

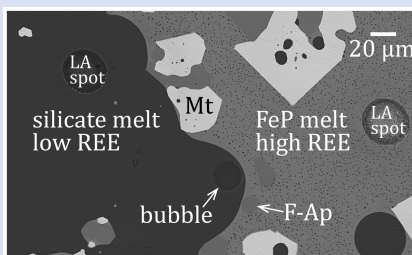
Silicate and iron phosphate melt immiscibility promotes REE enrichment

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Abstract



A surging rare earth element (REE) demand calls for finding new REE resources. Iron oxide-apatite (IOA) deposits have substantial REE potential, but their REE enrichment mechanisms remain uncertain, hindering REE exploration. The dominant process of IOA deposit formation is also hotly debated. Here, we use novel layered piston-cylinder experiments to address these questions. Seventeen magmatic FeP–Si immiscibility experiments, across 800–1150 °C, and at 0.4 and 0.8 GPa, reproduced many natural textural (*e.g.*, dendritic magnetite) and geochemical (*e.g.*, $D_{\text{Ti/Fe}}^{\text{LFeP-LSi}} < 1$) features of IOA deposits. Magmatic-hydrothermal fluid bubbles and iron oxide-bubble pairs formed as well. The results strongly support FeP–Si immiscibility as a controlling factor in IOA deposits, although not mutually exclusive with other models. Light REE partition into FeP liquids, preferentially to heavy REE, explaining the light REE enrichment of IOA deposits. Some $D_{\text{REE}}^{\text{LFeP-LSi}}$ values reach above 100, much higher than previously reported. Hence, any FeP rich rock that experienced magmatic Fe–Si immiscibility (*e.g.*, IOA, nelsonites) is expected to be light REE enriched and should be considered as a REE exploration target.

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Introduction

Rare earth elements (REEs; lanthanides + Y) are required for modern society to achieve a green energy transition. Iron oxide-apatite (IOA) deposits are globally distributed and formed from the Paleoproterozoic to the Pleistocene (Reich *et al.*, 2022; Yan and Liu, 2022). In IOA deposits, ubiquitous monazite was found in the ~1.88 Ga Kiruna deposit (Pålsson *et al.*, 2014; Yan *et al.*, 2023b), and a significant REE resource (>1 Mt rare earth metals) at Kiruna was recently reported (LKAB, 2023). In addition, iron oxide-phosphate (FeP) tephra containing monazite at the ~2 Ma El Laco deposit (Mungall *et al.*, 2018), REE-rich tailings in ~1.0 Ga deposits in the Adirondacks of New York (Taylor *et al.*, 2019), and a REE-rich breccia pipe containing ~12 wt. % REO at the ~1.4 Ga Pea Ridge deposit (Aleinikoff *et al.*, 2016) further demonstrate that IOA deposits typically contain substantial REE potential (Yan and Liu, 2022).

IOA deposits are related to magmatic rocks (*e.g.*, Troll *et al.*, 2019), yet exactly how they form is unclear. Previous studies suggest the involvement of iron-rich molten salts or hydrosaline liquids (*e.g.*, Bain *et al.*, 2020; Zeng *et al.*, 2024), magnetite-bubble flotation (*e.g.*, Knipping *et al.*, 2015), hydrothermal metasomatic replacement of lava flows (*e.g.*, Sillitoe and Burrows, 2002), with or without magmatic-hydrothermal fluids (*e.g.*, Rojas *et al.*, 2018). In addition, the immiscibility between iron oxide phosphate liquids and silicate magma (FeP–Si) is a commonly invoked process for the formation of IOA deposits (Naslund, 1983; Tornos

et al., 2016, 2024; Hou *et al.*, 2018; Keller *et al.*, 2022). However, the exact processes that control the ore-forming processes are hotly debated.

For FeP–Si liquid pairs, experimental studies showed a narrow miscibility gap in dry melts (*i.e.* the compositions of the silicate and FeP melts are closer; Fig. 1a), which widen with lower temperature, higher oxygen fugacity ($f\text{O}_2$), $a\text{H}_2\text{O}$, and higher F[−] or P₂O₅ contents (*e.g.*, Kamenetsky *et al.*, 2013; Hou *et al.*, 2018). For example, crustal inputs of S⁶⁺, F[−], H₂O, Fe and phosphate (*e.g.*, via sulfate-evaporites or ironstones) are suggested to widen the Fe–Si immiscibility width in IOA deposits (Lledo *et al.*, 2020; Pietruszka *et al.*, 2023; Tornos *et al.*, 2024). Preliminary work (*e.g.*, Schmidt *et al.*, 2006; Veksler *et al.*, 2006; Lester *et al.*, 2013) indicates that immiscible FeP melts incorporate more REEs than coexisting silicate melts (Fig. 1a). Reliable partition coefficients are only known for narrow immiscibility (nIM, Fig. 1a) conditions. Lester *et al.* (2013) obtained $D_{\text{REE}}^{\text{LFeP-LSi}}$ of ~3–40 at $D_{\text{SiO}_2}^{\text{LFeP-LSi}}$ of ~0.14–0.49 for moderate miscibility gaps (mIM). However, in the Lester *et al.* (2013) phosphate-bearing experiments, lower $D_{\text{SiO}_2}^{\text{LFeP-LSi}}$ values did not always correspond to higher $D_{\text{REE}}^{\text{LFeP-LSi}}$ values (Fig. 1a). For wide miscibility gaps (wIM), Lledo (2005) derived $D_{\text{Er}}^{\text{LFeP-LSi}}$ of 13, but a full set of REE partition coefficients for wide miscibility gaps is still undetermined. The main reasons are (1) few Fe–Si immiscibility experiments contain REEs (Yan and Liu, 2022), and (2) experimentally generated immiscible droplets are typically too small (unless a centrifuge

