

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 has been invoked, a lower overprint has 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 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 ⁸³. 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 ranges between 50 and 100 m ^{84,85}. The ore is hosted by metavolcanic rocks of andesitic to dacitic compositions that belong to the c. 1.91-1.87 Ga volcano-sedimentary succession of Bergslagen ^{40,86}.

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 ⁵. 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 ⁵. 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 ⁸⁷. The host rocks of the deposit consist of typical subduction zone andesites and dacites which have been hydrothermally altered with alteration increasing at depth ^{5,88,89}. Although hydrothermal activity was associated with the ore formation ^{5,88}, the ore at El Laco is supposed to have formed by dominantly magmatic processes, involving an iron oxide-rich magma and magmatic fluids ⁶². 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 ^{5,88}. 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 ^{5,62}. However, a hydrothermal origin is put forward on the basis of oxygen isotopes ³² arguing that the surprising isotopic homogeneity of magnetite samples at El Laco ($\sim +4.0$ ‰) 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- $\delta^{18}\text{O}$ hydrothermal fluid as transport agent

^{27,30,32} possibly also in some sort of evaporitic pan. 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 ^{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 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 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 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 zone, 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 ¹⁰⁹. 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 ¹⁰⁹. The Panzihua deposit is currently mined and holds a reserve of 1333 Mt of ore ¹⁰⁹. The two Panzihua samples of this study represent massive Ti-magnetite ore.

2.3 Ruotevare, Norrbotten, Sweden: The geology of the Ruotevare area in Norrbotten, northern Sweden, comprises ultrabasic rock types such as peridotite and pyroxenite, which are associated with anorthosite and gabbro of Precambrian age ^{110,111}. 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 ^{112,113}.

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 ^{114–116}. 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 late Sveconorwegian amphibolite facies metamorphism ^{114,116}. 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 ^{114,117}. The ore holds between 26 and 35 % “titanomagnetite” with a content of 28.7–32.3 % FeO ¹¹⁴. Within the ore are plagioclase-rich layers which give the appearance of a layered igneous intrusion ^{114,117}. The ore is supposed to have been formed as a magmatic cumulate which

resulted from gravitational settling within a gabbroic magma ^{114,116}. The sample in this study is a massive Ti-magnetite ore from the mine at Taberg.

2.5 Ulvön, Ångermanland, Central Sweden: The mineral ulvöspinel derives its name from the Ulvö island, where the layered igneous Ulvö Gabbro Complex is found ¹¹⁸ at the east coast of central Sweden. The intrusion consists of several gently dipping lopoliths, 30-80 km in diameter and 250-300 m in thickness ^{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 ¹²¹. These rocks are ~1.25 Ga old and have not been affected by regional metamorphic overprint or deformation ^{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 ^{121,122}. Such layers have also been mined for their metals ¹²¹. Other common minerals in the Ulvö Gabbro Complex are plagioclase (labradorite), olivine, and clinopyroxene ^{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 km²) and highest (3718 m) island of the island group, which is situated over the Canary hot spot ^{123,124}. Volcanic activity on the island dates back to >6.5 Ma and is today seen in several small volcanoes and the Teide-Pico Viejo edifice ¹²⁴. Samples for this study originate from dykes in the NE rift zone of the island. The samples comprise ankaramites and basanites ^{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 ¹²⁷. Four of these belts are dominated by sedimentary rocks, most commonly limestones and loose sediments ranging in age from the Triassic to recent ^{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 ^{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 ¹²⁷. The rocks have been affected by metamorphism represented by diabase and serpentinite ¹²⁷. The sample used in this study comes from a dolerite dyke near Agros in the central part of the Troodos complex 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 ¹³¹, whose current plume channel lies beneath the Vatnajökull glacier and represents the surface expression of the Mid-Atlantic ridge 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 ¹³¹. Volcanic eruptions, often of explosive nature due to lava-snow interaction, occur every three to four years ¹³³. The main eruption products are tholeiitic basalts as well as basaltic andesites 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 ^{135,136}, Agung ¹³⁷, Gede ¹³⁸, Kelut ¹³⁹ and Merapi 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 ^{141,142}. Calc-alkaline volcanism with dacites and andesites are the typical eruption products in most recent times ^{142,143}. Beside volcanic rocks, the area also hosts several gold, tin and copper deposits associated with subduction zone volcanism ¹⁴².

