representative of nature (e.g. 40 wt. % \( \text{P}_2\text{O}_5 \) in a starting melt) \(^{36,38} \). Such a composition contrasts with the host rocks to actual Kiruna-type deposits at Bafq, El Laco, Grängesberg and Kiruna. Using our new data to assess formation mechanisms, we can employ the isotope fractionation between immiscible Fe-rich melts and their silicate counterparts \(^{35,56} \). Assuming a hydrous system, the maximum fractionation for oxygen isotopes between an iron-rich melt and a silicate melt is 0.8 ‰ \(^{35} \). Testing if our massive magnetite samples are representative of an Fe-rich melt that formed from immiscibility should then produce associated equilibrium silicate melts with \( \delta^{18}\text{O} \) between -3.5 and +5.2 ‰. These values are out of the range of common intermediate igneous rocks \(^{57,58} \). Testing the same approach for the plutonic reference material (\( n=7 \)) produces two equilibrium melts (\( \delta^{18}\text{O} =+5.4 \) and +5.6 ‰) that both match a basaltic igneous composition (MORB = +5.7 ±0.4 ‰). The formation of Kiruna-type ores by liquid immiscibility is therefore not fully aligned with our data. Although this would, at first glance, favour cumulate processes over liquid immiscibility, there is probably uncertainty as to the natural fractionation of \( \delta^{16}\text{O} \) during liquid immiscibility and, to date, little information is available for Fe–isotopes in such situations. This leads us to encourage further tests in order to verify which of these two magmatic processes is more dominant in the formation of apatite-iron oxide systems. Future developments in the field of in-situ analysis of Fe-O isotope composition may hopefully help resolve small features such as thin, Ti-poor outer alteration rims as reported by e.g., Knipping et al. \(^{31} \) on magnetite samples from the Los Colorados apatite-iron-oxide deposit that these authors interpret to have bearing on the ore formation process. However, such textures cannot yet be analyzed for Fe and O isotopes in situ \(^{59} \), and in respect to our whole-grain results, such volumetrically small features would have a minimal effect on the bulk isotope signature of our samples.
In contrast to the massive ore samples, the vein and disseminated magnetites associated with apatite-iron oxide ores and low-\(^{18}\)O massive magnetite ores from Kiruna, Grängesberg and El Laco (i.e. \(\delta^{18}\)O\(_{\text{mgt}} < 0 \)‰, n=7) are not in equilibrium with recognized magmatic sources at the previously established temperatures. For these samples equilibrium with magmatic sources would only be obtained at temperatures below 400 °C (Supplementary Table 6). Notably, Fe-P-rich magmas can only be liquid down to \(~600\) °C \(^{34}\) implying that these magnetite samples cannot have formed directly from a magma. Moreover, the O isotope signatures in these magnetites overlap with those of our low-temperature and hydrothermal reference group and they can either be explained by a cooling magmatic fluid, or by a low-temperature hydrothermal system with external fluid influx. For El Laco, disequilibrium between high-temperature magmatic sources and a sub-set of low-\(^{18}\)O samples has previously been discussed and is attributed to late-stage or secondary processes \(^5\),\(^\)\(^\)\(^32\). The low-\(^{18}\)O magnetite samples from El Laco are also associated with considerable amounts of hematite that probably formed as a result of oxidation of magnetite by low-\(^{18}\)O, possibly meteoric-dominated, hydrothermal fluids at temperatures of \(\leq 150\) °C \(^5\),\(^\)\(^\)\(^32\). Meteoric fluids, particularly from higher altitudes such as the Andes, could cause such a negative shift in oxygen isotopes. However, these fluids would be Fe poor and may thus have only limited effect on iron isotope composition. For the isotope analysis great care was taken to avoid any direct hematite contamination of the samples, yet minor hematite formation along fractures in discrete magnetite grains is seen in some El Laco samples and may in part explain the larger spread in oxygen isotope data \(^5\),\(^\)\(^\)\(^14\),\(^\)\(^17\),\(^\)\(^18\),\(^\)\(^32\). Our iron isotope data, on the other hand, confirm a magmatic isotope signal throughout, i.e. even in the low-\(^{18}\)O samples. The low-\(^{18}\)O but magmatic \(\delta^{56}\)Fe magnetite compositions at El Laco are thus likely to represent overprint, remobilization and reprecipitation of an originally magmatic iron and oxygen signal by hydrothermal fluids that strongly affected oxygen isotopes in the magnetite, but had little effect on the iron isotopes \(^\)\(^14\),\(^\)\(^31\). The fluids affecting the ores may either have been derived from the cooling magmatic system or from an external fluid contribution during the evolution of the mineralization. Remarkably, hydrothermal overprint in the Kiruna Mining District in Sweden, for
instance, has now been suggested to post-date ore formation with up to 250 My \textsuperscript{52}. If this is correct, it implies that some non-magmatic (i.e. hydrothermal) isotope signals in apatite-iron-oxide ores may be entirely unrelated to the original mode of formation.

The Fe-O isotope data obtained on magnetite samples from apatite-iron oxide ores from Sweden, Chile and Iran are thus broadly consistent with the few available Fe-O isotope values from a) the literature (apatite-iron-oxide ores from USA and the Chilean Iron belt), and b) the volcanic and plutonic reference data in this study from various layered igneous intrusions (from China, South Africa and Sweden) and from recent volcanic provinces (Indonesia, Canary Islands, New Zealand, and Iceland). Moreover, the iron and oxygen isotopes of magnetite samples from apatite-iron oxide ores differ, for most samples, from magnetites produced by low temperature or hydrothermal processes (≤ 400°C). The iron and oxygen isotope data together with the calculated equilibrium sources are therefore in agreement with a predominantly (ortho-)magmatic origin (magma and high temperature magmatic fluids) for the investigated Kiruna-type deposits, rather than of a low-temperature hydrothermal one. While our data are very well suited to distinguish these broad formation conditions, they are not ideally suited to resolve the precise formation process and agent, i.e. we cannot distinguish magma versus high-temperature fluid or liquid immiscibility processes versus magnetite accumulation (Supplementary Fig. 2). Accepting an essentially magmatic nature of these deposits, a local hydrothermal overprint and replacement within a volcanic to sub-volcanic system would naturally be expected (Fig. 6), and will involve localized late-stage or secondary hydrothermal alteration and overprint \textsuperscript{1,18,32,41}. Hydrothermal alteration might locally be pronounced and may seem pervasive in places, as is known from many volcanic provinces \textsuperscript{60,61}. This by-product of otherwise ortho-magmatic formation processes must, however, not be confused with the main source signal of most Kiruna-type magnetite samples revealed in our study (Figs. 5 & 6).

Hydrothermally-formed magnetite is isotopically distinct and appears subordinate in our sample suite. The bulk of the Kiruna-type ore investigated thus formed in sub-volcanic...
environments under essentially high-temperature magmatic conditions, in line with the magmatic
school of thought \cite{3,5,14,17,18,31,62}. Precipitation of magnetite was either from iron-oxide-saturated
intermediate magmas or from immiscible Fe-rich melts that separated from broadly andesitic to
dacitic parent magmas and subsequent physical (either gravity or gas-driven) magnetite segregation
to form massive magnetite melts and mushes \cite{18,24,31,35,63}. Kiruna-type apatite-iron-oxide ores are
hence dominantly a magmatic phenomenon and they presumably continue to form in active arc- and
back-arc type sub-volcanic environments up to the present day. Our combined isotope data and
calculations represent a significant advance in the understanding of Kiruna-type ore deposits and
over-rules most arguments for a completely hydrothermal mode of formation. Moreover, we
provide a reference system for Fe-O isotopes in Kiruna-type ores against which future research can
test genetic concepts for low- versus high-temperature origin of as yet underexplored Kiruna-type
deposits.