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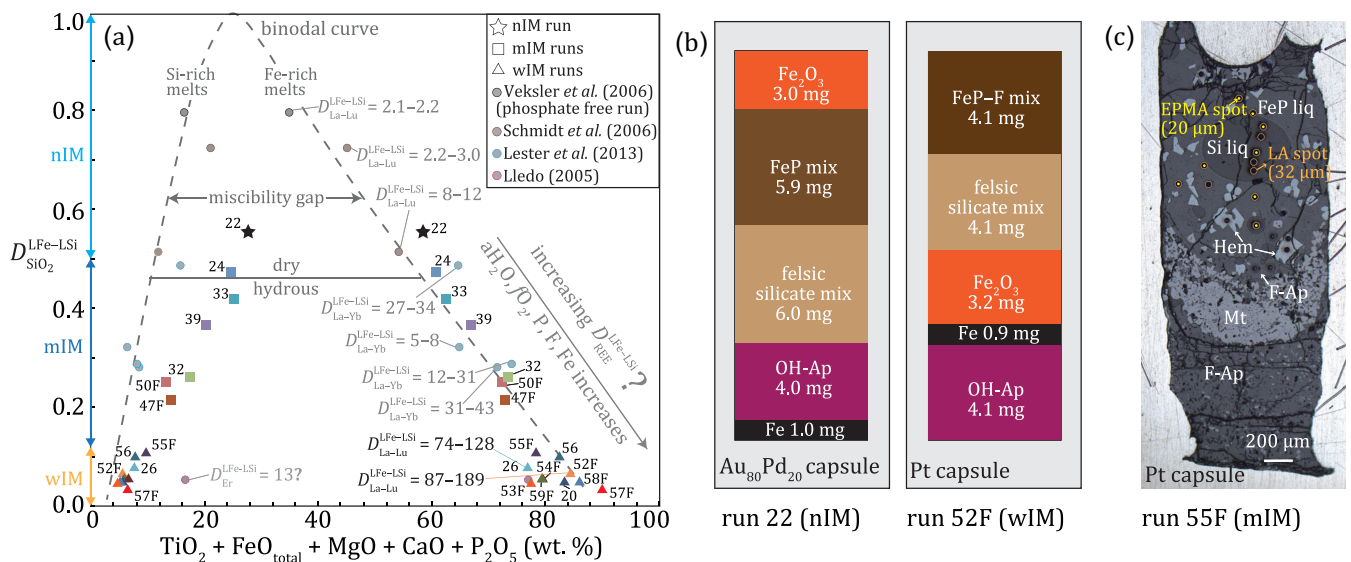


Figure 1 (a) Previous immiscibility experiments doped with trace elements, overlain by our new experiments (triangles, squares, and pentagons). Binodal curve and previous dry and hydrous experimental miscibility ranges are from [Kamenetsky et al. \(2013\)](#) and [Hou et al. \(2018\)](#). The width of the miscibility gap is affected by many variables (e.g., T , aH_2O , and others), and this projection captures the combined effect. (b) The layered set-up of representative experiments. (c) Reflected light image of experiment 55F, with analysis spots for Si and FeP liquids marked. Abbreviations: nIM, $0.5 \leq D_{SiO_2}^{LFe-LSi}$; mIM, $0.12 < D_{SiO_2}^{LFe-LSi} < 0.5$; wIM, $D_{SiO_2}^{LFe-LSi} \leq 0.12$; liq, liquid; F-Ap, fluorapatite; OH-Ap, hydroxyapatite; Mt, magnetite; Hem, hematite.

setup is used), complicating trace element analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) ([Schmidt et al., 2006](#); [Veksler et al., 2006](#)).

In this study, we address the origins and REE enrichment mechanisms of IOA deposits *via* a novel piston cylinder layered experimental design (Fig. 1b, c) followed by *in situ* analyses (Fig. 1c).

Methods

We conducted 17 FeP–Si immiscibility experiments over 800–1150 °C for 2–5 days (Fig. 1, Table 1), using a piston cylinder apparatus at the Research School of Earth Sciences, Australian National University (RSES, ANU). Starting materials included felsic silicate mix, FeP, and FeP–F compositions (Table S-1). Water was added in the form of solid hydroxides. These compositions were loaded into noble metal capsules (either Pt or AuPd) together with commercially available hydroxyapatite. Preliminary experiments using homogeneous starting materials resulted in tiny (mostly <5 μm) immiscible liquids. Therefore, subsequent experiments employed layered starting materials to obtain larger immiscible melts for easier geochemical analysis. Natural IOA deposits often contain coexisting hematite and magnetite ([Tornos et al., 2024](#); [Xu et al., 2024](#)). Therefore, we aimed to buffer oxygen fugacity at the magnetite–hematite (MH) oxygen buffer by adding layers of Fe³⁺O₃ and Fe⁰ powders, such that some hematite is reduced to magnetite *in situ*. Major and trace elements of immiscible liquids (three to eight points each) were measured using an electron probe microanalyser (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). Analytical spot sizes were typically 20 μm for EPMA and 32 μm for LA-ICP-MS.

Full details of the starting compositions, experimental procedures, geochemical analytical methods, resultant phases, their compositions, and calculated partition coefficients are available in the [Supplementary Information](#).