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 ¹⁴⁴. It is the largest currently active volcano on the Northern Island with the most recent eruption in 2007 and several other eruptive events during the last hundred years ^{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 ^{147,148}. Mt. Ruapehu is underlain by Mesozoic meta-greywacke, which in turn is underlain by oceanic, metamorphosed igneous crust ^{146,149}. The typical eruption products are subduction zone andesites and dacites with porphyritic textures ^{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 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 ^{152,153}. The major iron ore zones are northeast-striking, and variably, but steeply (to 80°) dipping towards the southeast 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 ^{86,153}. Later regional metamorphism to amphibolite facies grade, as well as three stages of ductile deformation have affected the older rocks in the area, including the Björnberget ore and its host rocks ^{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 ¹⁵⁴. 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 ¹⁵⁴. The dolomitic marbles at Dannemora are very dark-coloured due to a content of 5-30 % of fine magnetite ^{154,155}. The area has been affected by greenschist facies metamorphism during the Svecokarelian orogeny and deformed at least twice, leading to isoclinal folding ^{154,156}. 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 % ^{154,155}. 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 ¹⁵⁴. 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 ^{86,157}. 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 ¹⁵². 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 % ^{24,86,157}. 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 ¹⁵⁸. The iron content of the deposits lies between 30 % and 55 % ^{86,157}.

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Supplementary Tables

Supplementary Table 1. Oxygen and iron isotope analysis for magnetite from apatite-iron oxide ores and reference materials

Sample	Sample Description	Sample Provenance	$\delta^{18}\text{O}$ in ‰	2 σ	$\delta^{56}\text{Fe}$ in ‰	2 σ
<u>Apatite-iron oxide ore</u>						
Kiruna Mining District (KMD), Northern Sweden						
Kiruna-17NY28	Banded massive (Ap-)magnetite ore	Kiirunavaara mine, Kiruna	4.1	±0.2	0.19	±0.03
K-Mt-1 (907/75)	Massive magnetite ore	Kiirunavaara mine, Kiruna	-1.0	±0.2	0.20	±0.03
Ki-Mi-2a (1079/251)	Massive magnetite ore	Kiirunavaara mine, Kiruna	0.1	±0.2	0.21	±0.02
Ki-Mi-2b (1079/251)	Massive magnetite ore	Kiirunavaara mine, Kiruna	-0.7	±0.2	0.22	±0.04
K-Mt-1079/303	Massive magnetite ore	Kiirunavaara mine, Kiruna	-0.3	±0.2	0.27	±0.04
K-Mt-1079/437	Massive magnetite ore	Kiirunavaara mine, Kiruna	0.6	±0.2	0.16	±0.02
M1931*	Massive magnetite ore	Kiirunavaara mine, Kiruna	0.1	±0.2	-	-
M1937*	Skeletal magnetite ore	Kiirunavaara mine, Kiruna	1.4	±0.2	-	-
LVA-3	Massive magnetite ore	Luossavaara mine, Kiruna	1.2	±0.2	0.23	±0.02
LVA-FW-1	Massive magnetite ore	Luossavaara mine, Kiruna	1.4	±0.2	0.12	±0.04
LVA-FW-2	Massive magnetite ore	Luossavaara mine, Kiruna	1.2	±0.2	0.27	±0.03
K-Mt-3	Massive magnetite ore	Mertainen mine, Kiruna	1.9	±0.2	0.41	±0.03
K-Mt-4	Massive magnetite ore	Mertainen mine, Kiruna	1.6	±0.2	0.29	±0.03
M7557*	Massive magnetite ore	Rektorn mine, Kiruna	2.5	±0.2	-	-
Grängesberg Mining District (GMD), Central Sweden						
DC717-KES090068	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.2	±0.2	0.40	±0.03
DC717-KES090070	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.8	±0.2	0.24	±0.03
DC717-KES090072	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	0.9	±0.2	0.33	±0.03
DC717-KES090084	Magnetite vein in intermediate volcanic rock	Grängesberg mine, Grängesberg	-1.1	±0.2	0.11	±0.03
DC690-KES090011	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	2.8	±0.2	0.31	±0.03
DC690-KES090012	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.2	±0.2	0.31	±0.04
DC690-KES090020	Massive Ap-veined magnetite ore	Grängesberg mine, Grängesberg	1.1	±0.2	0.30	±0.04
DC690-KES090024	Massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.0	±0.2	0.26	±0.03
DC690-KES090027	Ap-veined/banded massive magnetite ore	Grängesberg mine, Grängesberg	1.2	±0.2	0.29	±0.03
DC690-KES090030	Silicate-spotted massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.8	±0.2	0.39	±0.04
DC690-KES090034	Coarse-grained Ap-spotted massive magnetite ore	Grängesberg mine, Grängesberg	0.5	±0.2	0.27	±0.03
DC690-KES090044	Disseminated magnetite in intermediate volcanic rock	Grängesberg mine, Grängesberg	-1.0	±0.2	0.24	±0.03
DC575-KES103011	Magnetite-dominated massive ore	Grängesberg mine, Grängesberg	1.8	±0.2	0.31	±0.03
DC575-KES103016	Coarse, massive (Ap-)magnetite ore	Grängesberg mine, Grängesberg	1.5	±0.2	0.27	±0.04
DC575-KES103003	Magnetite-dominated massive ore	Grängesberg mine, Grängesberg	0.2	±0.2	1.0	±0.03
KES091013b	Massive (Ap-)magnetite ore	Blötberget mine, Blötberget	0.1	±0.2	0.33	±0.03
El Lago Ap-Fe-oxide deposit, Chile						
EJ-LS-11-1	Massive magnetite ore	Laco Sur, El Lago	1.9	±0.2	0.28	±0.03
EJ-LS-11-2	Massive magnetite ore	Laco Sur, El Lago	-4.3	±0.2	0.24	±0.03
EJ-LS-11-3	Massive magnetite ore	Laco Sur, El Lago	-1.9	±0.2	0.36	±0.03
EJ-LS-11-4	Massive magnetite ore	Laco Sur, El Lago	4.2	±0.2	0.34	±0.03
LS-2	Massive magnetite ore	Laco Sur, El Lago ¹	4.3	±0.2	0.27	±0.03
LS-52	Massive magnetite ore	Laco Sur, El Lago ¹	4.4	±0.2	0.28	±0.03