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Author contributions

VRT, EJ and KH conceived the study. Field work was carried out by EJ, KH, KPN, SAM, UBA and VRT. Sample preparation was carried out by FW and SS. Isotope analyses were performed by CH, EK, FW and MAM. Modelling was performed by FW, VRT and CH and illustrations were prepared by FW and VRT. The manuscript was written by VRT and FW with contributions from all co-authors.

Additional information

Supplementary Information accompanies this paper.

Competing interests: The authors declare no competing interests.
Methods

Sampling. Samples from the Kiruna Mining District (n=11) come from the type locality for Kiruna-type apatite-iron-oxide ores at Kiirunavaara, Sweden, as well as from other apatite-iron-oxide deposits in the district, including magnetite dykes in the footwall of the smaller deposit at Luossavaara. as well as massive ore from the Mertainen and Rektorn deposits. Mineralised samples from the Grängesberg Mining District (GMD) were collected from three drillcores (DC), DC 690 (n=7), DC 717 (n=3) and DC 575 (n=3) that transect the deposit with a shallow plunge (< 20 °) and were drilled at 650 m (n=2) and 570 m below the surface respectively. In addition to massive apatite-iron-oxide samples, two Grängesberg samples were selected from magnetite veins and disseminations in the host rocks. One sample was collected from the smaller Blötberget apatite-iron-oxide deposit within the greater Grängesberg area and another from the nearby but contrasting marble-hosted hydrothermal/low-temperature iron oxide deposit at Björnberget (n=1). Samples from El Laco (n=6) were sampled at the surface and come from Laco Sur, the southern deposit in the area. To obtain a meaningful and widely applicable comparison of the apatite-iron-oxide ores with hydrothermal and magmatic reference samples, oxygen and iron isotope values were also determined on magnetite from massive ore from the iron oxide-polymetallic skarn deposit at Dannemora in Sweden (n=4), the banded iron formation at Striberg in Sweden (n=1), the layered igneous intrusion of Panzhihua in China (n=2), the Bushveld igneous complex in South Africa (n=1), the Swedish layered igneous intrusions of Taberg (n=1), Ulvön (n=1) and Ruoutevare (n=1), and from a gabbro bomb from Skjaldbreiður in Iceland (n=1). Samples representative of recent igneous magnetites were chosen from basaltic andesites from Indonesia (n=6), basalts and dolerite from the Canary Islands (n=3), dacites from New Zealand (n=2) and a dolerite from Troodos massif in Cyprus (n=1). An overview of the samples used in this study and details on their mineral assemblage and provenance is given in Supplementary Table 1. An outline of the geological setting of our sample suite is given in the Supplementary Information.
Iron isotope analysis. Analysis of the individual magnetite samples for Fe isotopes was dominantly carried out at the Victoria University in Wellington, New Zealand (n=47). The crystals were digested and chemically purified with concentrated HF and HNO$_3$ acid and the analysis was then done using a $^{57}$Fe–$^{58}$Fe double spike and a Nu Plasma MC-ICP-MS (Multicollector-Inductively Coupled Plasma Mass Spectrometer). As a standard the international IRMM-014 CRM material was used. Full details on the Fe isotope analysis are given in Millet et al. $^{64}$. All iron isotope data were recorded as $\delta^{56}$Fe, which is the deviation of $^{56}$Fe/$^{54}$Fe relative to the IRMM-014 CRM standard material. The average 2σ error during iron isotope analysis was 0.03 ‰.

A set of magnetite samples (n=11) was analysed for iron-isotopes by ALS Scandinavia Ltd. in Luleå, Sweden. The magnetite samples were prepared for analysis by microwave-assisted digestion in a HNO$_3$+HCl+HF mixture according to the method described in Ingri et al. $^{65}$. The isotope analysis was then carried out with a Thermo Scientific Neptune MC-ICP mass spectrometer. The $\delta^{56}$Fe-values were calculated with relation to the IRMM-014 CRM standard. The 2σ error was calculated from two independent consecutive measurements and was on average also about 0.03 ‰.

Six further magnetite samples were analyzed at the Vegacenter at the Swedish Museum of Natural History in Stockholm. The crystals were digested and chemically purified using concentrated HF and HNO$_3$ and 10M HCl acid following the procedures of Borrok et al. $^{66}$ and Millet et al. $^{64}$. The samples were diluted with 0.3 M HNO$_3$ to a concentration of 2-3 ppm before measurement. The Fe isotope analyses were performed on a Nu Plasma II HR-MC-ICP-MS in pseudo-high-resolution mode to resolve interfering species. The samples were corrected for mass bias using the standard-sample bracketing technique, normalizing to the IRMM-014 standard. The average 2σ external reproducibility for the samples was 0.06 ‰ for $\delta^{56}$Fe.

Oxygen isotope analysis. The analysis for oxygen isotopes was carried out at the University of Cape Town (South Africa) using a Finnigan DeltaXP dual inlet gas source mass spectrometer (n=59). For the oxygen analysis the magnetite samples were prepared by laser fluorination $^{67}$,
whereby they were reacted with 10 kPa of BrF₅, and the purified O₂ was collected onto a 5 Å molecular sieve in a glass storage bottle. As a reference and calibration standard Monastery garnet was used. All oxygen data were recorded in the usual δ¹⁸O notation relative to SMOW where δ¹⁸O = (R_{sample}/R_{standard} - 1) * 1000, and R = the measured ratio ¹⁸O/¹⁶O. All oxygen isotope data was obtained with a 2σ error of ≤0.2 ‰.

**Data availability:** The authors declare that all relevant data are available within the article and its supplementary information files.
References


timing of host-rock emplacement, hydrothermal alteration, and iron oxide-apatite
mineralization in the Kiruna District, Norrbotten, Sweden. *Econ. Geol.* **111**, 1595-1618
(2016). doi:10.2113/econgeo.111.7.1595

20. Westhues, A. *et al.* Tracing the fluid evolution of the Kiruna iron oxide apatite deposits using
zircon, monazite, and whole rock trace elements and isotopic studies. *Chem. Geol.* **466**, 303-

hydrothermal alteration and source regions for the Kiruna iron oxide-apatite ore (northern

of magnetite from magnetite-apatite mineralization and their host rocks: examples from

from Sri Lanka: Implications on Kiruna-type mineralization associated with ultramafic
6254


25. Parak, T. Kiruna iron ores are not intrusive-magmatic ores of the kiruna type *Economic

26. Nystrom, J. O. & Henriquez, F. Magmatic features of iron ores of the Kiruna type in Chile
doi:10.2113/gsecongeo.90.2.473

27. Sillitoe, R. H. & Burrows, D. R. New field evidence bearing on the origin of the El Laco


38. Hou, T. *et al.* Immiscible hydrous Fe-Ca-P melt and the origin of iron oxide-apatite ore


47. Dziony, W. *et al.* In-situ Fe isotope ratio determination in Fe-Ti oxides and sulfides from...


**Figure 1. Sample overview map.** a) Global map showing the different locations of origin for apatite-iron-oxide ore and reference samples. b) A close up view of the main part of the Fennoscandian Shield showing the sample locations for magnetites from Sweden.
Figure 2. Images of apatite-iron oxide ores in this study. False-colour BSE images of massive magnetite ore samples from a) and b) Kiruna, c) and d) Grängesberg e) and f) Bafq and d) and h) El Laco. Kiruna, Grängesberg and Bafq magnetite samples are homogeneous and commonly lack zonation or signs of alteration. El Laco (g and h), is exceptional in this respect as for some samples intra-crystal zonation is observed. As a supplement, regular greyscale BSE images for these samples are provided in Supplementary Fig. 1.
Figure 3. Iron isotope results from this study. Shown is the distribution of iron isotopes in magnetites from the Kiruna and Grängesberg districts, El Laco, and the Bafq district together with available literature data \[14,45,47,48\]. Reference fields for common hydrothermal and magmatic magnetites are shown for comparison \[39,45-47,51,69,70\]. Magnetites from apatite-iron oxide ores show a clear distinction from low-temperature or hydrothermal magnetites and overlap with the layered intrusions and volcanic reference magnetites (i.e. in the magmatic reference field). Data from Wang et al. \[45\] show the effects of a progressive transgression from ortho-magmatic processes to hydrothermal fluid evolution from originally higher to lower $\delta^{56}$Fe values and an originally magmatic fluid may thus evolve into a hydrothermal fluid. One hydrothermal sample from the highly altered, remobilized and recrystallized Mineville deposit in the USA ($\delta^{56}$Fe = -0.92‰, $\delta^{18}$O not available).
is not shown for simplification. Ve-Di samples represent vein and disseminated magnetites.

