



Integrated O, Fe, and Ti isotopic analysis elucidates multiple metal and fluid sources for magnetite from the Ernest Henry Iron oxide copper gold (IOCG) Deposit, Queensland, Australia

Christopher Emproto^{a,*}, Ryan Mathur^b, Adam Simon^a, Ilya Bindeman^c, Linda Godfrey^d,
Courtney Dhnaram^e, Vladimir Lisitsin^e

^a University of Michigan, Ann Arbor, MI, USA

^b Juniata College, Huntingdon, PA, USA

^c University of Oregon, Eugene, OR, USA

^d Rutgers University, New Brunswick, NJ, USA

^e Geological Survey of Queensland, City East, Queensland, Australia

ARTICLE INFO

Keywords:

IOCG
Ernest Henry
O isotopes
Fe isotopes
Ti isotopes

ABSTRACT

Iron oxide copper gold (IOCG) deposits are globally important sources of Cu; however, their origins remain poorly understood with respect to the metal and fluid sources involved in their formation. In this work, we utilize integrated Fe, Ti, and O isotopic data for magnetite to trace major metal and fluid inputs for the Proterozoic-aged Ernest Henry IOCG deposit—the largest known IOCG deposit in the Cloncurry District, Queensland, Australia. Magnetite separates from ore stage and pre-ore biotite-magnetite (bt-mgt) and magnetite-actinolite (mgt-act) alteration assemblages from Ernest Henry were analyzed for their O, Fe, and Ti isotope abundances, reported as $\delta^{18}\text{O}$ (VSMOW), $\delta^{56}\text{Fe}$ (IRMM-14), and $\delta^{49}\text{Ti}$ (OL-Ti). Select magnetite samples were also analyzed for ^{17}O (reported as $\Delta^{17}\text{O}_{0.5305}$) and range from -0.118 to -0.056‰ —suggesting evaporitic input. The $\delta^{18}\text{O}$ values from ore stage ($+1.57$ to $+7.36\text{‰}$), bt-mgt ($+0.34$ to $+5.68\text{‰}$), and mgt-act ($+1.68$ to $+2.10\text{‰}$) samples are consistent with a magmatic-hydrothermal origin for ore and pre-ore mineralizing fluids at Ernest Henry; non-magmatic $\delta^{18}\text{O}$ values $>c. 5\text{‰}$ may be explained through localized carbonate wall rock assimilation. Despite this, $\delta^{56}\text{Fe}$ values for ore stage (-0.50 to $+0.33\text{‰}$), bt-mgt (-0.65 to $+0.38\text{‰}$), and mgt-act (-0.26 to $+0.30\text{‰}$) magnetite are generally isotopically lighter than the accepted range ($c. +0.06$ to $+0.49\text{‰}$) for igneous and magmatic-hydrothermal magnetite and exhibit a relatively large range of $c. 1\text{‰}$, suggesting Fe source mixing within the deposit. Ore stage magnetite $\delta^{49}\text{Ti}$ (-1.64 to $+3.79\text{‰}$; avg: $+1.49\text{‰}$; $2\sigma = 2.63\text{‰}$) compositions are generally higher and more variable than either the bt-mgt (-0.44 to $+1.49\text{‰}$; avg: $+0.62\text{‰}$; $2\sigma = 1.13\text{‰}$) or mgt-act ($+0.27$ to $+1.89\text{‰}$; avg: $+1.05\text{‰}$; $2\sigma = 1.56\text{‰}$) and suggest that Ti isotope fractionation occurred due to differential mobility in the fluid. The data are best explained by models invoking both magmatic and non-magmatic metal and fluid input. Fluid flow channeled between the footwall and hanging wall shear zones introduced non-magmatic Fe that may have been leached from local mafic units by magmatic-hydrothermal fluids, resulting in neoformed and regeneratively replaced magnetite with magmatic $\delta^{18}\text{O}$, but non-magmatic $\delta^{56}\text{Fe}$ values during pre-ore alteration. These fluids may have mixed with Fe-poor evaporitic fluids prior to magnetite formation. Later magmatic Fe and O contributions during ore stage mineralization resulted in magnetite with variable $\delta^{56}\text{Fe}$ and irresolvable $\delta^{18}\text{O}$ overprinting. Ernest Henry is the first known example of an IOCG deposit with a major leached metal component identified through metal stable isotope geochemistry.

1. Introduction

Sustainable supplies of elements including Fe, Cu, rare earth

elements (REE), and other metals are required to build and maintain renewable energy in infrastructure. The demand for Cu alone is expected to increase by as much as 350 % by 2050 and finding new sources of Cu is

* Corresponding author.

E-mail address: cemproto@umich.edu (C. Emproto).

<https://doi.org/10.1016/j.oregeorev.2022.105170>

Received 26 May 2022; Received in revised form 14 October 2022; Accepted 24 October 2022

Available online 31 October 2022

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paramount to closing a potential supply and demand gap (Elshkaki et al., 2016). The Iron Oxide Copper Gold (IOCG) class of mineral deposits is an increasingly significant source of Cu and has strong exploration potential as new geochemical vectoring tools are developed and the origin of these deposits becomes clearer (Hitzman et al., 1992; Sillitoe, 2003; Barton, 2014). Deposits sharing the physical and geochemical characteristics of the IOCG class may be broadly described as hydrothermal, structurally controlled Fe oxide ($\pm$ Cu sulfide) mineralization enveloped by extensive Na-Ca-K alteration haloes and exhibiting characteristic elemental enrichment suites comprising Fe oxides (including magnetite and/or hematite), Cu, Au, Ag, REE, P, U, and Co (Hitzman et al., 1992; Sillitoe, 2003; Barton, 2014). Some workers consider iron oxide apatite (IOA)—or “Kiruna type”—deposits to be a subset within the IOCG clan, whereas others propose that IOA systems represent the deeper, hotter roots of IOCG deposits or that IOCG deposits form from the overprinting of IOA deposits by Cu-rich fluids (Barton, 2014; Simon et al., 2018; Rodriguez-Mustaza et al., 2020; del Real et al., 2021). Analogues in the Cretaceous Chilean Iron Belt suggest that IOCG deposits can form in continental arc environments associated with subduction zone magmatism; however, other tectonic environments are believed to be represented in the global IOCG suite—hinting that there may be multiple geologic pathways to IOCG-style mineralization and potentially inhibiting a “mineral systems” approach (Barton, 2014; Rodriguez-Mustaza et al., 2020; Groves et al., 2022).