Bafq Mining District, Iran

13.C.88	Massive magnetite ore	Sechahun, Bafq	2.4	±0.2	0.20	±0.06
13.C.106	Massive magnetite ore	Lakke Siah, Bafq	2.3	±0.2	0.26	±0.05
13.C.216	Massive magnetite ore	Chadormalu, Bafq	0.6	±0.2	0.24	±0.03
13.C.217	Massive magnetite ore	Chadormalu, Bafq	0.6	±0.2	0.32	±0.02
13.C.219	Massive magnetite ore	Chadormalu, Bafq	2.8	±0.2	0.27	±0.07
14.22	Massive magnetite ore	Esfordi, Bafq	3.4	±0.2	0.32	±0.01

Plutonic reference material

Ruotevare	Ti-magnetite, layered igneous intrusion	Kvikjokk, Norrbotten, Sweden ²	3.2	±0.2	0.31	±0.03
Ulvön	Ti-magnetite, layered igneous intrusion	Ulvön island, Ångermanland, Sweden ²	4.0	±0.2	0.13	±0.03
Taberg	Ti-magnetite, layered igneous intrusion	Iron mine, Taberg, Småland, Sweden ³	4.1	±0.2	0.23	±0.04
EM419	Massive Fe-Ti magnetite ore	Northern pit, Panzhihua, China ⁴	4.8	±0.2	0.61	±0.05
EM424	Massive Fe-Ti magnetite ore	Nalahe, Panzhihua, China ⁴	2.8	±0.2	0.12	±0.04
Bushveld	Massive magnetite ore	Upper Zone, Bushveld Complex, South Africa ⁴	1.8	±0.2	-	-
Gabbrobomb	Magnetite from a gabbro xenolith	NW-Flank, Skjaldbreiður, Iceland ³	4.6	±0.2	0.46	±0.03

Volcanic reference material

TEF-NER-18	Magnetite from an ankaramite dyke	NE Rift Zone, Tenerife, Spain	-	-	0.07	±0.05
TEF-NER-57B	Magnetite from an ankaramite dyke	NE Rift Zone, Tenerife, Spain	3.7	±0.2	0.16	±0.02
TEF-NER-70	Magnetite from a pyroxene phyric dyke	NE Rift Zone, Tenerife, Spain	3.7	±0.2	0.10	±0.02
MG-07	Igneous magnetite from dacite	S-Flank, Mt. Ruapehu, New Zealand ⁵	-	-	0.32	±0.03
MG-09	Igneous magnetite from dacite	S-Flank, Mt. Ruapehu, New Zealand ⁵	-	-	0.29	±0.03
Kelut A1	Igneous magnetite from basaltic andesite	Mt. Kelut, Java, Indonesia	-	-	0.10	±0.04
GD-D-2	Igneous magnetite from basaltic andesite	Gede Dome, Java, Indonesia	-	-	0.12	±0.03
AK-B1	Igneous magnetite from basaltic andesite	SE-Flank, Anak Krakatau, Indonesia	-	-	0.06	±0.03
AK-B3	Igneous magnetite from basaltic andesite	SE-Flank, Anak Krakatau, Indonesia	-	-	0.16	±0.03
A-BA-1	Igneous magnetite from basaltic andesite	Mt. Agung, Bali, Indonesia	-	-	0.18	±0.05
M-BA06-KA-3	Igneous magnetite from basaltic andesite	Mt. Merapi, Java, Indonesia	3.9	±0.2	0.17	±0.03
83/CRS/6	Igneous magnetite from a dolerite dyke	Agros, Troodos Massif, Cyprus ⁶	-	-	0.34	±0.03