Figure 4. Oxygen isotope results from this study. Oxygen isotopes of magnetite samples from Kiruna, Grängesberg, El Laco, the Chilean Iron Belt, the Pea Ridge and Pilot Knob deposits, and the Bafq district, are compared to reference samples from layered igneous intrusions, recent volcanic magnetites, and low-temperature or hydrothermal ore deposits. The range of typical igneous magnetite is outlined in the reference box. The majority of magnetite samples from apatite-iron oxide ores plot within the reference field for common magmatic $\delta^{18}O$-values and overlap with magnetite values from recent volcanic rocks and layered intrusions. The low-temperature or hydrothermal reference suite, together with low-temperature magnetite literature...
data\textsuperscript{14,44}, plot dominantly to the left of the magmatic magnetite field, with only one exception, a magnetite from the Fe-skarn deposit at Dannemora. This particular outlier comes from a part of the deposit (Konstång) which itself represents a geochemical anomaly within the Dannemora deposit.

Our values for El Laco overlap with results from previous studies\textsuperscript{5,14,17,18,32}.

**Figure 5.** Distribution of Fe and O isotope values of magnetite samples used in this study. The various magnetite samples can be divided into three groups according to their Fe-O isotope composition; i) high-temperature magmatic magnetites, ii) hydrothermal magnetite samples and iii)
low-temperature magnetite samples. Most of the magnetite compositions of the apatite-iron-oxide ores in this study lie within, or near, the reference field for igneous magnetite, and overlap with the plutonic and volcanic magnetite samples analysed as reference suite. See also Supplementary Note 1 and Supplementary Fig. 2 for a detailed assessment of temperature-dependent equilibrium compositions. Reference field for common igneous and hydrothermal magnetites are based on literature data 14,39,44,47,50,51.

Figure 6. Schematic representation of magmatic stages for Kiruna-type apatite-iron-oxide ores from this and other studies, and from the analyzed reference materials. Stages II and III comprise ortho-magmatic ore formation: with decreasing temperature and on-going crystallization in the melt, the volatile/fluid pressure will increase and magmatic fluids are being expelled into the surrounding rocks. Below ~600 °C (towards the end of stage III), the magmatic-derived volatile pressure may begin to decrease, allowing progressively more of available external fluids into the system that initiate hydrothermal activity (< 400 °C). Massive apatite-iron oxide ores appear to commence crystallization in the ortho-magmatic stages (Stages II and III), whereas vein and disseminated magnetites formed mainly during Stage IV (hydrothermal precipitation and...
replacement). This implies that the commonly observed hydrothermal signals in apatite-iron oxide ores are late-stage products that are results of syn- to post-magmatic hydrothermal processes active during the cooling of the volcanic system, or in some cases possibly reprecipitation during later overprints.
Supplementary Information

Supplementary Note 1: Sampling sites

1. Sampling locations for apatite-iron-oxide ores

1.1 Kiruna district, northernmost Sweden: The Kiirunavaara, Luossavaara and Mertainen deposits in the Kiruna Mining District in Lappland, northern Sweden are hosted by trachyandesites and rhyodacitic ignimbrites and tuffs with an age of 1.89 to 1.87 Ga \(^3,19,71-74\). These volcanic rocks are underlain by older greenstones which are supposed to have formed in an extensional setting \(^75\). Deformation in the area is generally non-penetrative, dominated by local shearing and brittle tectonics and while regional metamorphism in greenschist facies have been invoked an even lower overprint have been suggested at Kiirunavaara and Luossavaara \(^76,77\). The apatite-iron oxide ores in the Kiruna district are dominated by magnetite, with iron contents of 50-70 % and up to c. 20 % apatite \(^25\). The deposits of the Kiruna district hold pre-mining reserves of more than 2 billion tons of ore \(^5\). The ore bodies have been interpreted to be just like the El Laco deposit of primarily magmatic origin on the basis of geochemical and textural observations including nodular ore textures and oxygen isotopes \(^5,24,26,78-81\).

1.2 Grängesberg/Blötberget, Bergslagen, Central Sweden: The apatite-iron-oxide deposit at Grängesberg and the smaller Blötberget deposit are dominated by magnetite with subordinate hematite and additionally both oxides occur as associated veins and disseminations in the immediate host rocks \(^1,82\). In the massive ores, bands of fine-grained fluorapatite with associated REE phosphates as well as variable amounts of silicates are characteristic \(^41\). The main deposit at Grängesberg, the so called “Export Field” consists of iron oxide ores in the ratio of approximately 80 % magnetite and 20 % hematite. Hematite-dominated parts occur mostly in the structural footwall and in the vicinity of crosscutting pegmatite dykes. Alteration zones in the host rocks right next to the mineralisation comprise disseminated and discrete phyllosilicate (biotite, chlorite) and
amphibole-rich assemblages (so-called *sköl*) with variable amounts of iron oxides and fluorapatite. The mineralisation is stratiform and dips between 50° and 70° towards the south-east and could be followed for more than 900 m at the surface where its width ranged between 50 and 100 m. The ore is hosted by metavolcanic rocks of andesitic to dacitic compositions belonging to the c. 1.91-1.87 Ga volcano-sedimentary succession of Bergslagen.

### 1.3 El Laco, Pico Laco, Northern Chile:

The apatite-iron oxide ores of El Laco are situated in Northern Chile at the flank of the Pliocene Pico Laco volcanic complex. The area around El Laco hosts seven different deposits distributed over 30 km² with a total amount of 500 Mt of high grade (~60% Fe) ore. The ore consists mainly of magnetite, however, hematite is also present as an oxidation product. Fission track dating of apatite crystals within the El Laco ore gave an age estimation of 2.1± 0.1 Ma. The host rocks of the deposit consist of typical subduction zone andesites and dacites which have been hydrothermally altered with alteration increasing at depth. Although hydrothermal activity was associated with the ore formation, the ore at El Laco is supposed to have formed by dominantly magmatic processes, involving an iron oxide-rich magma and magmatic fluids. Textural analysis indicates that the ore resembles intrusive and extrusive magmatic activity, such as lava flows, pyroclastics and dykes, where the lava flow deposits are notably dominated by hematite. A magmatic origin is also supported by features of iron oxide (magnetite) lava bombs, *aa* and *pahoehoe* lavas as well as vesicle-like cavities in addition to geochemical data from oxygen isotope analysis. However, a hydrothermal origin is put forward on the basis of oxygen isotopes arguing that the surprising isotopic homogeneity of magnetite samples at El Laco (~ +4.0 ‰) could not result from magmatic processes as a wider range of values would be expected due to magma cooling and hydrothermal processes associated with volcanic activity. Instead, these authors propose an origin by hydrothermal replacement with some high-δ¹⁸O hydrothermal fluid as transport agent, possibly also in some sort of evaporitic...
The samples for this study represent massive magnetite ore from the Laco Sur apatite-iron oxide ore deposit at El Laco.