While the Cu-Au mineralization in IOCG systems is generally agreed upon to be hydrothermal, no consensus exists regarding the source(s) of their contained metals and their mobilizing fluids (Barton, 2014). This work utilizes a novel isotopic approach to test proposed IOCG formation models using spatially referenced samples of magnetite from the Proterozoic Ernest Henry deposit in the Cloncurry District, Queensland, Australia. The source of ore fluids or the Cloncurry IOCG deposits remains the topic of extensive debate and at least four broadly defined fluid sources are proposed for these systems including magmatic-hydrothermal fluids, basinal brines, and combinations of these with sedimentary pore fluids and metamorphic fluids (Barton and Johnson, 1996; Baker et al., 2001, 2008; Cave et al., 2018; Fisher and Kendrick, 2008; Schlegel et al., 2017, 2018). In the magmatic-hydrothermal model, the fluids and metals are sourced from an evolving silicate magma in the shallow crust (Hitzman et al., 1992; Sillitoe, 2003; Chiaradia et al., 2006; Pollard, 2006; Schlegel et al., 2017; Simon et al., 2018). The fluids in the basinal brine model comprise hypersaline connate fluids that scavenge metals from the shallow crust; a nearby intrusion provides heat to drive the convection of these fluids (Oreskes and Einaudi, 1992; Haynes et al., 1995; Barton and Johnson, 1996; Bastrakov et al., 2007; Xavier et al., 2008). Fluids in the sedimentary pore fluid model consist of sedimentary pore water potentially mixed with metamorphic-derived fluids (Fisher and Kendrick, 2008; Schlegel et al., 2018). The metamorphic fluid model proposes that devolatilization during regional prograde metamorphism of the local volcanic and sedimentary stratigraphy resulted in rock-bounded brines (Benavides et al., 2007; Kendrick et al., 2007; Fisher and Kendrick, 2008). Some models propose multiple fluid sources or precipitating Fe and Cu-Au mineralization with or without fluid mixing as the mineralization trigger (Baker et al., 2008; Fisher and Kendrick, 2008; Cave et al., 2018).

Hypothesized fluid compositions for Cloncurry IOCG deposits span from hot and hypersaline brines to cooler and less saline Cu-U-rich aqueous solutions (Williams et al., 2001; Baker et al., 2008; Torresi et al., 2012; Schlegel et al., 2018). A prevailing hypothesis of the ore fluid chemistry proposes that Cu-Au mineralization derived from the infiltration of hypersaline, NaCl- and CO₂-rich brines with relatively low (< c. 200 ppm) Cu concentrations at pressures of c. 1.3–3.7 kbar (Baker et al., 2008; Rusk et al., 2010). Although low (c. 150 ppm) Cu concentrations are consistent with hypotheses suggesting a crustally-derived fluid, in situ analyses have measured Cu concentrations of c. 3000 ppm in some fluid inclusions interpreted to be coeval with Cu-Au mineralization in Cloncurry IOCG deposits and may alternatively

suggest that Cu-poor fluid inclusions could simply be pre-mineralization fluid or post-mineralization “spent” fluid (Baker et al., 2008; Rusk et al., 2010; Schlegel et al., 2021). A clear understanding of the fluids is clouded by the presence of multiple different types of fluid inclusions including those with magmatic-hydrothermal and evaporitic signatures, respectively (Baker et al., 2008). The heterogeneous fluid compositions and provenance signatures within individual deposits have spurred some to hypothesize fluid mixing as an important process in IOCG formation (Fisher and Kendrick, 2008; Baker et al., 2008).

Here we present O, Fe, and Ti stable isotope data for magnetite from the world-class Ernest Henry IOCG deposit and integrate our data with existing spatial datasets from the deposit to evaluate existing models explaining the mineralization history and the source of successive fluid generations at Ernest Henry. Recently, Fe and O stable isotope pairs have been important evidence in inferring magmatic metal and fluid sources for magnetite from IOA and IOCG deposits (Bilenker et al., 2016; Childress et al., 2016, 2020a, b; Troll et al., 2019; Rodriguez-Mustaza et al., 2020, 2022). While O isotope compositions are sensitive to secondary alteration from hydrothermal and supergene fluids, Fe isotopic compositions are considered more steadfast under such conditions and are considered as a more reliable indicator of metal provenance (Bilenker et al., 2016; Troll et al., 2019). Like Fe, Ti isotope signatures are also thought to resist hydrothermal and metamorphic overprinting due to the low solubility of Ti and common Ti-bearing minerals in most fluids. In presenting the first published Ti isotope measurements from a mineralized system, we demonstrate that the above assumption is flawed, providing insight into Ti isotope fractionation in ligand-rich hydrothermal systems and opening the door for Ti isotopes as a vectoring method. The stable isotope data presented herein provide the opportunity to trace metal and fluid sources, fluid mixing, and the assimilation of host rock components via 3D spatial analysis to develop a clearer picture regarding the metallogeny and mineralization history of the Ernest Henry IOCG deposit.

2. Geologic background

The Ernest Henry deposit is a blind IOCG-style Cu-Au deposit hosted in southeast-dipping, sheared Proterozoic metavolcanic rocks of the Eastern Succession of the Mount Isa Inlier, northwest Queensland, Australia (Fig. 1) (Twyler, 1997; Ryan, 1998; Austin et al., 2021b). The Cloncurry District in the Eastern Succession hosts a series of IOCG deposits including Starra and Mount Elliott, however, Ernest Henry is the largest known IOCG deposit in the district and the second largest IOCG deposit in Australia (following Olympic Dam) with an initial resource estimate of 167 Mt of ore grading 1.1 % Cu and 0.54 g/t Au (Lilly et al., 2017; Ryan, 1998; Hutton et al., 2012). First discovered in 1991 through drilling of a magnetic anomaly target, the deposit has been operated commercially since 1998 (Webb and Rowston, 1995; Ryan, 1998; Schlegel et al., 2021). Economic Cu-Au mineralization at Ernest Henry occurs in a south-plunging pipe-like structure located between two southeast-dipping shear zones: the dotwall shear zone in the northwest and the hanging wall shear zone in the southeast (Webb and Rowston, 1995; Austin et al., 2021a, b). The Eastern Succession consists of volcanic and metamorphosed volcanic, evaporite, and carbonate units that were episodically deposited into an intracontinental rift basin between c. 1890–1610 Ma (Blake, 1987; Blake and Stewart, 1992; Foster and Austin, 2008). The metamorphosed volcanic suite hosting IOCG mineralization at Ernest Henry consists of a series of andesitic to dacitic lavas with minor basaltic units erupted as the temporal and petrologic equivalents of the c. 1745 Ma Mount Fort Constantine metavolcanic suite (Page and Sun, 1998). These rocks were later deformed during the Isan Orogeny, with peak metamorphic conditions attaining greenschist to amphibolite facies and undergoing regional sodic-calcic alteration due to structurally-channeled 400–500 °C brines during E-W shortening at c. 1585 Ma (de Jong and Williams, 1995). Economic Cu-Au mineralization at Ernest Henry likely occurred at c. 1530 Ma associated with