Low-temperature or hydrothermal magnetites

KES091007B	Calcite bearing-magnetite ore	Björnberget, Sweden	-0.8	±0.2	-0.02	±0.03
DM-1	Iron-skarn magnetite ore	Botenhäll, Dannemora, Sweden ⁷	-0.4	±0.2	-0.36	±0.03
DM-2	Iron-skarn magnetite ore	Norrnäs 3, Dannemora, Sweden ⁷	-0.7	±0.2	0.01	±0.03
DM-3	Iron-skarn magnetite ore	Konstäng, Dannemora, Sweden ⁷	2.1	±0.2	-0.43	±0.03
DM-4	Iron-skarn magnetite ore	Strömsmalmen, Dannemora, Sweden ⁷	-0.6	±0.2	-0.35	±0.03
EJ092008	Magnetite from a banded iron formation deposit	Striberg, Bergslagen, Sweden	-1.2	±0.2	-0.57	±0.03

* Data from Lundh (2014) (ref.¹⁵⁹)

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 Rauseus, Dannemora Mineral AB, Österbybruk, Sweden

Supplementary Table 1. Oxygen and iron isotope analysis for magnetite from apatite-iron oxide ores and reference materials

Supplementary Table 2. Results for the magma (900°C)/magmatic water (800°C) equilibrium re-calculation

Sample	Rock type	$\delta^{18}\text{O}$	$\delta^{56}\text{Fe}$	$\delta^{18}\text{O}$ andesite	Value fit	$\delta^{18}\text{O}$ dacite	Value fit	$\delta^{18}\text{O}$ water	Value fit	$\delta^{56}\text{Fe}$ water	$\delta^{56}\text{Fe}$ magma
Kiruna	Massive ore	4.1	0.19	8.1	✓	8.4	✓	9.3	✓	-0.05	0.16
K-Mt-1	Massive ore	-1.0	0.20	3.0	X	3.4	X	4.3	X	-0.04	0.17
Ki-Mi-2a	Massive ore	0.1	0.21	4.0	X	4.4	X	5.2	✓	-0.04	0.18
Ki-Mi-2b	Massive ore	-0.7	0.22	3.3	X	3.6	X	4.5	X	-0.02	0.19
K-Mt-1079/303	Massive ore	-0.3	0.27	3.6	X	4.0	X	4.9	X	0.03	0.24
K-Mt-1079/437	Massive ore	0.6	0.16	4.6	X	4.9	X	5.8	✓	-0.08	0.13
M1931	Massive ore	0.1	-	4.1	X	4.4	X	5.3	✓	-	-
M1937	Massive ore	1.4	-	5.4	X	5.7	✓	6.6	✓	-	-
LVA-3	Massive ore	1.2	0.23	5.2	X	5.5	X	6.4	✓	-0.02	0.19
LVA-FW-1	Massive ore	1.4	0.12	5.4	X	5.7	✓	6.6	✓	-0.12	0.09
LVA-FW-2	Massive ore	1.2	0.27	5.1	X	5.5	X	6.4	✓	0.03	0.24
K-Mt-3	Massive ore	1.9	0.41	5.9	✓	6.2	✓	7.1	✓	0.17	0.38
K-Mt-4	Massive ore	1.6	0.29	5.6	X	5.9	✓	6.8	✓	0.05	0.26
M7557	Massive ore	2.5	-	6.5	✓	6.8	✓	7.7	✓	-	-
DC717-KES090068	Massive ore	1.1	0.40	5.1	X	5.4	X	6.3	✓	0.16	0.37
DC717-KES090070	Massive ore	1.8	0.24	5.8	✓	6.1	✓	7.0	✓	-0.01	0.21
DC717-KES090072	Massive ore	0.9	0.33	4.8	X	5.2	X	6.1	✓	0.09	0.30
DC690-KES090011	Massive ore	2.8	0.31	6.7	✓	7.1	✓	8.0	✓	0.07	0.28
DC690-KES090012	Massive ore	1.2	0.31	5.2	X	5.5	X	6.4	✓	0.07	0.28
DC690-KES090020	Massive ore	1.1	0.30	5.0	X	5.4	X	6.3	✓	0.06	0.27
DC690-KES090024	Massive ore	1.0	0.26	5.0	X	5.3	X	6.2	✓	0.02	0.23
DC690-KES090027	Massive ore	1.2	0.29	5.2	X	5.5	X	6.4	✓	0.05	0.26
DC690-KES090030	Massive ore	1.8	0.39	5.8	✓	6.1	✓	7.0	✓	0.15	0.36
DC690-KES090034	Massive ore	0.5	0.27	4.5	X	4.8	X	5.7	✓	0.03	0.24
DC575-KES103003	Massive ore	1.8	0.31	5.7	✓	6.1	✓	7.0	✓	0.07	0.28
DC575-KES103011	Massive ore	1.5	0.27	5.5	X	5.8	X	6.7	✓	0.03	0.24
DC575-KES103016	Massive ore	0.1	0.33	4.1	X	4.4	X	5.3	✓	0.09	0.30
DC575-KES103003	Massive ore	0.2	1.0	4.2	X	4.5	X	5.4	✓	0.76	0.97
DC690-KES090044	Disseminated magnetite	-1.0	0.24	3.0	X	3.3	X	4.2	X	0.00	0.21
DC717-KES090084	Magnetite vein	-1.1	0.11	2.8	X	3.1	X	4.1	X	-0.13	0.08
EJ-LS-11-1	Massive ore	1.9	0.28	5.9	✓	6.2	✓	7.1	✓	0.04	0.25
EJ-LS-11-2	Massive ore	-4.3	0.24	-0.3	X	0.0	X	0.9	X	0.00	0.21
EJ-LS-11-3	Massive ore	-1.9	0.36	2.1	X	2.4	X	3.3	X	0.12	0.33
EJ-LS-11-4	Massive ore	4.2	0.34	8.1	✓	8.5	✓	9.4	✓	0.10	0.31
LS-2	Massive ore	4.3	0.27	8.2	✓	8.6	✓	9.5	✓	0.03	0.24
LS-52	Massive ore	4.4	0.28	8.4	✓	8.7	✓	9.6	✓	0.04	0.25
13.C.88	Massive ore	2.4	0.20	6.4	✓	6.7	✓	7.6	✓	-0.04	0.17
13.C.106	Massive ore	2.3	0.26	6.2	✓	6.6	✓	7.5	✓	0.02	0.23
13.C.216	Massive ore	0.6	0.24	4.5	X	4.9	X	5.8	✓	0.00	0.21