Assessment of Equilibrium

FeP and silicate liquids were observed in all experiments (Fig. 2). Immiscible liquid droplets were typically well separated (Figs. 1c, 2). Solid crystals were likewise well defined and sized from several to dozens of μm (Figs. 2, S-4). Liquid compositions are shown in [Figures 1 and 3](#) and in the [Supplementary Information](#). Typically, equilibrium between melts is confirmed by reversals, time-series comparisons, or by spatially consistent phase compositions within a single experimental capsule. Previous REE-bearing Fe–Si melt immiscibility experiments containing homogenised starting materials reached equilibrium in less than 1 h at ~1200 °C and 0.2 GPa ([Lester et al., 2013](#)). Here, we use spatially consistent compositions as an equilibrium indicator, because manually loaded miniscule powder layers are nearly impossible to consistently reproduce for a constant-composition reversal or time-series experiment. The ratio between the maximum and minimum contents of elements within liquid phase droplets, measured in different places (Figs. 1c, 2b, c, S-6, S-7) within the capsule, is used to show compositional consistency. For example, [Table 1](#) shows this ratio for Ce. The $Ce^{max/min}$ ratio across all FeP liquids ranges from 1.01 to 1.2 and is very close to unity (1.08 ± 0.07 , 1 s.d.) considering the measurement uncertainty of 0.01–0.1 (2 s.e.), demonstrating their homogeneous composition. For silicate liquids, the $Ce^{max/min}$ ratios are slightly more variable, presumably because of slower diffusion in the polymerised melt. Nevertheless, excluding the three most variable experiments (53F, 54F, and 59F), the $Ce^{max/min}$ ratio across all silicate liquids is 1.22 ± 0.26 (1 s.d.), again showing homogeneous compositions considering the measurement uncertainty of 0.01–0.3 (2 s.e.). Examples for additional consistent major and trace elements other than Ce are available in the [Supplementary Information](#). The overall consistency of major and trace elements ([Table 1](#), [Figs. S-6, S-7](#)), predictable temperature dependence of $D_{LFeP-LSi}^{LFeP-LSi}$ values for wIM and mIM runs ([Fig. S-8](#)), and deviation of final liquid elemental contents from starting compositions ([Fig. 3](#)) indicate adequate chemical

Table 1 Summary of experimental conditions and products.

No.	Starting layers' mass (mg) FeP, Si, Hem, Fe, OH-Ap	P GPa	T °C	Duration days	Resultant Phases	Imm. width	Ce of Si liq (max/min)	Ce of FeP liq (max/min)	Equilibrated?
58F [^]	4.4(F [^]), 4.3, 2.7, 1.5, 4.1	0.4	800'	5	Mt , F-Ap, whit, Si liq, FeP liq, FeP crystal	wIM	n.a.	n.a.	n.a.
57F	4.4(F), 4.3, 2.5, 1.7, 4.2	0.8	800'	5	Mt , F-Ap, Si liq, FeP liq, FeP crystal	wIM	n.a.	n.a.	n.a.
22	5.9, 6.0, 3.0, 1.0, 4.0	0.4	900	5	Mt , Si liq, FeP liq	nIM	1.1 ± 0.1 [#]	1.18 ± 0.04	Yes
53F	4.0(F), 4.0, 2.7, 1.3, 4.0	0.4	900'	4	Mt, Hem , F-Ap, q, Si liq, FeP liq, FeP crystal	wIM	5.5 ± 0.3	1.01 ± 0.04	No
26	4.8, 5.1, 3.3, 1, 5.1	0.8	900'	4	Hem , whit, Si liq, FeP liq	wIM	1.1 ± 0.1	1.1 ± 0.1	Yes
52F	4.4(F), 4.1, 3.2, 0.9, 4.1	0.8	900'	4	Mt , F-Ap, Si liq, FeP liq	wIM	1.3 ± 0.3	1.02 ± 0.08	Yes
20	4.9, 5.1, 3.7, 1.4, 5	0.4	1000'	3	Mt, Hem , OH-Ap, q, Si liq, FeP liq	wIM	n.a.	n.a.	n.a.
54F	4.3(F), 4.3, 3.3, 1.0, 4.1	0.4	1000'	3	Hem , F-Ap, Si liq, FeP liq	wIM	4.1 ± 0.2	1.04 ± 0.02	No
59F	4.2(F), 4.1, 2.6, 1.4, 4.1	0.4	1000'	3	Mt, Hem , F-Ap, q, Si liq, FeP liq	wIM	2.3 ± 0.2	1.03 ± 0.04	No
55F	4.6(F), 4.6, 3.5, 1.0, 4.5	0.8	1000'	3	Mt, Hem , F-Ap, Si liq, FeP liq	wIM	1.1 ± 0.1	1.1 ± 0.1	Yes
56	4.2, 4.2, 2.9, 1.2, 4.1	0.8	1000'	3	Mt , Whit, OH-Ap, Si liq, FeP liq	wIM	1.9 ± 0.18	1.05 ± 0.03	Yes
47F	4.2(F), 4, 3.2, 1.0, 4.0	0.4	1100'	2	Mt , F-Ap, Si liq, FeP liq	mIM	1.5 ± 0.1	1.08 ± 0.05	Yes
24	4.0, 4.0, 3.0, 1.1, 4.0	0.8	1100	4	Mt , OH-Ap, Si liq, FeP liq	mIM	1.03 ± 0.05	1.04 ± 0.08	Yes
50F	3.6 (F), 3.2, 2.4, 0.7, 3.2	0.8	1100'	2	Mt , F-Ap, Si liq, FeP liq	mIM	1.1 ± 0.1	1.03 ± 0.03	Yes
32	4.4, 5.5, 1.2, 3.5(Mt), 4.9	0.4	1150	3	Mt, Hem , whit, Si liq, FeP liq	mIM	1.07 ± 0.08	1.2 ± 0.1	Yes
33	4.2, 5.3, 0.8, 4(Mt), 4.7	0.8	1150	3	Hem , OH-Ap, Si liq, FeP liq	mIM	1.2 ± 0.1	1.04 ± 0.03	Yes
39	3.7, 5.6, 3.1, 1.5, 4.8	0.8	1150	3	Mt , whit, Si liq, FeP liq	mIM	1.05 ± 0.05	1.02 ± 0.03	Yes

Fe-oxide phases as an indicator for fO_2 are marked in bold.

[^] 'F' suffix indicates fluoride-bearing experiments by using the FeP–F composition (e.g., 58F, 52F, 50F).