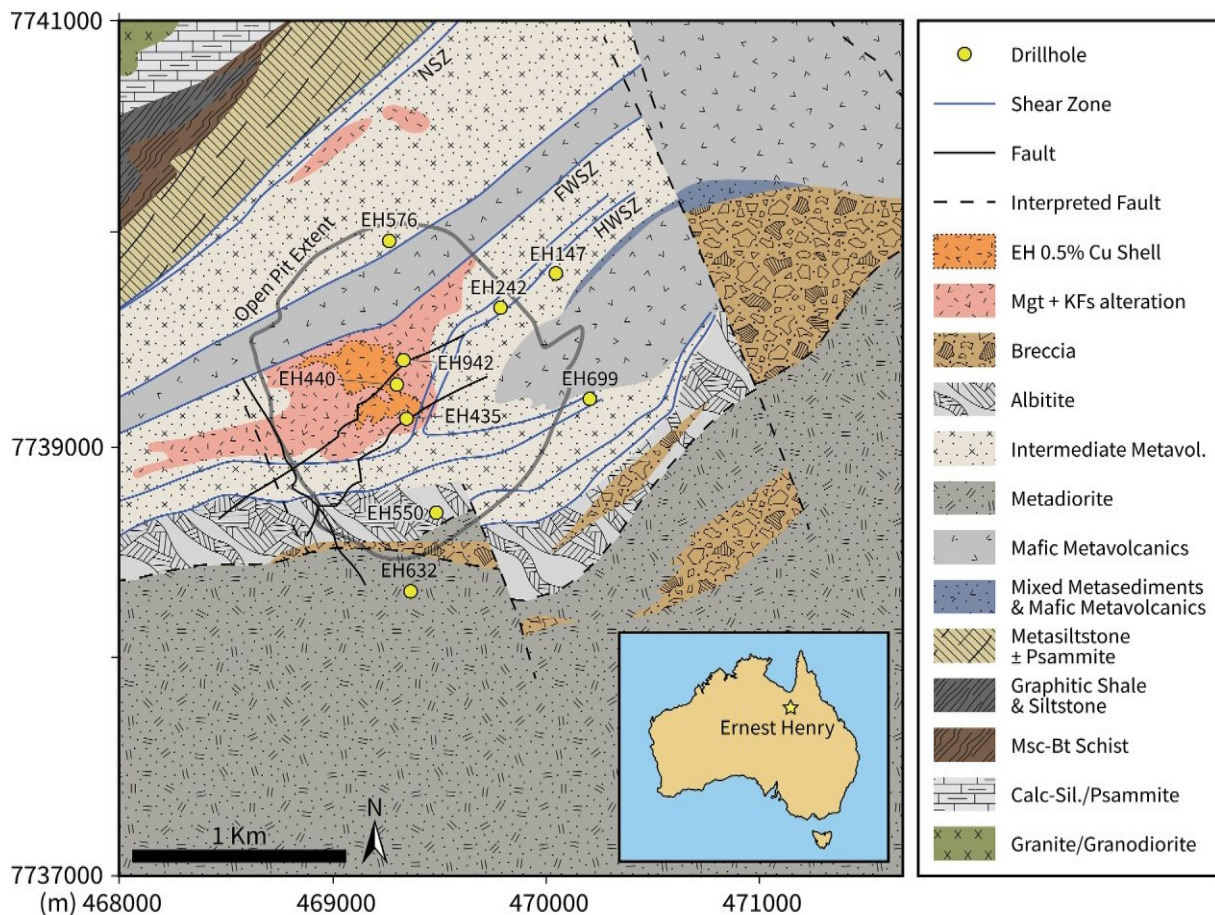


Fig. 1. Plan view of the subsurface geology of the Ernest Henry IOCG deposit. The extent of the deposit is represented by the 0.5% Cu shell (EH 0.5% Cu Shell). Modified after O'Brien (2016). FWSZ: Footwall shear zone; HWSZ: Hanging wall shear zone; NSZ: North shear zone.

the intrusion of A-type granitoids of the Williams-Naraku suite in the Mount Isa Inlier (Ryan, 1998; Belousova et al., 2001; Mark et al., 2006b; Cave et al., 2018).

Magnetite at Ernest Henry occurs within several mineralogically distinct assemblages including biotite-magnetite (bt-mgt), magnetite-actinolite (mgt-act), and ore stage assemblages. Bt-mgt, K-Mn-Fe, and mgt-act alteration directly preceded ore mineralization, as the reported U-Pb titanite age interpreted to represent bt-mgt alteration ($1514 \pm 11/-8$ Ma) is nearly within error of the interpreted age of regional A-type granitic magmatism (c. 1530 Ma) inferred to be the source of Cu in the district (Mark et al., 2006b). Biotite-magnetite alteration was subsequently overprinted by K-Mn-Fe alteration consisting of additional biotite and magnetite alongside K-feldspar, carbonates, and minor garnet (Schlegel et al., 2018). The timing of mgt-act alteration is unclear, but veins of magnetite-actinolite appear to cross-cut areas of bt-mgt mineralization in deeper portions of the orebody (Ernest Henry Mining, personal communication 2022). Minor chalcopyrite occurs within the mgt-act mineralization, which may indicate that mgt-act alteration represents early Cu mineralization at Ernest Henry (Mark et al., 2006b; Schlegel et al., 2021). During later ore stage mineralization, magnetite formed alongside K-feldspar, chalcopyrite, pyrite, and native Au (Mark et al., 2006b; Schlegel et al., 2021). The ore zone was then variably overprinted by later carbonate veining and post-mineralization alteration (Schlegel et al., 2021).

At shallower levels of the Ernest Henry deposit, mineralization is primarily present as infill between rounded clasts of potassically altered metavolcanic host rocks, whereas at depth, both infill and partial replacement of clasts are present (Rusk et al., 2010). Previous interpretations of the mineralized breccia at Ernest Henry involved an

explosive-implosive eruptive model or ore mineralization caused by fluid over pressurization due to the mixing of magmatic-hydrothermal fluid with basinal brine, inspiring a diatreme-like structural interpretation of the deposit (Oliver et al., 2006; Mark et al., 2006a; Rusk et al., 2010; Cave et al., 2018). The hypothesis that brecciation was synchronous with Fe and Cu-Au mineralization was supported by the occurrence of rounded clasts of pyrite, chalcopyrite, and magnetite within the lower levels of the breccia as well as the partial replacement of clasts within it (Rusk et al., 2010). More recent interpretations instead favor brecciation due to fluid-driven failure under generally ductile conditions during regional metamorphism of the Mount Isa Inlier prior to c. 1530 Ma Cu-Au mineralization followed by post-mineralization brittle deformation (Marshall and Oliver, 2008; Cave et al., 2018; Austin et al., 2021a, b). Despite intense cross-disciplinary scrutiny since shortly after its discovery, understanding of the mineralization history at Ernest Henry enjoys no broad consensus and continues to evolve to reconcile geochronological, geochemical, and petrographic data (Baker et al., 2008; Cave et al., 2018; Austin et al., 2021a, b; Schlegel et al., 2021, 2022).

3. Methods

Core and rock chip samples from the Ernest Henry deposit were provided by the Geological Survey of Queensland (GSQ) for analysis. Samples were sourced from a series of drill cores traversing different sections of the ore deposit and comprise a representative suite of lithologies from the Ernest Henry ore stage, bt-mgt, and mgt-act alteration assemblages found throughout and adjacent to the deposit. Drill cores EH576 and EH942 intersect the nearby Erebus prospect c. 1 km NNW of

the Ernest Henry orebody (c. 550 m depth) and exhibit mag-tact and bi-mgt alteration interpreted as related to equivalent alteration occurring closer to the orebody. Ore stage magnetite samples are interpreted to be petrogenetically related to economic Cu-Au mineralization (Schlegel et al., 2021; this study). More detailed petrography data for most samples included in this work are presented in Schlegel et al. (2021); see Appendix Table S1 for additional sample information. Magnetite textures and mineral associations were assessed on polished samples using scanning electron microscopy backscattered electron imaging (SEM-BSE) methods at the Electron Microbeam Analysis Lab (EMAL) at the University of Michigan using a JEOL JSM-7800FLV field emission scanning electron microscope.