13.C.217	Massive ore	0.6	0.32	4.6	X	4.9	X	5.8	✓	0.08	0.29
13.C.219	Massive ore	2.8	0.27	6.8	✓	7.1	✓	8.0	✓	0.03	0.24
14.22	Massive ore	3.4	0.32	7.4	✓	7.7	✓	8.6	✓	0.08	0.29

Oxygen:

1. $1000\ln\alpha_{(\text{mt-basalt})} = -3.4\text{‰}$; $1000\ln\alpha_{(\text{mt-andesite})} = -4.0\text{‰}$; $1000\ln\alpha_{(\text{mt-dacite})} = -4.3\text{‰}$; regular range of basalts, arc andesites/dacites +5.7 to +8 ‰ (ref.^{57,58,160})

2. $1000\ln\alpha_{(\text{mt-water } 800^{\circ}\text{C})} = -5.2\text{‰}$; regular range for magmatic waters 5-10 ‰ (ref.^{161,162})

Iron:

1. $1000\ln\alpha_{(\text{mt-magma})} = 0.03\text{‰}$; regular range of arc andesites/dacites +0.00 to +0.12 ‰ (ref.³⁹)

2. $1000\ln\alpha_{(\text{mt-water } 800^{\circ}\text{C})} = 0.24\text{‰}$; regular range for magmatic waters 0.00 to -0.35‰ (ref.^{39,70})

✓ = in equilibrium with magma/magmatic water ; X= not in equilibrium with common magmatic values

Supplementary Table 2. Results for the magma (900°C)/magmatic water (800°C) equilibrium re-calculation

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

Sample	Rock type	$\delta^{18}\text{O}$	$\delta^{56}\text{Fe}$	$\delta^{18}\text{O}$ water	Value fit	$\delta^{56}\text{Fe}$ water
Ki-Mi-2a	Massive ore	0.1	0.21	6.3	✓	-0.14
K-Mt-1079/437	Massive ore	0.6	0.16	6.8	✓	-0.19
M1931	Massive ore	0.1	-	6.3	✓	
DC690-KES090034	Massive ore	0.5	0.27	6.7	✓	-0.08
DC575-KES103003	Massive ore	0.2	1.0	6.4	✓	0.65
DC575-KES103016	Massive ore	0.1	0.33	6.3	✓	-0.02
13.C.216	Massive ore	0.6	0.24	6.8	✓	-0.11
13.C.217	Massive ore	0.6	0.32	6.8	✓	-0.03

Oxygen: $1000\ln\alpha_{(\text{mt-water } 625^\circ\text{C})} = -6.2 \text{ ‰}$ (ref.¹⁶¹)