' Two-step experiments: first heated to 1200 at 150 °C/min and held 20 min for melt homogenisation, then cooled to the target temperature at 40 °C/min (2.5–10 min) and held for 2–5 days.

[#] $C_{e}^{max/min}$ shown as max/min value ± 2 s.e., with 2 s.e. derived from measurement uncertainty.

Abbreviations: Mt, magnetite; OH-Ap, hydroxyapatite; F-Ap, fluorapatite; Hem, hematite; liq, liquid; whit, whitlockite; q, quartz; wIM, wide immiscibility ($D_{SiO_2}^{LFe-LSi} \leq 0.12$); nIM, narrow immiscibility ($0.5 \leq D_{SiO_2}^{LFe-LSi}$); mIM, moderate immiscibility ($0.12 < D_{SiO_2}^{LFe-LSi} < 0.5$); n.a., not applicable.

exchange and equilibrium between the two liquids, despite the layered experimental design. According to this criterion, immiscible liquids in nIM (22), mIM (24, 33, 39, 32, 50F, 47F) and most of the wIM (52F, 26, 55F, 56) runs reached or were very close (47F, 56) to equilibrium (Table 1). The immiscible liquids of experiments 53F, 54F and 59F showed complex semi-equilibrated conditions using this criterion (Figs. S-9, S-10). Three experiments (20, 57F, 58F) did not contain liquid phases with sufficient size for multiple analyses and were excluded from D calculations. However, their textures were informative.

In Fe–Si immiscibility experiments at 0.1 GPa and ~1000 °C by Hou *et al.* (2018)—which excluded REEs and contained homogenised starting materials—immiscible FeP liquids contained μ m-scale unidentified droplets (their Figs. 1a, d). We encountered similar textures. Rarely, small inclusions (either crystals or liquid droplets) interfered with EPMA and LA-ICP-MS analyses. For nIM run 22, μ m-sized silicate droplets were included within FeP liquids (Fig. 2d). For the mIM runs, FeP liquids contained μ m-sized minerals, silicate droplets, and bubbles (Fig. 2g–j). Similarly, for wIM runs, FeP liquids contained μ m-sized silicate droplets and bubbles (Fig. 2a–c, e, f). This cross-contamination resulted in some partition coefficients being closer to unity, making the real $D_{REE}^{LFe-LSi}$ values even higher than the already high values we are reporting (Fig. 3d, e). $D_{REE}^{LFe-LSi}$ values of our nIM and mIM runs (Fig. 3d, e) thereby represent lower bound values. For wIM experiments, their low-REE silicate droplets and bubbles were included in a high-REE FeP host, and there is an order of magnitude difference for most element concentrations between the two liquids. Therefore, we consider the contamination-driven effect of lowering $D_{REE}^{LFe-LSi}$ to be negligible

for wIM runs. In contrast to the common silicate inclusions within FeP liquids, the opposite was rare. Analysed regions of silicate liquids contained few, if any, FeP liquid droplet impurities (Fig. 2). When present, they were sufficiently large and rare (Fig. 2d, h) to facilitate straightforward analyses of silicate liquid without compromising measurements with spuriously high REE contents.

Five experiments resulted in obvious coexisting magnetite and hematite, and hence their fO_2 is buffered by MH, around 4.5 log units higher than the nickel–nickel oxide (NNO) buffer at our run conditions based on buffer curves determined using the online oxygen fugacity buffer calculator (<https://fo2.rses.anu.edu.au/fo2app/>, accessed 15 August 2024). Magnetite and hematite were distinguished based on contrasting optical properties in reflected light and Raman spectra (Figs. 1c, S-1). Other single-iron oxide experiments (Table 1) were likely to be close to the MH-buffer since they were prepared in a similar way, such that redox-sensitive elements were still expected to behave as if the runs were MH-buffered. The high oxidation state of the experiments prevented substantial Fe loss to the noble metal capsules, with typical values of ~2 wt. % Fe, and up to a maximum of ~8.4 wt. % Fe, alloyed with capsule materials at the capsule–experiment contact, whereas Fe was below detection limit further away (Fig. S-3).

Chemical Composition of Immiscible Liquids

Elemental systematics in our experiments are consistent with FeP–Si immiscibility during the formation of IOA deposits.