1.4 Bafq, Central Iran:

The Bafq-Saghand metallogenic zone is located in the Kashmar-Kerman Tectonic Zone (KKTZ) in Central Iran and comprises about 34 recorded iron ore mineralizations with nearly ~1500 Mt ore with an average grade of 55% Fe\textsuperscript{90,91}. Among these deposits, larger apatite-iron-oxide ores that are currently mined include Chadormalu, Choghart, Se-Chahun, Lakke Saih and Esfordi. Some deposits, such as Esfordi and Gazestan, have high-grade apatite mineralizations and represent important phosphorus resources.

The deposits show a spectrum of mineralization styles such as massive orebodies, metasomatic replacements, stockworks and veins. The dominant minerals are magnetite, apatite and actinolite. Although the main Fe mineral is magnetite, all gradations towards hematite (through martitization) occur\textsuperscript{92}.

Most of the iron ore bodies occur as dome-shaped discordant to concordant structures, which consist mostly of lenses or irregular masses of massive magnetite surrounded by ore breccia and disseminated magnetite in the host rocks. In some places irregular bodies of massive magnetite are enclosed by a stockwork of magnetite, actinolite and apatite veins. An important feature of these deposits is that they frequently display gradational contacts with their host rocks. Sharp contacts are generally restricted to structurally controlled zones\textsuperscript{92}. The apatite-iron-oxide mineralizations in the Bafq-Saghand zone are hosted by dolomitic and rhyolitic rocks of Cambrian Volcano-Sedimentary Units (CVSU).

The geological setting of the KKTZ is linked to a major episode of late Neoproterozoic to Early Cambrian orogenic activity in an active continental-margin environment\textsuperscript{43}.

The Origin of low-Ti apatite-iron oxide deposits of the Bafq-Saghand area has long been a matter of debate. In this case, several models have been proposed for these deposits which include i)
carbonatitic magmatism \(^{93-95}\), ii) liquid immiscibility \(^96\), iii) magmatic \(^{11,97}\), iv) alkaline magmatism \(^{42}\), v) magmas of the Kiruna-type \(^98\), vi) hydrothermal Kiruna-type \(^{92,99-101}\), vii) banded iron formations \(^{102,103}\) and viii) magmatic-hydrothermal \(^{91}\).

2. Sampling locations for Layered Igneous Intrusion reference materials

2.1 Bushveld, South Africa: The magnetite sample in this study comes from the Rustenburg Layered Suite (RLS) of the Bushveld complex, which is an 8 km thick succession of layered mafic and ultramafic rocks with an age of about 2.1 Ga \(^{104,105}\). The RLS is divided up into the Lower, Critical, Main and Upper zones, with the Critical Zone being the economically most important one since it holds the world’s largest chromite and platinum-group element deposits \(^{106}\). However, magnetite is mined within the Upper Zone, which contains about 20 m in total thickness of pure magnetite in the form of several magnetite layers within 2 km thick magnetite-bearing gabbroic rocks \(^{107}\). The magnetite layers vary in thickness between 0.1 and 10 m and contain some silicates, mostly plagioclase feldspar \(^{105}\). The most prominent layer is called the Main Magnetite Layer from which the magnetite used in this study originates. The magnetite layers in the Upper zone are of magmatic origin and are assumed to have been formed by cycles of magma mixing of different FeO-rich magmas and subsequent cumulate emplacement \(^{108}\).

2.2 Panzhihua, Sichuan Province, China: The layered igneous intrusion of Panzhihua is located in the Panxi Mining District, Sichuan Province, in South West China and is part of the Emeishan Large Igneous Province. It is a relatively unmetamorphosed and undeformed, 2 km thick, sill-like gabbroic intrusion which dips about 50°-60° towards the NW and extends about 19 km from NE to SW \(^{109}\). The intrusion is concordantly emplaced within late Neoproterozoic dolomite limestones, permian syenites and Triassic shales and coal measures and is itself 263 Ma old \(^{109}\). The intrusion is divided into four zones based on differences in internal structure and iron oxide mineralizations.
These four zones are the marginal, lower, middle and upper zone. Iron ore occurs in the lower and middle zones. The mineralizations consist of both, massive lens-shaped or tabular ore bodies up to 60 m in thickness as well as disseminated ore. The massive ore bodies consist of >80% Ti-magnetite with variable amounts of clinopyroxene, plagioclase, and olivine. The average ore grade comprises 43 wt % FeO, 11.68 wt % TiO₂, and 0.30 wt % V₂O₅. On the basis of texture (e.g. vesicles), geochemistry and the absence of evidence for a skarn origin, the mineralization is interpreted to have formed from an oxide enriched melt. The Panzhihua deposit is currently mined and holds a reserve of 1333 Mt of ore. The two Panzhihua samples of this study represent massive Ti-magnetite ore.

### 2.3 Ruoutevare, Norrbotten, Sweden:
The geology of the Ruoutevare area in Norrbotten northern Sweden comprises ultrabasic rock types such as peridotite and pyroxenite, which are associated with anorthosite and gabbro of Precambrian age. Associated with the gabbro intrusion is a deposit of iron ore in the form of Ti-bearing magnetite layers with a grade of 54.2 wt. % FeO and 11 wt. % TiO₂.

### 2.4 Taberg mine, Småland, Sweden:
The Fe-Ti mineralization at Taberg is located in southern Sweden, about 12 km to the south of Lake Vättern, within the Protogine Zone, a 1.2 Ga old. 20 km wide and several 100 km long belt of ductile and brittle deformation. The ore deposit consists of 1.2 Ga old troctolites (e.g. olivine gabbro) with high contents of Ti-rich magnetite ("titanomagnetite") and which have been affected by the late Sveconorwegian amphibolite facies metamorphism. The ore body has a dimension of c. 1 x 0.4 km and is hosted by an amphibolitised gabbro-dolerite, which has intruded the surrounding Småland granites. The ore holds between 26 and 35 % "titanomagnetite” with a content of 28.7–32.3 % FeO (Sandecki 2000). Within the ore are plagioclase-rich layers which give the appearance of a layered igneous intrusion. The ore is supposed to have been formed as a magmatic cumulate which resulted...
from gravitational settling within a gabbroic magma\textsuperscript{114,116}. The sample in this study is a massive Ti-
magneite ore from the mine at Taberg.

2.5 Ulvön, Ångermanland, Central Sweden: The mineral ulvöspinel derive its name after the
Ulvö island, where the layered igneous Ulvö Gabbro/dolerite Complex is found\textsuperscript{118} at the east coast
of central Sweden. The intrusion consists of several gently dipping lopoliths, 3080 km in diameter
and 250-300 m in thickness\textsuperscript{119,120}. These gabbroic lopoliths contain alternate bands of mafic and
more felsic layers with thicknesses between 0.5 cm and 1 m, likely a result of magmatic cumulus
processes\textsuperscript{121}. These rocks are ~1.25 Ga old and have not been affected by regional metamorphic
overprint or deformation\textsuperscript{120,121}. Ti-magnetite occurs in distinct layers, like for example in the
rhythmically layered zone of Norra Ulvön, which contains up to 10 cm thick bands with >50 % Fe-
Ti oxides\textsuperscript{121,122}. Such layers have also been mined for their metals\textsuperscript{121}. Other common minerals in
the Ulvö Gabbro Complex are plagioclase (labradorite), olivine, and clinopyroxene\textsuperscript{119,121}. The
sample used in this study is a massive Ti-magnetite ore from Norra Ulvön.