Iron: $1000\ln\alpha_{(\text{mt-water } 625^\circ\text{C})} = 0.35 \text{ ‰}$ (ref.³⁹)

✓ = in equilibrium with magma/magmatic water ; X= not in equilibrium with common magmatic values (ref.^{70,162})

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

Supplementary Table 4. Results for the volcanic and plutonic reference material equilibrium re-calculation

Sample	Rock type	$\delta^{18}\text{O}$	$\delta^{56}\text{Fe}$	$\delta^{18}\text{O}$ basalt	$\delta^{56}\text{Fe}$ magma
TEF-NER-57B	Magnetite from an ankaramite dyke	3.7	0.16	7.1	0.13
TEF-NER-70	Magnetite from a pyroxene phyric dyke	3.7	0.10	7.1	0.07
M-BA06-KA-3	Igneous magnetite from basaltic andesite	3.9	0.17	6.2	0.14
TEF-NER-18	Magnetite from an ankaramite dyke	-	0.07	7.0	0.04
Kelut A1	Igneous magnetite from basaltic andesite	-	0.10	7.0	0.07
GD-D-2	Igneous magnetite from basaltic andesite	-	0.12	7.5	0.09
AK-B1	Igneous magnetite from basaltic andesite	-	0.06	6.4	0.03
AK-B3	Igneous magnetite from basaltic andesite	-	0.16	6.4	0.13
A-BA-1	Igneous magnetite from basaltic andesite	-	0.18	6.7	0.15
Gabbrobomb	Magnetite from a gabbro xenolith	4.6	0.46	8.0	0.43
Ruotevare	Ti-magnetite, layered igneous intrusion deposit	3.2	0.31	6.6	0.28
Ulvön	Ti-magnetite, layered igneous intrusion deposit	3.9	0.13	7.4	0.10
Taberg	Ti-magnetite, layered igneous intrusion deposit	4.1	0.23	7.5	0.20
EM419	Massive Fe-Ti magnetite ore	4.8	0.61	8.3	0.58
EM424	Massive Fe-Ti magnetite ore	2.8	0.12	6.2	0.09

Oxygen: $1000\ln\alpha_{(\text{mt-basalt})} = -3.4\text{‰}$; $1000\ln\alpha_{(\text{mt-andesite})} = -4.0\text{‰}$; $1000\ln\alpha_{(\text{mt-dacite})} = -4.3\text{‰}$; regular range of basalts, arc andesites/dacites $+5.7$ to $+8\text{‰}$ (ref.^{57,58,160})

Iron: $1000\ln\alpha_{(\text{mt-magma})} = 0.03\text{‰}$; regular range of arc andesites/dacites $+0.00$ to $+0.12\text{‰}$ (ref.³⁹)

For volcanic samples where no $\delta^{18}\text{O}$ -value was obtained estimates for magma $\delta^{18}\text{O}$ were taken from Jolis (2013) (ref.¹⁶³).

Supplementary Table 4. Results for the volcanic and plutonic reference material equilibrium re-calculation

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

Sample	$\delta^{18}\text{O}$	$\delta^{56}\text{Fe}$	$\delta^{18}\text{O}$ water	$\delta^{56}\text{Fe}$ water	$\delta^{18}\text{O}$ andesite	$\delta^{56}\text{Fe}$ magma
Los Colorados, Chilean Iron Belt (Bilenker et al. 2016)						
05-3.30	2.41	0.22	6.9	-0.13	6.4	0.19
05-20.7	3.04	0.09	7.5	-0.26	7.0	0.06
05-32	2.75	0.22	7.3	-0.13	6.8	0.19
05-52.2	3.17	0.14	7.7	-0.21	7.2	0.11
05-72.9	2.36	0.13	6.9	-0.22	6.4	0.1
05-82.6	2.76	0.08	7.3	-0.27	6.8	0.05
05-90	2.99	0.21	7.5	-0.14	7.0	0.18
05-106	2.78	0.12	7.3	-0.23	6.8	0.09
05-126.15	2.48	0.1	7.0	-0.25	6.5	0.07
04-38.8	2.04	0.18	6.5	-0.17	6.0	0.15
04-66.7	1.92	0.18	6.4	-0.17	5.9	0.15
04-129.3	2.62	0.22	7.1	-0.13	6.6	0.19
04-104.4	2.43	0.24	6.9	-0.11	6.4	0.21
Pea Ridge and Pilot Knob (Childress et al. 2016)						
PR18	2.12	0.35	8.3	0	4.9	0.32
PR-64A	4.87	0.2	11.1	-0.15	7.7	0.17
PR-77A	5.11	0.21	11.3	-0.14	7.9	0.18
PR-82A	5.9	0.1	12.1	-0.25	8.7	0.07
PR-82B	7.03	0.07	13.2	-0.28	9.8	0.04
PR-37	4.5	0.07	10.7	-0.28	7.3	0.04
PR-144	5.04	0.26	11.2	-0.09	7.8	0.23
PK-1145-965.8	6.68	0.19	12.9	-0.16	9.5	0.16
PK-1145-979.5	6.21	0.24	12.4	-0.11	9.0	0.21