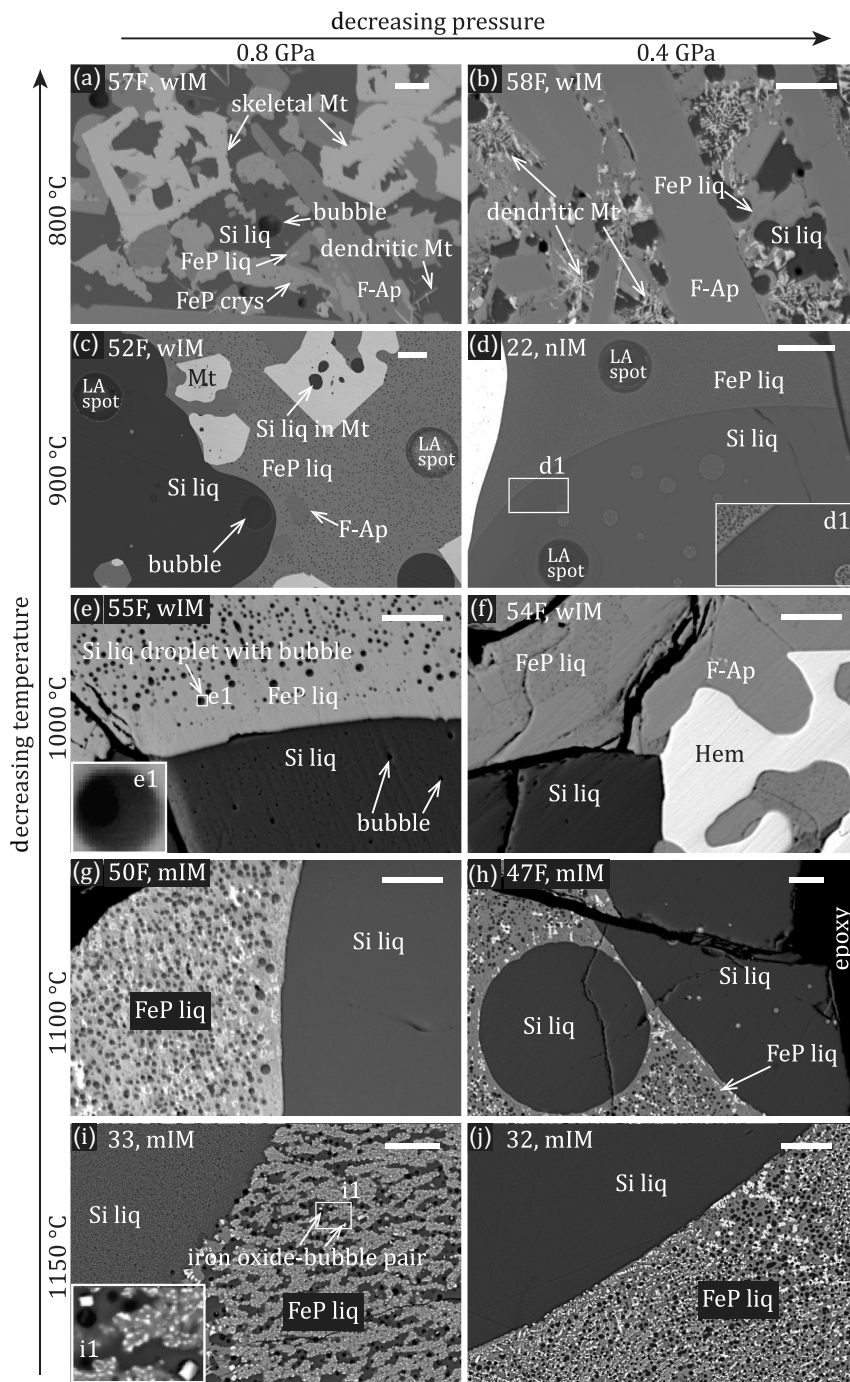


Figure 2 Backscattered images of mineral phases and melt textures from representative experiments. Silicate liquids contain $\mu\text{-sized}$ Fe-rich droplets at the highest temperatures and pressures (0.8 GPa, 1150 °C; i). FeP liquids contain (or mix with) minerals and silicate liquid droplets, but such contaminants decrease with IM degree, temperature, and pressure (i to c). FeP liquids crystallise substantially between 900 and 800 °C. Scale bar is 20 μm . Abbreviations: liq, liquid; Mt, magnetite; Hem, hematite; F-Ap, fluorapatite; crys, crystal.

We find that $D_{\text{F}}^{\text{LFeP-LSi}}$, $D_{\text{MgO}}^{\text{LFeP-LSi}}$, $D_{\text{CaO}}^{\text{LFeP-LSi}}$, and $D_{\text{P}_2\text{O}_5}^{\text{LFeP-LSi}}$ are all above 1 (Fig. 3, Table S-2), consistent with diopside ($\text{CaMgSi}_2\text{O}_6$), actinolite [$\text{Ca}_2(\text{Mg,Fe})_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$], and fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] as common minerals in IOA deposits. Trace element partition coefficients (Fig. 3) likewise support Th, Co, and V (likely as V^{5+}) enrichment in IOA deposits (Reich *et al.*, 2022; Tornos *et al.*, 2024). Despite $D_{\text{TiO}_2}^{\text{LFeP-LSi}} > 1$ (Fig. 3), $D_{\text{Ti/Fe}}^{\text{LFeP-LSi}}$ is below 1 (Fig. 3e), causing Ti/Fe of the FeP liquid to be lower than that of the silicate liquid. Thus, FeP–Si immiscibility dilutes Ti in the FeP liquid relative to Fe, consistent with the typically low Ti contents of IOA magnetite.

FeP–Si Immiscibility Textures

Our experiments show several textural interactions between felsic melt and Fe–Ca–P-rich phases. The experimental temperatures of 800–1150 °C are within the typical homogenisation temperature ranges for melt inclusions in IOA deposits (700–1145 °C; Xie *et al.*, 2019; Bain *et al.*, 2020; Pietruszka *et al.*, 2023; Xu *et al.*, 2024). We observed common silicate liquid droplets in FeP liquids (Fig. 2c, e–j). If such droplets were trapped during magnetite formation (Fig. 2c), then this potentially explains the Si-rich melt inclusions observed in magnetite from the El Laco massive ores (Tornos *et al.*, 2024) and quartz