3. Sampling locations for volcanic reference materials

3.1 Canary Islands: Tenerife located in the centre of the Canary archipelago is the largest (2058
km\textsuperscript{2}) and highest (3718 m) of the island group which is situated over the Canary hot spot\textsuperscript{123,124}. Volcanic activity on the island dates back to about 6.5 Ma and is today seen in several small
volcanoes and the Teide-Pico Viejo edifice\textsuperscript{124}. Samples for this study originate from dykes in the
NE rift zone on the island. The samples comprise ankaramites and basanites\textsuperscript{125,126}.

3.2 Cyprus: The island of Cyprus is located in a zone of underthrusting in the eastern part of the
Mediterranean Sea, where the African plate is being pushed into the Eurasian plate. It can be
divided into five more or less parallel belts, which trend approximately eastwards and are convex
towards the south\textsuperscript{127}. Four of these belts are dominated by sedimentary rocks, most commonly
limestones and loose sediments ranging in age from the Triassic to recent\textsuperscript{127,128}. The fifth belt, the Troodos igneous massif, is dominated by mafic and ultramafic igneous rocks and represents an ophiolite sequence obducted during the alpine orogeny\textsuperscript{127,129}. The Troodos massif is about 11 km thick and divided up into basic and ultrabasic rocks in the center, the sheeted intrusive complex and the peripheral pillow lavas\textsuperscript{127}. The rocks have been affected by metamorphism represented by diabase and serpentinite\textsuperscript{127}. The sample used in this study comes from a dolerite dyke near Agros in the central part of the Troodos complex\textsuperscript{130}.

3.3 Iceland: The volcanic island of Iceland is located directly over the point in the North Atlantic, where asthenospheric flow interacts with a deep seated mantle plume\textsuperscript{131}, whose current plume channel lies beneath the Vatnajökull glacier and represents the plate boundary of the Mid-Atlantic ridge\textsuperscript{132}. Extensive volcanism is common on the island with more than 18 active volcanoes, which are often associated with rift zones and their volcanic fissure swarms\textsuperscript{131}. Volcanic eruptions, often of explosive nature due to lava-snow interaction, occur every three to four years\textsuperscript{133}. The main eruption products are tholeiitic basalts as well as basaltic andesites\textsuperscript{134}. The magnetite sample used in this study comes from a basaltic lava bomb erupted from the Skjaldbreiður volcano in SW Iceland.

3.4 Indonesia: The investigated magnetite samples come from the Anak Krakatau\textsuperscript{135,136}, Agung\textsuperscript{137}, Gede\textsuperscript{138}, Kelut\textsuperscript{139} and Merapi\textsuperscript{140} volcanoes on the Indonesian Islands of Java and Bali. These are part of the Western Sunda-Banda arc, which developed during the Cenozoic through subduction of the Indian-Australian plate under the Eurasian plate\textsuperscript{141,142}. Calc-alkaline volcanism with dacites and andesites are the typical eruption products in most recent times\textsuperscript{142,143}. Beside volcanic rocks, the area also hosts several gold, tin and copper deposits associated with subduction zone volcanism\textsuperscript{142}. 

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3.5 New Zealand: Mount Ruapehu is a 2797 m high stratovolcano at the southern end of the Taupo Volcanic Zone (TVZ) on the North Island of New Zealand\(^\text{144}\). It is the largest and currently active volcano on the Northern Island with the most recent eruption in 2007 and several other eruptive events during the last hundred years\(^\text{145,146}\). Volcanic activity in the TVZ is associated with the subduction of the Pacific Plate beneath the Australian Plate along the Hikurangi-Kermadec Trench system\(^\text{147,148}\). Mt. Ruapehu is underlain by Mesozoic meta-greywacke, which in turn is underlain by oceanic, metamorphosed igneous crust\(^\text{146,149}\). The typical eruption products are subduction zone andesites and dacites with porphyritic textures\(^\text{150,151}\). The magnetite content of the volcanic rocks at Mt. Ruapehu varies between less than 1 % and up to 6 % and is just over 1% on average\(^\text{146}\). Samples used in this study are two dacite rocks that come from the southern Flank of Mt. Ruapehu.

4. Sampling sites for low-temperature hydrothermal ore deposit reference materials

4.1 Björnberget mines, Grängesberg Mining District, Bergslagen, Central Sweden: The Björnberget mines are located c. 3 km east-southeast of the Grängesberg Export field in the northwestern part of the Bergslagen ore province, south central Sweden. The magnetite-dominated iron ores occur as in part carbonate-banded, skarn-associated types, which may locally progress into true skarn iron ores\(^\text{152,153}\). The major iron ore zones are northeast-striking, and variably, but steeply (to 80°) dipping towards the southeast\(^\text{152}\). The ore-bearing carbonates and skarns of the Björnberget mines are in turn hosted by c. 1.91-1.88 Ga old felsic metavolcanic rocks (rhyolitic to rhyodacitic in composition), which are variably altered, but of which more well-preserved types exhibit what can be interpreted as primary laminations\(^\text{86,153}\). Later regional metamorphism to amphibolite facies grade, as well as three stages of ductile deformation has affected the older rocks in the area, including the Björnberget ore and its host rocks\(^\text{85,86}\).

4.2 Dannemora mine, Bergslagen, southcentral Sweden: The Dannemora skarn iron ore deposit is situated in the eastern part of the Bergslagen ore province. It consists of 25 iron ore bodies, which
are typically enriched in manganese, and some smaller sulphide deposits, which are all hosted by c. 1.9 Ga old meta-volcanic and meta-sedimentary rocks. These include meta-dacites and meta-rhyolites as well as calcitic and dolomitic meta-limestones (marbles). The latter can locally exhibit preserved stromatolitic textures. The metavolcanic rocks have been interpreted as pyroclastic flow and air-fall deposits which together with the limestones were deposited in open marine, lagoonal and terrestrial (subaerial) environments. The dolomitic marbles at Dannemora are very dark-coloured due to a content of 5-30 % of fine magnetite. The area has been affected by greenschist facies metamorphism during the Svecokarelian orogeny and deformed at least twice, leading to isoclinal folding. The iron ore at Dannemora consists to a great extent of massive strata-bound magnetite ore dipping 65-70° to the west, within an east-south-east syncline, and has an iron content of between 30 and 50 %. The formation of the ore is believed to relate to circulating metal-bearing hydrothermal fluids. These fluids altered silica-rich units in the area and formed the major, mineralised skarn units through extensive reactions with the pre-existing limestones. In some cases fluid rock interaction and evaporation may have altered the fluid composition and led to enrichment of heavier elements and isotopes. The Dannemora samples used in this study are all calcite-bearing magnetite ores and come from various locations in the Dannemora mine (see Supplementary Table 1).

4.3 Striberg mine, Bergslagen, Central Sweden: Banded Iron Formations (BIF), such as the deposit at Striberg, are found in the Bergslagen ore province, and are hosted by the 1.91-1.88 Ga old metavolcanic rocks. In the Striberg area, extensive banded iron formations occur associated with skarn iron ores, in a complexly folded and deformed succession. The succession shows a main structural trend in a northwest-southeasterly direction, and with moderately steep (c. 45-60°) dips to the northeast. The main Striberg deposit consists mainly of alternating quartz and hematite-rich layers, normally of 1-10 mm thickness, and the silica content varies between 18 % and 28 %. Typical for BIF deposits, there is a dominance of hematite as the main Fe-bearing
mineral, however, magnetite is also present as an alteration product of the latter, and in some BIF ore types at Striberg the hematite has been completely converted to magnetite\textsuperscript{158}. The iron content of the deposits lies between 30% and 55%\textsuperscript{86,157}. 
Supplementary Tables and Figures

Supplementary Fig. 1
Greyscale BSE images of samples presented in Fig. 2, taken with a Field Emission-EPMA JXA-8530F JEOL hyperprobe. Except for some samples from El Laco, all chosen magnetite ores appear homogeneous with no discernable zonation or rims of alteration. Sample numbers: a) and b) K-MT-1079-303 c and d) KES090020 e) 13-C-219 f) 13-C-219 g and h) LS-11-4.