Oxygen:

1. $1000\ln\alpha_{(\text{mt-andesite})} = -4.0\text{‰}$ (ref.¹⁴) or -2.8‰ (ref.⁴⁸)
2. $1000\ln\alpha_{(\text{mt-water } 625^{\circ}\text{C})} = -4.5\text{‰}$ (ref.¹⁴) or -6.2‰ (ref.⁴⁸)

Iron:

1. $1000\ln\alpha_{(\text{mt-magma})} = 0.03\text{‰}$ (ref.³⁹)
2. $1000\ln\alpha_{(\text{mt-water } 625^{\circ}\text{C})} = 0.35\text{‰}$ (ref.³⁹)

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

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

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

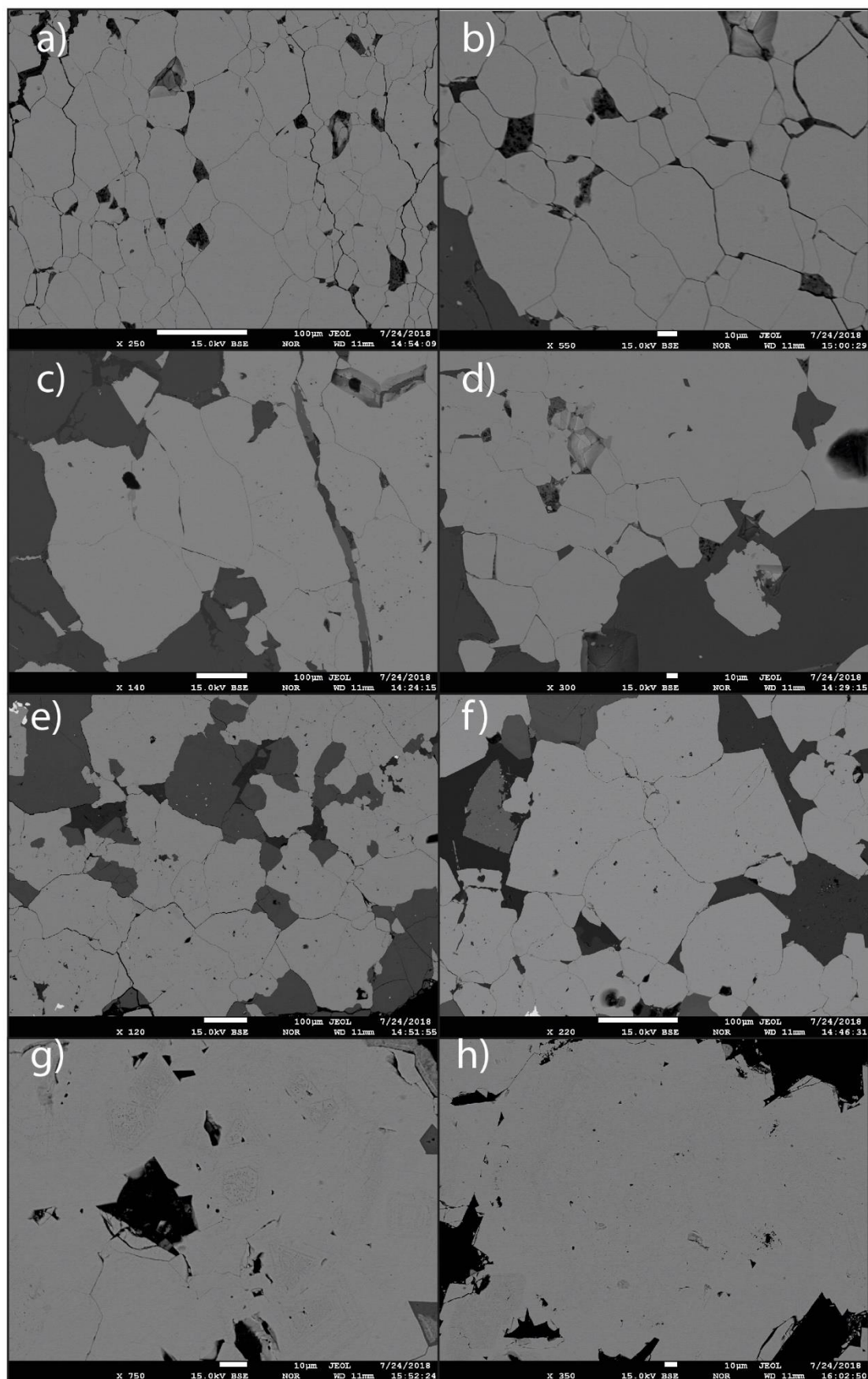
Oxygen: $1000\ln\alpha_{(\text{mt-water } 375^\circ\text{C})} = -7.8 \text{ ‰}$ (ref.¹⁶¹)