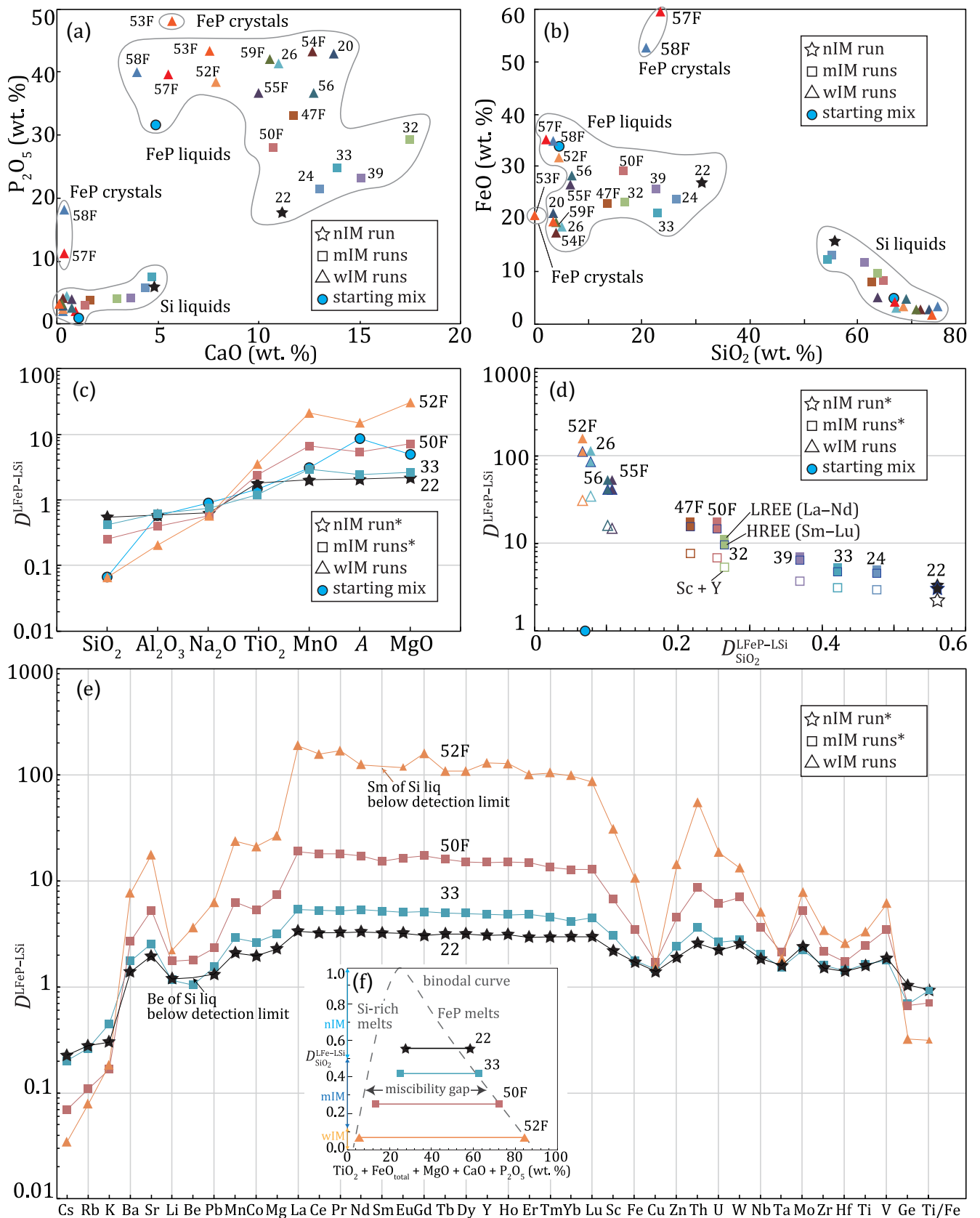


Figure 3 (a, b) $\text{CaO}-\text{P}_2\text{O}_5$ and $\text{SiO}_2-\text{FeO}_t$ plot of two liquids and FeP crystals; (c) major element partitioning of 11 runs (Table 1); and (e) trace element partitioning between immiscible Si- and FeP-rich melts of representative experiments, with the inset (f) showing immiscibility widths. Starting felsic silicate and FeP mix were plotted. *Partition coefficients might be closer to 1 due to impurities in FeP liquids for nIM and mIM runs (Fig. 2), see text for details.

inclusions in earliest-formed magnetite in the El Romel deposit (Rojas *et al.*, 2018). Moreover, imperfect separation of silicate liquid droplets for FeP liquids (Fig. 2) indicates that FeP melts may carry silicate even under wide immiscibility conditions where SiO₂ is nearly insoluble in FeP melts. This may lead to the formation of actinolite, pyroxene, or even quartz, consistent with their occurrence in IOAs (e.g., Nyström and Henríquez, 1994; Mungall *et al.*, 2018; Reich *et al.*, 2022), and particularly in their REE-rich portions (e.g., “Per Geijer” type ore bodies, e.g., Henry, Rektorn and Nukutus, in the Kiruna deposit; Nyström and Henríquez, 1994; LKAB, 2023), which are otherwise expected to be silicate-poor according to wIM equilibrium compositions. FeP liquid droplets surrounded by felsic liquid (Fig. 2d) resemble melt inclusions in feldspar from El Laco (Tornos *et al.*, 2016; Pietruszka *et al.*, 2023).

Skeletal or dendritic magnetite (Fig. 2a, b), generated by rapid quenching of 800 °C runs, remarkably similar to magnetite textures observed in the El Laco and Kiruna IOA deposits (Nyström and Henríquez, 1994), indicating that quenching (and, by implication, probable eruption) of FeP-rich melts occurred during IOA formation. Experiments 53F (0.4 GPa, 900 °C), 57F (0.8 GPa, 800 °C), and 58F (0.4 GPa, 800 °C) yielded FeP liquids and FeP crystals (Figs. 2a, b, 3a, b, S-4), similar to two unidentified FeP phases of El Laco (Xie *et al.*, 2019).

These textural similarities (Fig. S-11) and temperature overlaps suggest our experimental scenarios (narrow to wide FeP–Si immiscibility) may accurately mimic natural processes. The experiments also contain bubbles and iron oxide–bubble pairs indicative of hydrothermal fluid saturation (e.g., Fig. 2c, e, i). Sulfate–evaporite assimilation is hypothesised to be conducive to FeP–Si immiscibility (Pietruszka *et al.*, 2023; Tornos *et al.*, 2024). Iron-bearing hydrosaline liquids, recently proposed to be important for IOA formation (Zeng *et al.*, 2024), were also observed to coexist with immiscible FeP- and Si-rich liquids at El Laco deposit (Pietruszka *et al.*, 2023). Our suggested processes do not preclude—and are in fact compatible with—other proposed processes, such as Fe-rich magmatic hydrothermal fluids (Rojas *et al.*, 2018), iron oxide–bubble pairs (Knipping *et al.*, 2015), Fe-bearing hydrosaline liquids (Zeng *et al.*, 2024), and possibly evaporite assimilation (Pietruszka *et al.*, 2023).