Supplementary Fig. 2

Equilibrium source calculations for Fe and O isotopes. a) Calculated isotopic compositions of magma in equilibrium with magnetite samples from volcanic and plutonic reference materials at...
magmatic T (> 800 °C). Calculated isotopic compositions of magma or fluid in equilibrium with magnetite samples from the Kiruna (b), Grängesberg (c), El Laco and Bafq Mining Districts (d) and Chilean Iron Belt, Pea Ridge and Pilot Knob apatite-iron oxide ore 14,48 compared to the reference fields for common magmatic and hydrothermal sources 5,39,54,57,58,69,70,162,164–168. Some of the calculated ore forming magmas and fluids that are in equilibrium with apatite-iron oxide ore magnetites are enriched in 56Fe relative to common magmatic sources and plot above the currently accepted reference fields for intermediate magmas and high-temperature magmatic fluids. This may be the result of fractionation of the heavy isotope into the melt during early silicate crystallization in some mafic melts and consequently subsequent magnetite crystals may be enriched in the heavy iron isotope 46 (see text for details). Vein, disseminated and overprinted ore samples (Ve-Di) show equilibrium with common magmatic sources only at low-temperatures (<400 °C) representing a secondary component under more hydrothermal conditions (f). For simplification only values with δ56Fe ≤ +0.6 are plotted.
Table 1. Oxygen and iron isotope analysis for magnetite from apatite-iron oxides and reference materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Description</th>
<th>Sample Provenance</th>
<th>δ^{18}O in ‰</th>
<th>2σ</th>
<th>δ^{67}Fe in ‰</th>
<th>2σ</th>
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<td><strong>Apatite-iron oxide ore</strong></td>
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<td><em>Kiruna Mining District (KMD), Northern Sweden</em></td>
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<td>Kiruna-17NY28</td>
<td>Banded massive (Ap-)magnetite ore</td>
<td>Kiirunavaara mine, Kiruna</td>
<td>4.1 ±0.2</td>
<td>0.19 ±0.03</td>
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<td>K-Mt-1 (907/75)</td>
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<td>-1.0 ±0.2</td>
<td>0.20 ±0.03</td>
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<td>Ki-Mi-2a (1079/251)</td>
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<td>0.21 ±0.02</td>
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<td>Ki-Mi-2b (1079/251)</td>
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<td>Kiirunavaara mine, Kiruna</td>
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<td>0.22 ±0.04</td>
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<td>Kiirunavaara mine, Kiruna</td>
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<td>0.27 ±0.04</td>
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<td>0.16 ±0.02</td>
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<td>M1937*</td>
<td>Skeletal magnetite ore</td>
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<td>0.23 ±0.02</td>
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<td>DC690-KES090011</td>
<td>Massive (Ap-)magnetite ore</td>
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<td>0.31 ±0.03</td>
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<td>DC690-KES090012</td>
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<td>DC690-KES090020</td>
<td>Massive Ap-veined magnetite ore</td>
<td>Grängesberg mine, Grängesberg</td>
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<td>DC690-KES090027</td>
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<td>Silicate-spotted massive (Ap-)magnetite ore</td>
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<td><strong>El Laco Ap-Fe-oxide deposit, Chile</strong></td>
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<td>EJ-LS-11-1</td>
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<td>Laco Sur, El Laco</td>
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<td>0.28 ±0.03</td>
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<td>EJ-LS-11-2</td>
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<td>Laco Sur, El Laco</td>
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<td>LS-2</td>
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<td>13.C.88</td>
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<td>Reference</td>
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<td>Fe</td>
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<td>Ruoutevare</td>
<td>Ti-magnetite, layered igneous intrusion</td>
<td>Kvikjokk, Norrbotten, Sweden</td>
<td>3.2</td>
<td>±0.2</td>
<td>0.31</td>
<td>±0.03</td>
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<td>Ulvön</td>
<td>Ti-magnetite, layered igneous intrusion</td>
<td>Ulvön island, Ångermanland, Sweden</td>
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<td>±0.2</td>
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<td>±0.03</td>
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<td>Taberg</td>
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<td>Iron mine, Taberg, Småland, Sweden</td>
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<td>EM419</td>
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<td>Northern pit, Panzhuhua, China</td>
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<td>EM424</td>
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<td>Bushveld</td>
<td>Massive magnetite ore</td>
<td>Upper Zone, Bushveld Complex, South Africa</td>
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<td>Gabbrobomb</td>
<td>Magnetite from a gabbro xenolith</td>
<td>NW-Flank, Skjaldbreiður, Iceland</td>
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<td>TEF-NER-18</td>
<td>Magnetite from an ankaramite dyke</td>
<td>NE Rift Zone, Tenerife, Spain</td>
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<td>TEF-NER-57B</td>
<td>Magnetite from an ankaramite dyke</td>
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<td>TEF-NER-70</td>
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<td>MG-07</td>
<td>Igneous magnetite from dacite</td>
<td>S-Flank, Mt. Ruapehu, New Zealand</td>
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<td>MG-09</td>
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<td>S-Flank, Mt. Ruapehu, New Zealand</td>
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<td>Kelut A1</td>
<td>Igneous magnetite from basaltic andesite</td>
<td>Mt. Kelut, Java, Indonesia</td>
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<td>Igneous magnetite from basaltic andesite</td>
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<td>AK-B1</td>
<td>Igneous magnetite from basaltic andesite</td>
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<td>AK-B3</td>
<td>Igneous magnetite from basaltic andesite</td>
<td>SE-Flank, Anak Krakatau, Indonesia</td>
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<td>A-BA-1</td>
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<td>Calcite bearing-magnetite ore</td>
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<td>±0.2</td>
<td>0.01</td>
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<td>DM-3</td>
<td>Iron-skarn magnetite ore</td>
<td>Konstäng, Dännemora, Sweden</td>
<td>2.1</td>
<td>±0.2</td>
<td>-0.43</td>
<td>±0.03</td>
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<td>Iron-skarn magnetite ore</td>
<td>Strömsmalm, Dännemora, Sweden</td>
<td>-0.6</td>
<td>±0.2</td>
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<td>±0.03</td>
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<tr>
<td>EJ092008</td>
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<td>-1.2</td>
<td>±0.2</td>
<td>-0.57</td>
<td>±0.03</td>
</tr>
</tbody>
</table>

* Data from Lundh (2014) (ref.135)