Stable isotope data were obtained from magnetite mineral separates prepared through magnetic separation of crushed rock samples. Due to the small (< 100 µm) average grain size of magnetite in most samples, magnetite separates were obtained through a series of magnetic separations without hand picking. Magnetic separates were successively reduced to powder using a pestle and mortar over several crushing steps between each additional magnetic separation to remove impurities liberated during crushing and obtain the purest possible magnetite fractions. Magnetite separates rather than whole rock powders were utilized for analysis due to the highly heterogeneous nature of ore mineralization observed at Ernest Henry. The Ti budget at Ernest Henry is likely significantly impacted by biotite, with a lesser influence from ilmenite, rutile, and titanite (Schlegel et al., 2021). However, the targeting of a single mineral phase facilitates comparison across the different assemblages found throughout and near the deposit and further enables comparison with magnetite isotope data from the literature. All magnetite sampled for this study appeared fresh without any obvious signs of oxidation or surface weathering.

Magnetite O isotope compositions were measured at the University of Oregon using BrF₅ in a laser fluorination line connected to a Thermo MAT 253 gas isotope ratio mass spectrometer (IRMS) operated in dual inlet mode. Approximately 2 mg of magnetite mineral separates were used for each analysis. Magnetite samples were pretreated overnight to obtain a clean blank prior to analysis, ensuring that any reactive secondary phases were removed by the BrF₅ pretreatment. The Gore Mountain garnet (GMG) standard (+6.52‰) and UWG-2 garnet (+5.8‰) were measured before, during, and following sample analyses (Loewen and Bindeman, 2016). Long-term monitoring of errors on these standards yields an average 2σ of ±0.08‰ δ¹⁸O for the laboratory and methodology. Yields (µmol/mg of O₂ gas extracted) were checked using a Baratron gauge; yields for δ¹⁸O analyses are presented in Table S2. For triple O analyses, the generated gas was sent through a 9 m gas chromatographic zeolite column with a 5 Å molecular sieve to remove NF₃ contaminants and then frozen within the zeolite. A timed 20 min LN₂-slush accompanied each analysis to further prevent any contamination. The gas was then run for 3 to 8 cycles of 8 sample-standard comparison (24 or 64 repetitions; 32 or most samples); standard mass spectrometric errors for δ¹⁷O_{0.5305} on these were in the vicinity of 0.01‰. The San Carlos olivine (SCO) was used as a triple O standard and its values were 0.051 ± 0.01‰, in agreement with Miller et al. (2020). Normalization of δ¹⁷O to this was 0.01‰ and δ¹⁸O of SCO during the δ¹⁷O sessions was in 4.9–5.5‰ range.

Sample dissolution and column chemical separation for Fe and Ti isotope analyses were carried out at Juniata College following the methodology of Mathur et al. (2022). A total of c. 50 mg of magnetite from each sample were dissolved in a 4 ml solution of 25 % 15.2 M HNO₃ and 75 % 10 M HCl over a hot plate. Separate solutions for Fe and Ti isotopes were obtained through a two-step purification process using Bio-Rad AG MP-1 (HCl form, 100–200 mesh) and prepacked Eichrom TODGA anion exchange resins. During the first step, Fe is separated from the sample solution and retained on the Bio-Rad AG MP-1 column resin using procedures identical to that of Mar'echal et al. (1999) and Mathur et al. (2005); Fe is retrieved from the resin using a 2 M HCl elution step. During the second column step, the sample solution is loaded onto a

prepacked TODGA column and rinsed with ultrapure water and HNO₃ prior to Ti elution using HNO₃ and 1 % hydrogen peroxide. Isobaric element abundances and yields from the chromatography were monitored to ensure negligible concentrations and >91 % yields using inductively coupled plasma optical emission spectrometry (ICP-OES) via an Agilent 5900 ICP-OES instrument at Juniata College. All concentrations were calculated with calibration curves between 0.5 and 20 ppm with values corrected using Y as an internal standard.

Isotope sample solutions were analyzed using multi-collector inductively coupled mass spectrometry (MC-ICP-MS) Neptune MC-ICP-MS at Rutgers University and Washington State University. Titanium was measured on both instruments and further descriptions of the process and instrument parameters are provided in Mathur et al. (2022). The instrumentation setup for Ti was identical to that of Zhu et al. (2002) and mass bias was corrected by standard sample bracketing. The bracketing Ti isotope standard used for this study was graciously donated by N. Dauphas at the University of Chicago (Greber et al., 2021; Zhang et al., 2011). The 2σ error for the Ti isotope analyses was determined to be ±0.14‰ via multiple, full procedural measurements of a solid synthetic Fe-Ti oxide standard.

The Fe isotope solutions were measured at Washington State University with instrumentation setup and data reduction identical to Yesavage et al. (2016). Iron isotope samples were measured in duplicate, and the reported value is an average of the two measurements. The 2σ for each sample is lower than the reported error below. The NIST SRM 3126a Fe isotope standard was monitored throughout the analytical session and produced a δ⁵⁶Fe = +0.29 ± 0.07‰ (2σ; N=14) which is within the error of previously reported values. Given this sample was measured the most throughout the measuring sessions, the error for all samples is assumed to be ±0.07‰. Several previously measured magnetite values reported in the literature were replicated to further assess the reproducibility of the technique; these data are presented in Appendix Table S3. Most samples were reproduced within or nearly within error, although sample heterogeneity may explain additional minor discrepancies (Knipping et al., 2019). The largest difference between our replicate and the published value was +0.16‰ for sample LC-05-82.6 where our measured δ⁵⁶Fe value was 0.08‰ whereas Bilenker et al. (2016) report a δ⁵⁶Fe value of +0.08 ± 0.03‰; Knipping et al. (2019) analyzed this sample using in situ laser ablation techniques and observed heterogeneity outside of the analytical error with respect to the core and rim (Table S3).

4. Results

Representative SEM-BSE images of magnetite are presented in Fig. 2. Several styles of magnetite were observed during SEM-BSE imaging. In most samples, magnetite is closely associated with titanite and Mn-rich ilmenite (Fig. 2). Magnetite generally contains few inclusions, although some samples host abundant inclusions of K-feldspar or albite (Fig. 2b, c). Minor inclusion phases include chalcopyrite, Mn-rich ilmenite, pyrite, and titanite. Magnetite is commonly associated with titanite and ilmenite and may be rimmed by titanite. Quartz occurs as fracture fillings and along grain boundaries in magnetite clusters. No major element zoning in magnetite was observed using SEM X-ray energy dispersive spectroscopy (XEDS) mapping and SEM-BSE imaging.

Magnetite sample information and δ¹⁸O, δ⁵⁶Fe, and δ⁴⁹Ti data are presented in Table 1; triple O isotope data are presented in Table 2. Magnetite stable isotope compositions are reported and discussed relative to Vienna standard mean ocean water (VSMOW), Standard 14 from the Institute for Reference Materials and Measurements (IRMM-14), and the Origins Laboratory Ti (OL-Ti) standard for δ¹⁸O, δ⁵⁶Fe, and δ⁴⁹Ti, respectively. For δ⁵⁶Fe and δ⁴⁹Ti data, only data displaying mass dependent fractionation were included.