REE Enrichment in IOAs and Fe-REE Associations

Figure 3c–e shows $D_{\text{LREE}}^{\text{LFeP-LSi}}$ values of different immiscibility widths, where the gap widens with evolution or cooling (Fig. 1). The general trend is that, with a wider miscibility gap, REE partition more strongly into FeP relative to silicate melts. Our results show that $D_{\text{LREE}}^{\text{LFeP-LSi}}$ and $D_{\text{HREE}}^{\text{LFeP-LSi}}$ can reach above 100 for wide immiscibility (wIM in Fig. 3d, e), so the previously reported $D_{\text{FeP}}^{\text{LFeP-LSi}}$ of 13 for wide immiscibility (Lledo, 2005) is unrealistically low. We find that $D_{\text{LREE}}^{\text{LFeP-LSi}}$ values are higher than $D_{\text{HREE}}^{\text{LFeP-LSi}}$, regardless of immiscibility width (Fig. 3d), similar to the findings of Lester *et al.* (2013). The ubiquitous enrichment of LREE relative to HREE in IOA deposits is consistent with this finding and indicates FeP–Si immiscibility is likely a dominant process in IOA deposit formation. Magnetite does not host significant REE; hence, REE in IOA deposits are mainly hosted in phosphates, such as apatite, monazite, and xenotime (Yan and Liu, 2022). Generally, IOA deposits with large iron tonnages and highly evolved portions of IOA deposits (e.g., Pea Ridge, Kiruna, Carmen, and the Fresia deposits) should have higher phosphate contents, and thereby higher REE potential (Yan *et al.*, 2023a).

Other FeP-rich rocks understood to be related to magmatic Fe–Si immiscibility (e.g., nelsonites, Fe–Ti–V deposit such as Panzhihua) experienced a lower immiscibility degree (Lledo *et al.*, 2020) and therefore REE in their Fe-rich parts were less enriched compared to IOA deposits.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2436>.



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References

- ALEINIKOFF, J.N., SELBY, D., SLACK, J.F., DAY, W.C., PILLERS, R.M., *et al.* (2016) U–Pb, Re–Os, and Ar/Ar geochronology of rare earth element (REE)-rich breccia pipes and associated host rocks from the Mesoproterozoic Pea Ridge Fe–REE–Au deposit, St. Francois Mountains, Missouri. *Economic Geology* 111, 1883–1914. <https://doi.org/10.2113/econgeo.111.8.1883>
- BAIN, W.M., STEELE-MACINNIS, M., LI, K., LI, L., MAZDAB, F.K., MARSH, E.E. (2020) A fundamental role of carbonate–sulfate melts in the formation of iron oxide–apatite deposits. *Nature Geoscience* 13, 751–757. <https://doi.org/10.1038/s41561-020-0635-9>
- HOU, T., CHARLIER, B., HOLTZ, F., VEKSLER, I., ZHANG, Z., *et al.* (2018) Immiscible hydrous Fe–Ca–P melt and the origin of iron oxide–apatite ore deposits. *Nature Communications* 9, 1415. <https://doi.org/10.1038/s41467-018-03761-4>
- KAMENETSKY, V.S., CHARLIER, B., ZHITOVA, L., SHARYGIN, V., DAVIDSON, P., FEIG, S. (2013) Magma chamber–scale liquid immiscibility in the Siberian Traps represented by melt pools in native iron. *Geology* 41, 1091–1094. <https://doi.org/10.1130/g34638.1>
- KELLER, T., TORNOS, F., HANCHAR, J.M., PIETRUSZKA, D.K., SOLDATI, A., *et al.* (2022) Genetic model of the El Laco magnetite–apatite deposits by extrusion of iron-rich melt. *Nature Communications* 13, 6114. <https://doi.org/10.1038/s41467-022-33302-z>
- KNIPPING, J.L., BILENKER, L.D., SIMON, A.C., REICH, M., BARRA, F., *et al.* (2015) Giant Kiruna-type deposits form by efficient flotation of magmatic magnetite suspensions. *Geology* 43, 591–594. <https://doi.org/10.1130/g36650.1>
- LESTER, G.W., KYSER, T.K., CLARK, A.H., LAYTON-MATTHEWS, D. (2013) Trace element partitioning between immiscible silicate melts with H₂O, P, S, F, and Cl.