Iron: $1000\ln\alpha_{(\text{mt-water } 375^\circ\text{C})} = 0.5 \text{ ‰}$ (ref.³⁹)

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

Supplementary Figures

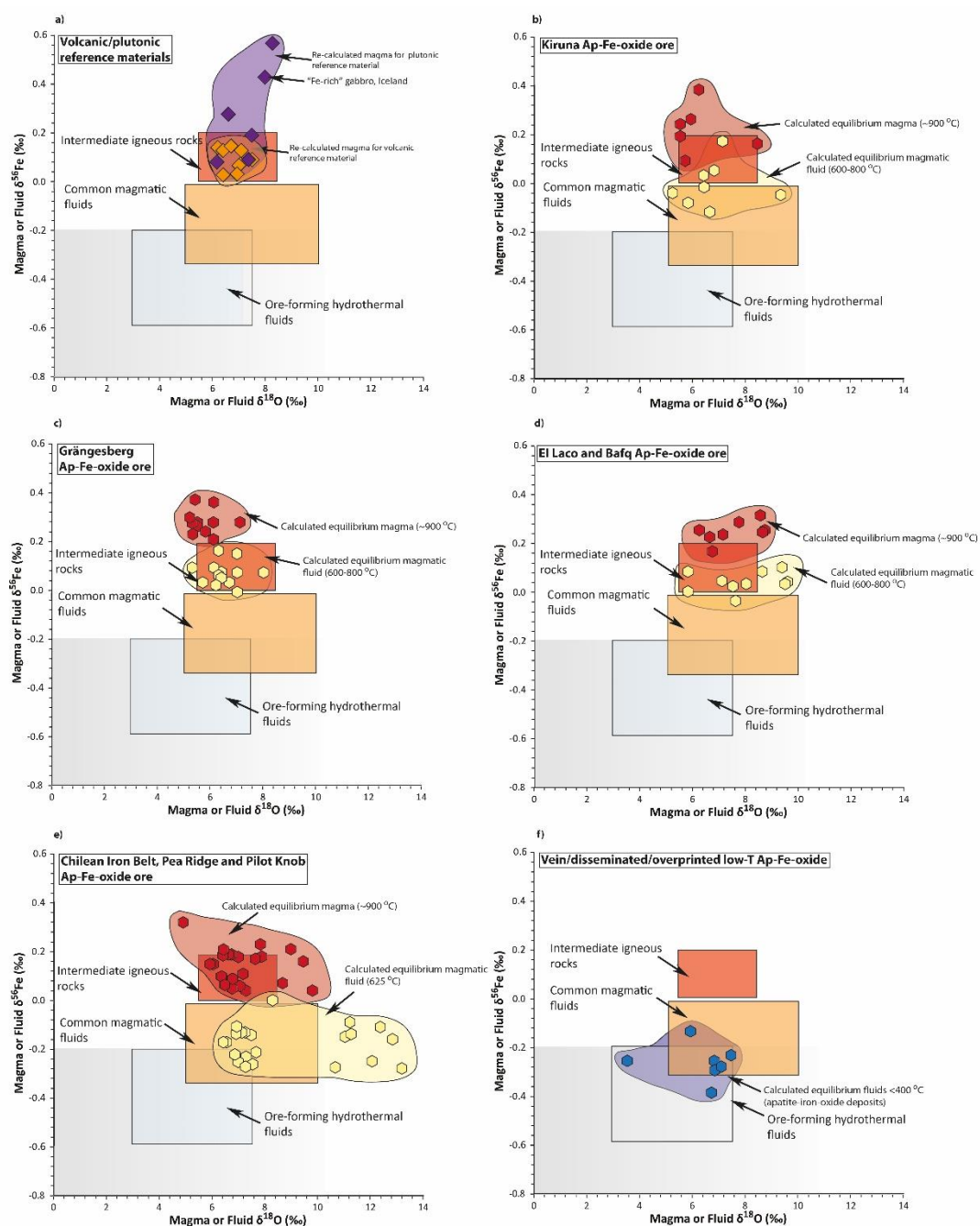
Supplementary Fig.1



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



Supplementary Fig. 2

Equilibrium peaa 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 ^{56}Fe 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 fluid sources only at low-temperatures (<400 °C), representing a secondary component under more hydrothermal conditions (f). For simplification only values with $\delta^{56}\text{Fe} \leq +0.6$ are plotted.