The magnetite δ¹⁸O values range from +1.57 to +7.36‰ with an average δ¹⁸O of +2.97 ± 2.66‰ (2σ; N=21) for ore stage magnetite, +0.34 to +5.68‰ with an average δ¹⁸O of +2.07 ± 2.52‰ (2σ; N=20)

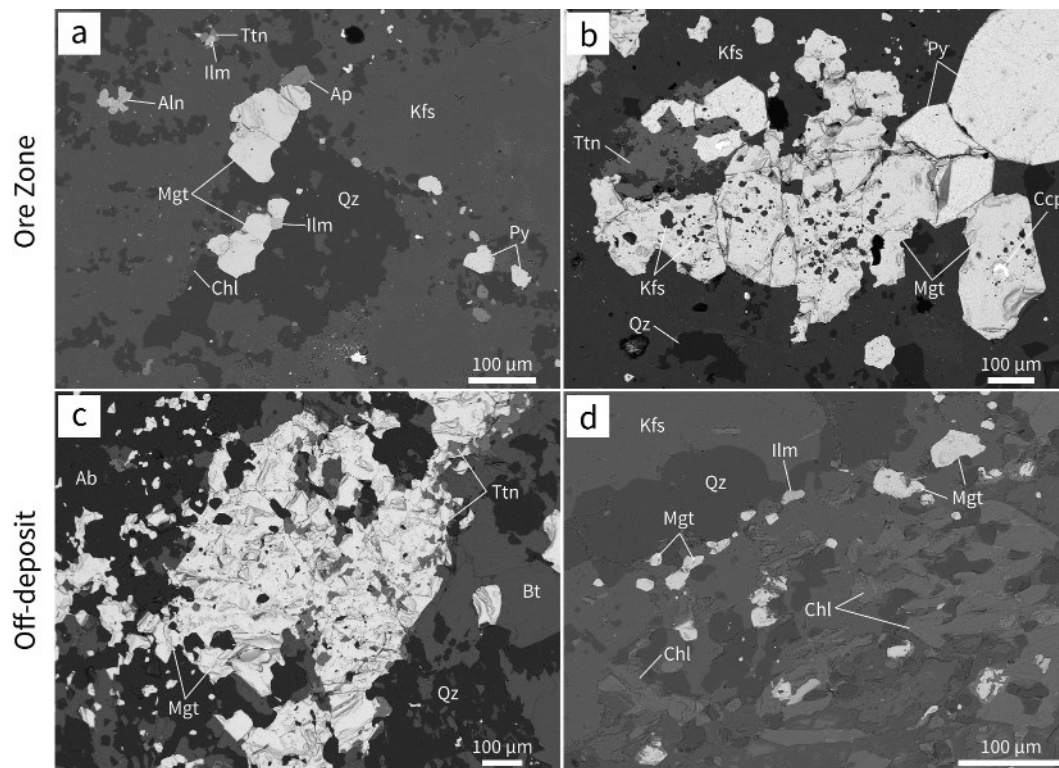


Fig. 2. SEM-BSE images of magnetite and associated minerals from ore stage samples EH191 (a) and EH164 (b), bt-mgt sample EH117 (c) and mgt-act sample MS_EHM213 (d). Ab: albite; Aln: allanite; Ap: apatite; Bt: biotite; Ccp: chalcopryrite; Chl: chlorite; Ilm: ilmenite; Kfs: K-feldspar; Mgt: magnetite; Py: pyrite; Qz: quartz; Ttn: titanite.

bt-mgt magnetite, and $+1.68$ to $+2.10\%$ with an average $\delta^{18}\text{O}$ of $+1.96 \pm 0.38\%$ (2σ ; $N=4$) mgt-act magnetite. Magnetite $\delta^{18}\text{O}$ values from all samples primarily fall within the range consistent with igneous and magmatic-hydrothermal magnetite ($c. +1$ to $+4.5\%$) (Taylor, 1967, 1968; Bilenker et al., 2016; Troll et al., 2019). However, two ore stage magnetite samples (EH209: $+5.47\%$; EH211: $+7.36\%$) and one bt-mgt sample (MS_EHM255: $+5.675\%$) exhibit higher $\delta^{18}\text{O}$ values than those consistent with a magmatic origin and two bt-mgt samples plot at $\delta^{18}\text{O}$ values lower than the magmatic origin range; all other pre-ore samples exhibit $\delta^{18}\text{O}$ values consistent with the range of magmatic magnetite. The $\delta^{18}\text{O}$ range (0.42%) of mgt-act magnetite is remarkably narrow compared to the bt-mgt and ore stage magnetite. The ore stage magnetite samples plotting outside the magmatic origin range are from the deepest sampled parts of the EH435 drill core—which plunges sub-vertically through the center of the orebody; magnetite samples from this drill core show monotonically increasing $\delta^{18}\text{O}$ values with depth (Fig. 4). No other drill core shows this monotonic relationship, although the highest $\delta^{18}\text{O}$ values are generally found at depth in the drill cores accessing the ore zone (Fig. 4). Ore stage samples analyzed for triple oxygen isotopes yielded $\Delta^{17}\text{O}$ values of $0.094 \pm 0.043\%$ (2σ ; $N=7$) and two bt-mgt samples yielded $\Delta^{17}\text{O}$ values of 0.073% and 0.069% , respectively (Fig. 5).

The magnetite $\delta^{56}\text{Fe}$ values range from -0.50 to $+0.33\%$ with an average $\delta^{56}\text{Fe}$ of $-0.09 \pm 0.52\%$ (2σ ; $N=8$) for ore stage magnetite, -0.65 to $+0.38\%$ with an average $\delta^{56}\text{Fe}$ of $-0.26 \pm 0.30\%$ (2σ ; $N=13$) for the bt-mgt magnetite, and -0.26 to $+0.30\%$ with an average $\delta^{56}\text{Fe}$ of $-0.03 \pm 0.49\%$ (2σ ; $N=4$) for mgt-act magnetite. Magnetite $\delta^{56}\text{Fe}$ values are generally lower than the range proposed for magmatic magnetite ($c. +0.06$ to $+0.49\%$ $\delta^{56}\text{Fe}$). Only a few ore stage magnetite samples exhibit $\delta^{56}\text{Fe}$ and $\delta^{18}\text{O}$ pairs that plot within or nearly within the ranges of magmatic magnetite (Fig. 6) (Bilenker et al., 2016; Troll et al., 2019). The ore zone magnetite samples with magmatic $\delta^{56}\text{Fe}$ values were obtained from the deep portion of the EH550 drill core

where the drill intersects the 0.5% Cu zone defining the economic portion of the orebody. Iron isotope data from outside of the hanging wall and footwall shear zones with respect to the Ernest Henry deposit are generally isotopically heavier than data from within the region bounded by both shear zones (Fig. 4).

The magnetite $\delta^{49}\text{Ti}$ values range from -1.64 to $+3.79\%$ with an average $\delta^{49}\text{Ti}$ of $-1.49 \pm 2.63\%$ (2σ ; $N=16$) for ore stage magnetite, -0.44 to $+1.49\%$ with an average $\delta^{49}\text{Ti}$ of $+0.62 \pm 1.13\%$ (2σ ; $N=11$) for bt-mgt magnetite, $+0.27$ to $+1.89\%$ with an average $\delta^{49}\text{Ti}$ of $+1.05 \pm 1.56\%$ (2σ ; $N=4$) for mgt-act magnetite. The highest $\delta^{49}\text{Ti}$ values are generally observed in magnetite from deeper parts of the drilled portion of the Ernest Henry deposit (Fig. 4). The range of Ti isotope compositions within magnetite from the Ernest Henry orebody encompasses and exceeds the range of Ti isotope compositions reported for both terrestrial and extraterrestrial bulk rock materials (Fig. 3). However, the pre-ore magnetite $\delta^{49}\text{Ti}$ values primarily fall within the range of bulk rock $\delta^{49}\text{Ti}$ or terrestrial igneous rocks with the exception of one bt-mgt sample (MS_EHM_152: -0.44%) (Millet et al., 2016; Aarons et al., 2020). There is a loose correlation between $\delta^{49}\text{Ti}$ and $\delta^{18}\text{O}$ for ore stage magnetite (Fig. 7a), however, no clear relationship is observed between $\delta^{49}\text{Ti}$ and $\delta^{56}\text{Fe}$ (Fig. 7b).