1. Samples donated by Dr. Jan-Olov Nyström, Naturhistoriska Riksmuseet, Stockholm, Sweden
2. Samples from the sample collection of the Geological Survey of Sweden, Uppsala, Sweden
3. Sample from the sample collection, Department of Earth Science, Uppsala University, Sweden
4. Samples collected and donated by Prof. Nicholas Arndt, Université Joseph Fourier, Grenoble, France
5. Samples donated by Prof. John Gamble, Department of Geology, Victoria University of Wellington, New Zealand
6. Samples donated by Prof. Christopher J. Stillman, Department of Geology, Trinity College Dublin, Ireland
7. Samples donated by Gunnar Rausene at Dännemora Mineral AB, Österbybruk, Sweden
### Supplementary Table 2. Results for the magma (900°C)/magmatic water (800°C) equilibrium re-calculation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>δ(^{18})O</th>
<th>δ(^{86})Fe</th>
<th>δ(^{18})O value fit</th>
<th>δ(^{18})O dacite</th>
<th>δ(^{18})O water</th>
<th>δ(^{18})O water fit</th>
<th>δ(^{56})Fe water</th>
<th>δ(^{56})Fe magma</th>
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<td>3.0</td>
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<td>0.21</td>
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<td>0.31</td>
<td>5.7</td>
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<td>✓</td>
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<td>0.24</td>
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<td>8.2</td>
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<td>13.C.216</td>
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<td>0.24</td>
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<td>Massive ore</td>
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<td>0.32</td>
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<td>13.C.219</td>
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<td>0.27</td>
<td>6.8</td>
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<td>7.1</td>
<td>✓</td>
<td>8.0</td>
<td>0.03</td>
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<td>14.22</td>
<td>Massive ore</td>
<td>3.4</td>
<td>0.32</td>
<td>7.4</td>
<td>✓</td>
<td>7.7</td>
<td>✓</td>
<td>8.6</td>
<td>0.08</td>
</tr>
</tbody>
</table>

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50
Oxygen:
1. $1000\ln \alpha_{\text{mt-basalt}} = -3.4 \%_o$; $1000\ln \alpha_{\text{mt-andesite}} = -4.0 \%_o$; $1000\ln \alpha_{\text{mt-dacite}} = -4.3 \%_o$; regular range of basalts, arc andesites/dacites $+5.7$ to $+8 \%_o$ (ref.\textsuperscript{37,58,160})
2. $1000\ln \alpha_{\text{mt-water 800°C}} = -5.2 \%_o$; regular range for magmatic waters $5$-$10 \%_o$ (ref.\textsuperscript{161,162})

Iron:
1. $1000\ln \alpha_{\text{mt-magma}} = 0.03 \%_o$; regular range of arc andesites/dacites $+0.00$ to $+0.12 \%_o$ (ref.\textsuperscript{39})
2. $1000\ln \alpha_{\text{mt-water 800°C}} = 0.24 \%_o$; regular range for magmatic waters $0.00$ to $-0.35 \%_o$ (ref.\textsuperscript{39,70})

\(\checkmark\) = in equilibrium with magma/magmatic water; \(X\) = not in equilibrium with common magmatic values

Supplementary Table 3. Results for the magmatic water (625°C) equilibrium re-calculation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>$\delta^{18}$O</th>
<th>$\delta^{56}$Fe</th>
<th>$\delta^{18}$O water</th>
<th>Value fit</th>
<th>$\delta^{56}$Fe water</th>
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<tr>
<td>Ki-Mi-2a</td>
<td>Massive ore</td>
<td>0.1</td>
<td>0.21</td>
<td>6.3</td>
<td>(\checkmark)</td>
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</tr>
<tr>
<td>K-Mt-1079/437</td>
<td>Massive ore</td>
<td>0.6</td>
<td>0.16</td>
<td>6.8</td>
<td>(\checkmark)</td>
<td>-0.19</td>
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<tr>
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<td>Massive ore</td>
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<td>-</td>
<td>6.3</td>
<td>(\checkmark)</td>
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<td>0.27</td>
<td>6.7</td>
<td>(\checkmark)</td>
<td>-0.08</td>
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<td>DC575-KES103003</td>
<td>Massive ore</td>
<td>0.2</td>
<td>1.0</td>
<td>6.4</td>
<td>(\checkmark)</td>
<td>0.65</td>
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<tr>
<td>DC575-KES103016</td>
<td>Massive ore</td>
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<td>0.33</td>
<td>6.3</td>
<td>(\checkmark)</td>
<td>-0.02</td>
</tr>
<tr>
<td>13.C.216</td>
<td>Massive ore</td>
<td>0.6</td>
<td>0.24</td>
<td>6.8</td>
<td>(\checkmark)</td>
<td>-0.11</td>
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<tr>
<td>13.C.217</td>
<td>Massive ore</td>
<td>0.6</td>
<td>0.32</td>
<td>6.8</td>
<td>(\checkmark)</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Oxygen: $1000\ln \alpha_{\text{mt-water 625°C}} = -6.2 \%_o$ (ref.\textsuperscript{161})
Iron: $1000\ln \alpha_{\text{mt-water 625°C}} = 0.35 \%_o$ (ref.\textsuperscript{39})

\(\checkmark\) = in equilibrium with magma/magmatic water; \(X\) = not in equilibrium with common magmatic values (ref.\textsuperscript{39,162})
Supplementary Table 4. Results for the volcanic and plutonic reference material equilibrium re-calculation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>δ¹⁸O</th>
<th>δ⁵⁶Fe</th>
<th>δ¹⁸O basalt</th>
<th>δ⁵⁶Fe magma</th>
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<tbody>
<tr>
<td>TEF-NER-57B</td>
<td>Magnetite from an ankaramite dyke</td>
<td>3.7</td>
<td>0.16</td>
<td>7.1</td>
<td>0.13</td>
</tr>
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<td>TEF-NER-70</td>
<td>Magnetite from a pyroxene phyrict dyke</td>
<td>3.7</td>
<td>0.10</td>
<td>7.1</td>
<td>0.07</td>
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<tr>
<td>M-BA06-KA-3</td>
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<td>3.9</td>
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<td>-</td>
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<td>Kelut A1</td>
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<td>-</td>
<td>0.10</td>
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<td>GD-D-2</td>
<td>Igneous magnetite from basaltic andesite</td>
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<td>AK-B1</td>
<td>Igneous magnetite from basaltic andesite</td>
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<td>Gabbrobomb</td>
<td>Magnetite from a gabbro xenolith</td>
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<td>Ruoutevare</td>
<td>Ti-magnetite, layered igneous intrusion deposit</td>
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<td>6.6</td>
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<tr>
<td>Ulvön</td>
<td>Ti-magnetite, layered igneous intrusion deposit</td>
<td>3.9</td>
<td>0.13</td>
<td>7.4</td>
<td>0.10</td>
</tr>
<tr>
<td>Taberg</td>
<td>Ti-magnetite, layered igneous intrusion deposit</td>
<td>4.1</td>
<td>0.23</td>
<td>7.5</td>
<td>0.20</td>
</tr>
<tr>
<td>EM419</td>
<td>Massive Fe-Ti magnetite ore</td>
<td>4.8</td>
<td>0.61</td>
<td>8.3</td>
<td>0.58</td>
</tr>
<tr>
<td>EM424</td>
<td>Massive Fe-Ti magnetite ore</td>
<td>2.8</td>
<td>0.12</td>
<td>6.2</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Oxygen: **1000ln(αbasalt)=−3.4‰; 1000ln(αandesite)=−4.0‰; 1000ln(αdacite)=−4.3‰**; regular range of basalts, andesites/dacites +5.7 to +8‰ (ref. 57,58,160
Iron: 1000ln(αmagma)=0.03‰; regular range of arc andesites/dacites +0.00 to +0.12‰ (ref. 39)
For volcanic samples where no δ¹⁸O-value was obtained estimates for magma δ¹⁸O were taken from Jolis (2013) (ref. 16).