- Chemical Geology* 357, 178–185. <https://doi.org/10.1016/j.chemgeo.2013.08.021>
- LKAB (2023) *Europe's largest deposit of rare earth metals is located in the Kiruna area*. Press release, 12 January 2023, Luossavaara Kiirunavaara AB, Luleå, Sweden. <https://mb.cision.com/Main/11419/3696865/1777621.pdf>
- LLEDO, H.L. (2005) *Experimental studies on the origin of iron deposits; and mineralization of Sierra La Bandera, Chile*. Ph.D. thesis, State University of New York at Binghamton.
- LLEDO, H.L., NASLUND, H.R., JENKINS, D.M. (2020) Experiments on phosphate–silicate liquid immiscibility with potential links to iron oxide apatite and nelsonite deposits. *Contributions to Mineralogy and Petrology* 175, 111. <https://doi.org/10.1007/s00410-020-01751-8>
- MUNGALL, J.E., LONG, K., BRENNAN, J.M., SMYTHE, D., NASLUND, H.R. (2018) Immiscible shoshonitic and Fe-P-oxide melts preserved in unconsolidated tephra at El Laco volcano, Chile. *Geology* 46, 255–258. <https://doi.org/10.1130/g39707.1>
- NASLUND, H.R. (1983) The effect of oxygen fugacity on liquid immiscibility in iron-bearing silicate melts. *American Journal of Science* 283, 1034–1059. <https://doi.org/10.2475/ajs.283.10.1034>
- NYSTRÖM, J.O., HENRIQUEZ, F. (1994) Magmatic features of iron ores of the Kiruna type in Chile and Sweden; ore textures and magnetite geochemistry. *Economic Geology* 89, 820–839. <https://doi.org/10.2113/gsecongeo.89.4.820>
- PÄLSSON, B.I., MARTINSSON, O., WANHAINEN, C., FREDRIKSSON, A. (2014) Unlocking rare earth elements from European apatite-iron ores. *Proceedings of the 1st European Rare Earth Resources Conference*, 4–7 September 2014, Milos, Greece, 211–220. <https://eurare.org/docs/eres2014/fifthSession/BertilPalsson.pdf>
- PIETRUSZKA, D.K., HANCHAR, J.M., TORNOS, F., WIRTH, R., GRAHAM, N.A., *et al.* (2023) Magmatic immiscibility and the origin of magnetite-(apatite) iron deposits. *Nature Communications* 14, 8424. <https://doi.org/10.1038/s41467-023-43655-8>
- REICH, M., SIMON, A.C., BARRA, F., PALMA, G., HOU, T., BILENKER, L.D. (2022) Formation of iron oxide–apatite deposits. *Nature Reviews Earth & Environment* 3, 758–775. <https://doi.org/10.1038/s43017-022-00335-3>
- ROJAS, P.A., BARRA, F., DEDITIUS, A., REICH, M., SIMON, A., *et al.* (2018) New contributions to the understanding of Kiruna-type iron oxide-apatite deposits revealed by magnetite ore and gangue mineral geochemistry at the El Romeral deposit, Chile. *Ore Geology Reviews* 93, 413–435. <https://doi.org/10.1016/j.oregeorev.2018.01.003>
- SCHMIDT, M.W., CONNOLLY, J.A.D., GÜNTHER, D., BOGAERTS, M. (2006) Element partitioning: the role of melt structure and composition. *Science* 312, 1646–1650. <https://doi.org/10.1126/science.1126690>
- SILLITOE, R.H., BURROWS, D.R. (2002) New field evidence bearing on the origin of the El Laco magnetite deposit, northern Chile. *Economic Geology* 97, 1101–1109. <https://doi.org/10.2113/gsecongeo.97.5.1101>
- TAYLOR, R.D., SHAH, A.K., WALSH, G.J., TAYLOR, C.D. (2019) Geochemistry and geophysics of iron oxide-apatite deposits and associated waste piles with implications for potential rare earth element resources from ore and historical mine waste in the eastern Adirondack highlands, New York, USA. *Economic Geology* 114, 1569–1598. <https://doi.org/10.5382/econgeo.4689>
- TORNOS, F., VELASCO, F., HANCHAR, J.M. (2016) Iron-rich melts, magmatic magnetite, and superheated hydrothermal systems: The El Laco deposit, Chile. *Geology* 44, 427–430. <https://doi.org/10.1130/g37705.1>
- TORNOS, F., HANCHAR, J.M., STEELE-MACINNIS, M., CRESPO, E., KAMENETSKY, V.S., CASQUET, C. (2024) Formation of magnetite-(apatite) systems by crystallizing ultrabasic iron-rich melts and slag separation. *Mineralium Deposita* 59, 189–225. <https://doi.org/10.1007/s00126-023-01203-w>
- TROLL, V.R., WEIS, F.A., JONSSON, E., ANDERSSON, U.B., MAJIDI, S.A., *et al.* (2019) Global Fe-O isotope correlation reveals magmatic origin of Kiruna-type apatite-iron-oxide ores. *Nature Communications* 10, 1712. <https://doi.org/10.1038/s41467-019-09244-4>
- VEKSLER, I.V., DORFMAN, A.M., DANYUSHEVSKY, L.V., JAKOBSEN, J.K., DINGWELL, D.B. (2006) Immiscible silicate liquid partition coefficients: implications for crystal-melt element partitioning and basalt petrogenesis. *Contributions to Mineralogy and Petrology* 152, 685–702. <https://doi.org/10.1007/s00410-006-0127-y>
- XIE, Q., ZHANG, Z., HOU, T., CHENG, Z., CAMPOS, E., *et al.* (2019) New insights for the formation of kiruna-type iron deposits by immiscible hydrous Fe-P melt and high-temperature hydrothermal processes: evidence from El Laco deposit. *Economic Geology* 114, 35–46. <https://doi.org/10.5382/econgeo.2019.4618>
- XU, X., BAIN, W.M., TORNOS, F., HANCHAR, J.M., LAMADRID, H.M., *et al.* (2024) Magnetite-apatite ores record widespread involvement of molten salts. *Geology* 52, 417–422. <https://doi.org/10.1130/g51887.1>
- YAN, S., LIU, W. (2022) Rare earth elements in the iron-oxide apatite (IOA) deposit: insights from apatite. *International Geology Review* 64, 3230–3247. <https://doi.org/10.1080/00206814.2022.2028198>
- YAN, S., WAN, B., ANDERSSON, U.B. (2023a) Apatite age and composition: A key to the geological history of the Malmberget Iron-Oxide-Apatite (IOA) deposit and the region. *Journal of Geochemical Exploration* 252, 107267. <https://doi.org/10.1016/j.jexplo.2023.107267>
- YAN, S., WAN, B., ANDERSSON, U.B. (2023b) Hydrothermal circulation at 1.8 Ga in the Kiruna area, northern Sweden, as revealed by apatite geochemical systematics. *Precambrian Research* 395, 107151. <https://doi.org/10.1016/j.precamres.2023.107151>
- ZENG, L.-P., ZHAO, X.-F., SPANDLER, C., MAVROGENES, J.A., MERNAGH, T.P., *et al.* (2024) The role of iron-rich hydrosaline liquids in the formation of Kiruna-type iron oxide–apatite deposits. *Science Advances* 10, eadk2174. <https://doi.org/10.1126/sciadv.adk2174>