5. Discussion

5.1. Textural analysis

Although individual grains were interpreted to be homogeneous with respect to major elements, it is possible that different isotopic populations of magnetite could be represented in an individual datum. The utility of these measurements lies in assessing the distribution of these different populations throughout the deposit. The textures of the ore breccia have been interpreted by early workers to indicate a high energy, explosive genesis, although a diatreme-like origin has been

Table 1

Magnetite Ti, Fe, and O isotopic compositions and sample information.

Alteration	Drillhole	Sample	From (m)	To (m)	$\delta^{18}\text{O}$	$\delta^{56}\text{Fe}$	$\delta^{49}\text{Ti}$
bt-mt	EH147	MS_EHM152	100.1	100.5	1.35	0.07	0.44
bt-mt	EH147	MS_EHM157	146.3	146.97	2.06	0.18	0.48
bt-mt	EH147	MS_EHM159	184.6	185.5	2.03	0.46	1.44
bt-mt	EH242	EH248	72.05	72.2	2.23	0.17	0.59
ore	EH242	EH263	234.65	234.8	2.08–0.46		
bt-mt	EH435	EH187	103.45	103.6	1.19	0.65	0.25
ore	EH435	EH191	154.95	155.1	2.18	0.5	0.64
ore	EH435	EH197	229.7	229.9	2.31	0.13	1.84
ore	EH435	EH199	257.9	258.05	2.6–1.23		
ore	EH435	EH205	353	353.15	3.48–1.21		
ore	EH435	EH209	434.6	434.6	5.47–		–
ore	EH435	EH211	484.85	485	7.36	0.31	1.59
ore	EH440	MS_EHM250	96	96.3	2.9–		–
ore	EH440	MS_EHM251	136.87	138.98	1.98–1.16		
ore	EH440	MS_EHM254	235.95	236.12	2.16–		–
bt-mt	EH440	MS_EHM255	335.44	335.51	5.68	0.11–	
bt-mt	EH550	EH100	193.2	193.35	0.34	0.38	0.31
mt-act	EH550	EH107	242.7	242.8	1.98	0.3	0.27
bt-mt	EH550	EH117	399.5	399.65	1.88–		–
bt-mt	EH550	EH127	479.6	479.75–0.38			0.32
ore	EH550	EH147	697.5	697.65	2.07	0.13	1.39
ore	EH550	EH151	729.65	729.8	2.61	0.18	1.29
ore	EH550	EH152	736.1	736.25	2.67–3.03		
ore	EH550	EH157	794.2	794.35	3.15–		–
ore	EH550	EH164	871.5	871.65	1.57	0.33	0.37
ore	EH550	EH168	923.25	923.4	2.73–		–
ore	EH550	EH175	995.86	995.98	3.61	0.04	2.38
bt-mt	EH576	MS_EHM209	470.35	470.75	2.26–0.85		
mt-act	EH576	MS_EHM213	657.2	657.55	1.68	0.17	0.52
mt-act	EH576	MS_EHM219	811.35	811.8	2.1	0.03	1.52
bt-mt	EH576	MS_EHM221	842.75	843.15	2.52	0.07	1.08
mt-act	EH632	MS_EHM071	888.65	889.3	2.07	0.26	1.89
ore	EH632	MS_EHM079	982.59	998.1	3.1–3.79		
ore	EH632	MS_EHM083	1064.75	1064.9	4.11	0.09	3.57
ore	EH632	MS_EHM089	1173.98	1174.1	2.26–		–
ore	EH632	MS_EHM090	1186.7	1187.55–		–0.66	
bt-mt	EH632	MS_EHM099	1314.7	1314.7	3.65–		–
bt-mt	EH699	MS_EHM109	244	244.5	2	0.09–	
bt-mt	EH699	MS_EHM120	627.3	309.6	1.41	0.07	0.46
bt-mt	EH699	MS_EHM136	917.6	628.35	1.53	0.02–	
bt-mt	EH699	MS_EHM140	1062.8	918.2	0.9	0.13	1.49
ore	EH942	MS_EHM182	750.5	750.9	1.93–1.53		

Table 2

Magnetite triple O isotopic compositions and sample information. Errors are discussed in the text.

Sample	Alteration	$\delta^{18}\text{O}$	$\delta^{18}\text{O}_A$	$\delta^{17}\text{O} \pm \Delta$	$\delta^{17}\text{O}, 2\sigma$	n
EH197	ore	2.31	2.03	0.056	0.008	3
EH211	ore	7.36	9.93	0.1	0.022	4
MS_EHM079	ore	3.1	2.97	0.105	0.012	8
MS_EHM083	ore	4.11	4.12	0.113	0.022	4
EH205	ore	3.48	4.4	0.085	0.013	4
EH209	ore	5.47	6.03	0.118	0.009	8
EH251	ore	1.71	1.68	0.079	0.008	4
MS_EHM221	bt-mgt	2.52	1.65	0.069	0.014	4
MS_EHM099	bt-mgt	3.65	3.65	0.073	0.001	8

challenged based upon the preservation of pre-mineralization structures such as the metasedimentary inter-lens (Oliver et al., 2006; Cave et al., 2018). The spatial isotopic relationships, most clearly observed in the O isotope gradient in drillhole EH435, demonstrate that some degree of chemical organization remains in the ore zone that has not been completely obscured by brecciation. This observation is consistent with a non-explosive brecciation model and/or with our ore stage magnetite data recording post-brecciation processes (Austin et al., 2021a, b).

5.2. O isotopes

The O isotope systematics of terrestrial igneous rocks are well-constrained, and O isotope compositions have been used to argue for a magmatic-hydrothermal origin for IOCG deposits (Childress et al., 2020b; Rodriguez-Musta et al. 2020, 2022). The dearth of samples plotting at lower $\delta^{18}\text{O}$ values than the range consistent with a magmatic-hydrothermal origin suggest that Ernest Henry magnetite does not have a major meteoric O component nor was it affected by post-mineralization alteration from meteoric water (Bilenker et al., 2016; Troll et al., 2019). Importantly, the pre-ore magnetite samples also exhibit $\delta^{18}\text{O}$ values consistent with a magmatic-hydrothermal origin, suggesting that the fluids responsible for the regional Na-Ca alteration and pre-ore bt-mgt and mgt-act alteration were either magmatic or fully equilibrated with igneous rocks (Bilenker et al., 2016; Childress et al., 2016). The relatively narrow range (0.32‰) of mgt-act magnetite compared to ore stage (5.79‰) and bt-mgt (5.34‰) magnetite could indicate that the fluids responsible for bt-mgt and ore mineralization experienced O source mixing within or near the deposit.