Supplementary Table 5. Results for equilibrium re-calculation of literature data

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹⁸O</th>
<th>δ⁵⁶Fe</th>
<th>δ¹⁸O water</th>
<th>δ⁵⁶Fe water</th>
<th>δ¹⁸O andesite</th>
<th>δ⁵⁶Fe magma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Los Colorados, Chilean Iron Belt (Bilenker et al. 2016)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>05–3.30</td>
<td>2.41</td>
<td>0.22</td>
<td>6.9</td>
<td>-0.13</td>
<td>6.4</td>
<td>0.19</td>
</tr>
<tr>
<td>05–20.7</td>
<td>3.04</td>
<td>0.09</td>
<td>7.5</td>
<td>-0.26</td>
<td>7.0</td>
<td>0.06</td>
</tr>
<tr>
<td>05–32</td>
<td>2.75</td>
<td>0.22</td>
<td>7.3</td>
<td>-0.13</td>
<td>6.8</td>
<td>0.19</td>
</tr>
<tr>
<td>05–52.2</td>
<td>3.17</td>
<td>0.14</td>
<td>7.7</td>
<td>-0.21</td>
<td>7.2</td>
<td>0.11</td>
</tr>
<tr>
<td>05–72.9</td>
<td>2.36</td>
<td>0.13</td>
<td>6.9</td>
<td>-0.22</td>
<td>6.4</td>
<td>0.1</td>
</tr>
<tr>
<td>05–82.6</td>
<td>2.76</td>
<td>0.08</td>
<td>7.3</td>
<td>-0.27</td>
<td>6.8</td>
<td>0.05</td>
</tr>
<tr>
<td>05–90</td>
<td>2.99</td>
<td>0.21</td>
<td>7.5</td>
<td>-0.14</td>
<td>7.0</td>
<td>0.18</td>
</tr>
<tr>
<td>05–106</td>
<td>2.78</td>
<td>0.12</td>
<td>7.3</td>
<td>-0.23</td>
<td>6.8</td>
<td>0.09</td>
</tr>
<tr>
<td>05–126.15</td>
<td>2.48</td>
<td>0.1</td>
<td>7.0</td>
<td>-0.25</td>
<td>6.5</td>
<td>0.07</td>
</tr>
<tr>
<td>04–38.8</td>
<td>2.04</td>
<td>0.18</td>
<td>6.5</td>
<td>-0.17</td>
<td>6.0</td>
<td>0.15</td>
</tr>
<tr>
<td>04–66.7</td>
<td>1.92</td>
<td>0.18</td>
<td>6.4</td>
<td>-0.17</td>
<td>5.9</td>
<td>0.15</td>
</tr>
<tr>
<td>04–129.3</td>
<td>2.62</td>
<td>0.22</td>
<td>7.1</td>
<td>-0.13</td>
<td>6.6</td>
<td>0.19</td>
</tr>
<tr>
<td>04–104.4</td>
<td>2.43</td>
<td>0.24</td>
<td>6.9</td>
<td>-0.11</td>
<td>6.4</td>
<td>0.21</td>
</tr>
<tr>
<td>Pea Ridge and Pilot Knob (Childress et al. 2016)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR18</td>
<td>2.12</td>
<td>0.35</td>
<td>8.3</td>
<td>0</td>
<td>4.9</td>
<td>0.32</td>
</tr>
<tr>
<td>PR-64A</td>
<td>4.87</td>
<td>0.2</td>
<td>11.1</td>
<td>-0.15</td>
<td>7.7</td>
<td>0.17</td>
</tr>
<tr>
<td>PR-77A</td>
<td>5.11</td>
<td>0.21</td>
<td>11.3</td>
<td>-0.14</td>
<td>7.9</td>
<td>0.18</td>
</tr>
<tr>
<td>PR-82A</td>
<td>5.9</td>
<td>0.1</td>
<td>12.1</td>
<td>-0.25</td>
<td>8.7</td>
<td>0.07</td>
</tr>
<tr>
<td>PR-82B</td>
<td>7.03</td>
<td>0.07</td>
<td>13.2</td>
<td>-0.28</td>
<td>9.8</td>
<td>0.04</td>
</tr>
<tr>
<td>PR-37</td>
<td>4.5</td>
<td>0.07</td>
<td>10.7</td>
<td>-0.28</td>
<td>7.3</td>
<td>0.04</td>
</tr>
</tbody>
</table>

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Oxygen:
1. $1000 \ln (\alpha_{\text{mt-andesite}}) = -4.0 \%$ (ref. 14) or $-2.8 \%$ (ref. 46)
2. $1000 \ln (\alpha_{\text{mt-water 625°C}}) = -4.5 \%$ (ref. 14) or $-6.2 \%$ (ref. 46)

Iron:
1. $1000 \ln (\alpha_{\text{mt-magma}}) = 0.03 \%$ (ref. 39)
2. $1000 \ln (\alpha_{\text{mt-water 625°C}}) = 0.35 \%$ (ref. 39)

### Supplementary Table 6. Results for hydrothermal fluid (375°C) equilibrium re-calculation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}$O</th>
<th>$\delta^{56}$Fe</th>
<th>$\delta^{18}$O fluid</th>
<th>$\delta^{56}$Fe fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>KES090044</td>
<td>-1.0</td>
<td>0.24</td>
<td>6.80</td>
<td>-0.26</td>
</tr>
<tr>
<td>KES090084</td>
<td>-1.1</td>
<td>0.11</td>
<td>6.70</td>
<td>-0.39</td>
</tr>
<tr>
<td>EJ-LS-11-2</td>
<td>-4.3</td>
<td>0.24</td>
<td>3.50</td>
<td>-0.26</td>
</tr>
<tr>
<td>EJ-LS-11-3</td>
<td>-1.9</td>
<td>0.36</td>
<td>5.90</td>
<td>-0.14</td>
</tr>
<tr>
<td>K-mt-1</td>
<td>-0.95</td>
<td>0.20</td>
<td>6.9</td>
<td>-0.30</td>
</tr>
<tr>
<td>Ki-mi-2b</td>
<td>-0.69</td>
<td>0.22</td>
<td>7.1</td>
<td>-0.28</td>
</tr>
<tr>
<td>K-mt-1079/303</td>
<td>-0.33</td>
<td>0.27</td>
<td>7.5</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

Oxygen: $1000 \ln (\alpha_{\text{mt-water 375°C}}) = -7.8 \%$ (ref. 181)
Iron: $1000 \ln (\alpha_{\text{mt-water 375°C}}) = 0.5 \%$ (ref. 39)


81. Andersson, U.B. Coeval iron oxide and silicate magmas; structural evidence for immiscibility and mingling at Kiirunavaara and Luossavaara, Sweden. 12th SGA Biennial


90. Torab, F.M. Geochemistry and metallogeny of magnetite apatite deposits of the Bafq Mining


121. Larson, S. Å, Hogmalm, K. J. & Meurer, W. P. Character and significance of spectacular layering features developed in the thin, alkali-basaltic sills of the Ulv?? Gabbro Complex,

1148 122. Larson, S. Å. & Magnusson, K.-Å. The magnetic and chemical character of Fe-Ti oxides in

1150 123. Carracedo, J. C. *et al.* Hotspot volcanism close to a passive continental margin: the Canary

1152 124. Ancochea, E. *et al.* Volcanic evolution of the island of Tenerife (Canary Islands) in the light

1154 125. Deegan, F. M. *et al.* Crustal versus source processes recorded in dykes from the Northeast

1156 126. Delcamp, A. *et al.* Dykes and structures of the NE rift of Tenerife, Canary Islands: A record
1157 of stabilisation and destabilisation of ocean island rift zones. *Bull. Volcanol.* **74**, 963–980
1158 (2012).

1159 127. Gass, I. G. & Masson-Smith, D. The Geology and Gravity Anomalies of the Troodos Massif,

1161 128. Henson, F. R. S., Browne, R. V. & McGinty, J. A synopsis of the stratigraphy and geological


1171 133. Gudmundsson, M. T. *et al.* Eruptions of eyjafjallajökull Volcano, Iceland. in *Eos* **91**, 191
1172 (2010).


166. Rieger, A. A., Marshik, R. & Diaz, M. The evolution of the hydrothermal IOCG system in the Mantoverde district, northern Chile: New evidence from microthermometry and stable...