While the samples with $\delta^{18}\text{O}$ values lower than the magmatic origin range may be explained through minor alteration by meteoric water, those plotting at higher $\delta^{18}\text{O}$ values cannot be explained through this mechanism (Bilenker et al., 2016; Childress et al., 2020a). Although there may be some degree of sample contamination from closely associated carbonate minerals in EH209 and EH211 that could not be removed by pretreatment, similar values for magnetite from the

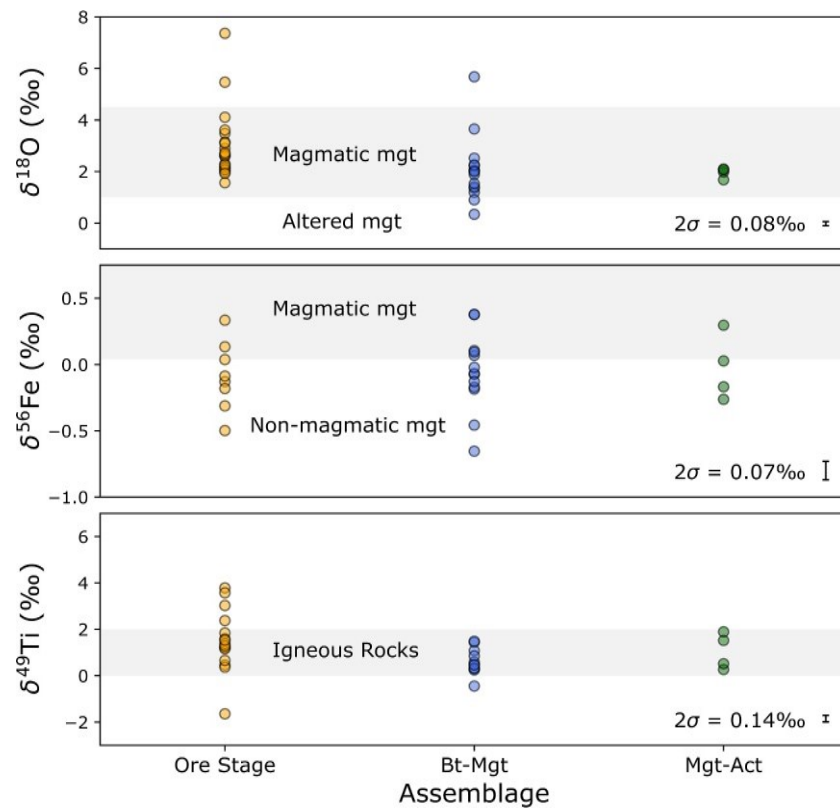


Fig. 3. Magnetite $\delta^{18}\text{O}$, $\delta^{56}\text{Fe}$, and $\delta^{49}\text{Ti}$ data by alteration assemblage. Gray bars plotted using igneous magnetite O and Fe ranges given in [Bilenker et al. \(2016\)](#) and [Troll et al. \(2019\)](#) and Ti whole rock data compiled in [Aarons et al. \(2020\)](#).

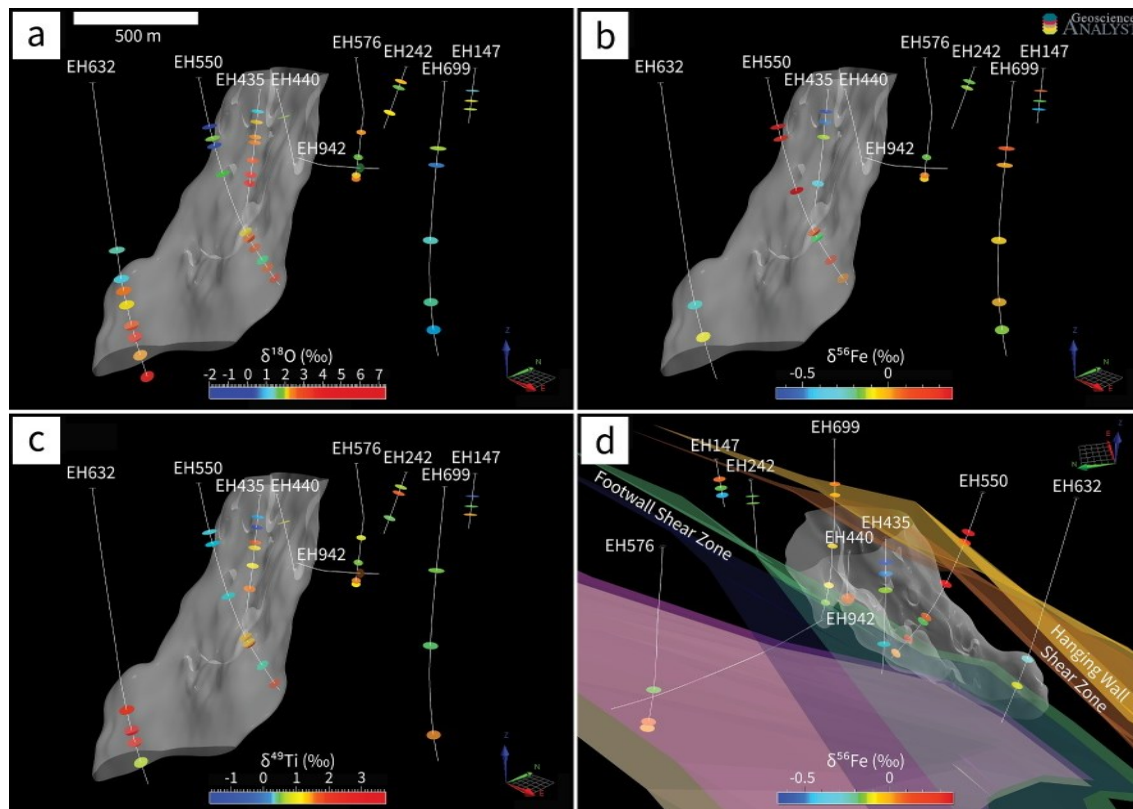


Fig. 4. Spatial O (a), Fe (b), and Ti (c) isotope data plotted with drill hole outlines (white lines) and the 0.5 % Cu equivalent shell (gray volume). Shear zones are shown in (d) relative to the deposit. 0.5 % Cu equivalent shell, drill collar, and drill survey data provided by GSQ. The length of the 0.5 % Cu equivalent shell spans 1244 m from 122 m above sea level at the upper truncation to 1122 m below sea level at the lower truncation.

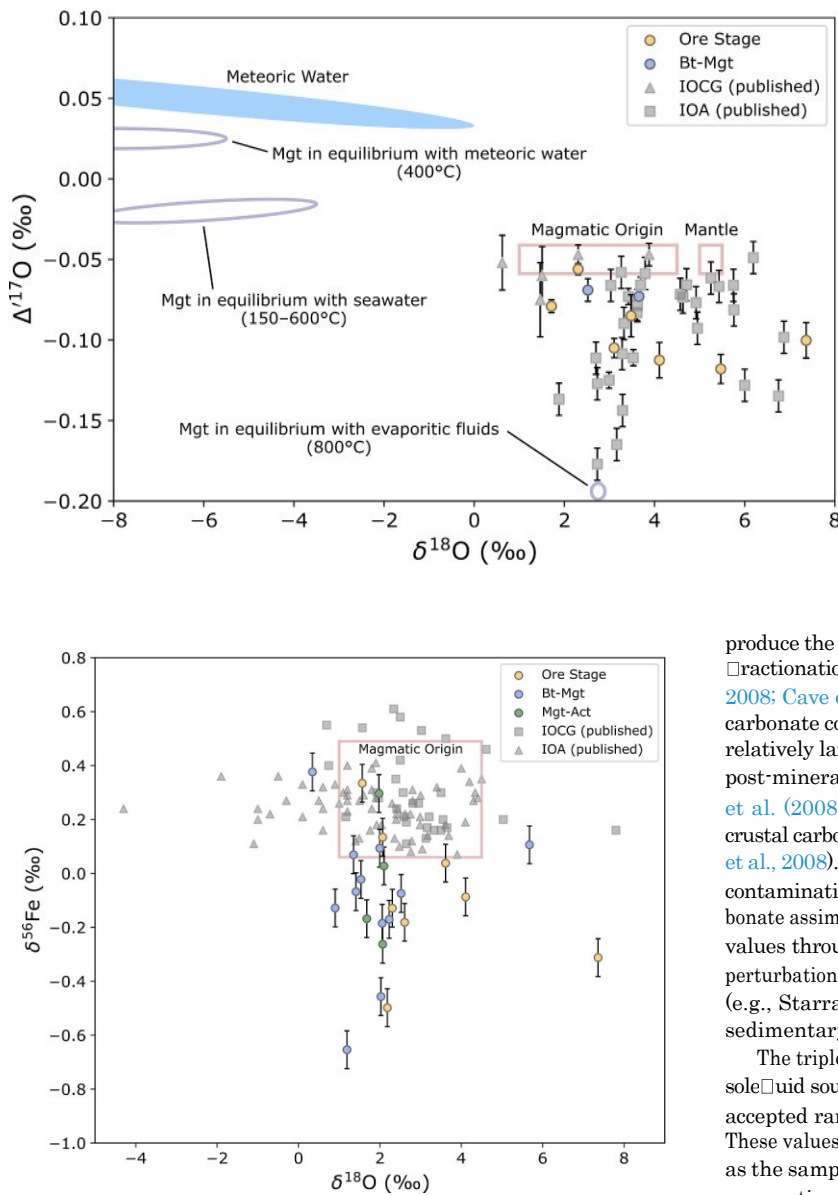


Fig. 6. Magnetite Fe and O isotope data for ore zone and pre-ore samples. Published IOCG magnetite values provided by Rodriguez-Mustaza et al. (2020, 2022) and Childress et al. (2020b) for samples from the Candelaria, Mina Justa, and Mantoverde IOCG deposits, respectively; IOA magnetite values are from Bilinker et al. (2016) and Troll et al. (2019) for samples from the Los Colorados, El Laco, Kiruna District, Grangesberg District, and Baq District IOA deposits. Magmatic origin box established using data from Taylor et al. (1967, 1968), Heimann et al. (2008), and Weis (2013). The $\delta^{18}\text{O}$ errors are smaller than the marker size.

Candelaria IOCG deposit in Chile reported by Rodriguez-Mustaza et al. (2020) were attributed by them to interactions with carbonate wall rocks present in the volcanic-sedimentary sequence at shallow levels of the deposit. Cave et al. (2018) published a modified map created by Ernest Henry Mining that reports a dolomitic marble breccia in/near the region of the deposit accessed by the deeper portion of the EH435 drill core; the inter-lens structure also contains carbonaceous sediments (Cave et al., 2018). Decarbonation reactions may have produced an isotopically heavy fluid (with respect to O), which likely mixed with the ore fluid as it was ascending prior to magnetite regenerative mineral replacement in shallower levels of the deposit (Taylor and O'Neil, 1977). For a mixture between a magmatic fluid with a $\delta^{18}\text{O}$ value of $\sim 1\text{‰}$ and marble with a $\delta^{18}\text{O}$ of $\sim 20\text{‰}$, c. 33 % assimilation is required to

Fig. 5. Triple O data plotted as $\Delta^{17}\text{O}_{0.5305}$ vs $\delta^{18}\text{O}$ values for samples from this study plotted alongside published data from Peters et al. (2020), Childress et al. (2020a), and Rodriguez-Mustaza et al. (2022). The magmatic origin and mantle fields are derived from data presented in Taylor (1968), Pack et al. (2016), Sharp et al. (2018), Troll et al. (2019), Miller et al. (2020), Bindeman (2021), and Peters et al. (2020). Magnetite equilibrium fields are based on data from Peters et al. (2020). The $\delta^{18}\text{O}$ error bars are smaller than the marker size.

produce the highest $\delta^{18}\text{O}$ value observed ($+7.36\text{‰}$) assuming negligible fractionation between magnetite and the fluid (Marshall and Oliver, 2008; Cave et al., 2018; Rodriguez-Mustaza et al., 2020). Mid-crustal carbonate contributions have previously been suggested to explain the relatively large CO_2 budget of the Cu-Au ore fluids, although syn- and post-mineralization carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values reported in Oliver et al. (2008) are consistent with mantle-derived fluids rather than crustal carbonates as the major CO_2 source (Kendrick et al., 2007; Oliver et al., 2008). The localization of our high $\delta^{18}\text{O}$ values is consistent with contamination from a small-volume host rock unit, as large-scale carbonate assimilation deeper in the system would have likely affected $\delta^{18}\text{O}$ values throughout the orebody (Oliver et al., 2008). Similarly localized perturbations of C and S isotopic data in other Cloncurry IOCG deposits (e.g., Starra and Osborne) have been attributed to local input from sedimentary units (Davidson and Dixon, 1992; Mark et al., 2000).

The triple O isotope data are not consistent with a silicate melt as the sole fluid source, as the $\Delta^{17}\text{O}$ for all but one sample plot outside of the accepted range for purely magmatic magnetite (Peters et al., 2020). These values are likely also affected by localized host rock assimilation, as the samples that plot between c. 1–3‰ $\delta^{18}\text{O}$ have $\Delta^{17}\text{O}$ close to the magmatic origin box, whereas the samples with $\delta^{18}\text{O} > 3\text{‰}$ plot discordantly to the bulk of samples in plots of $\delta^{56}\text{Fe}$ vs $\delta^{18}\text{O}$ and $\delta^{49}\text{Ti}$ vs $\delta^{18}\text{O}$ (Figs. 6 and 7a). The spread in $\Delta^{17}\text{O}$ for Ernest Henry magnetite is similar to that observed by Peters et al. (2020) in magnetite from the Baq District IOA deposits in Iran and attributed by those authors to input from evaporitic fluids. In contrast, triple O data for magnetite from the Mina Justa IOCG deposit in Peru reported in Rodriguez-Mustaza et al. (2022) are consistent with a silicate melt as the principal fluid source and suggest that evaporitic/basinal brine input is not a ubiquitous characteristic of IOCG systems. Although Baker et al. (2008) identified fluid inclusions with Br/Cl ratios consistent with evaporitic fluids in Cloncurry IOCG deposits (including at Ernest Henry), higher Cu concentrations were found in fluid inclusions that exhibited Br/Cl ratios indicative of a magmatic origin. These findings imply that evaporitic fluids were likely unimportant for transporting Cu and Au at Ernest Henry. A fluid mixing model supported by our data and that of previous studies involves Cu-Au-bearing magmatic-derived fluids mixing with a basinal brine that may or may not include metamorphic breakdown/devolatilization products (Baker et al., 2008; Schlegel et al., 2020). The spatial variability of $\Delta^{17}\text{O}$ remains poorly constrained and further work is needed to fully understand the importance of evaporitic fluids at Ernest Henry.

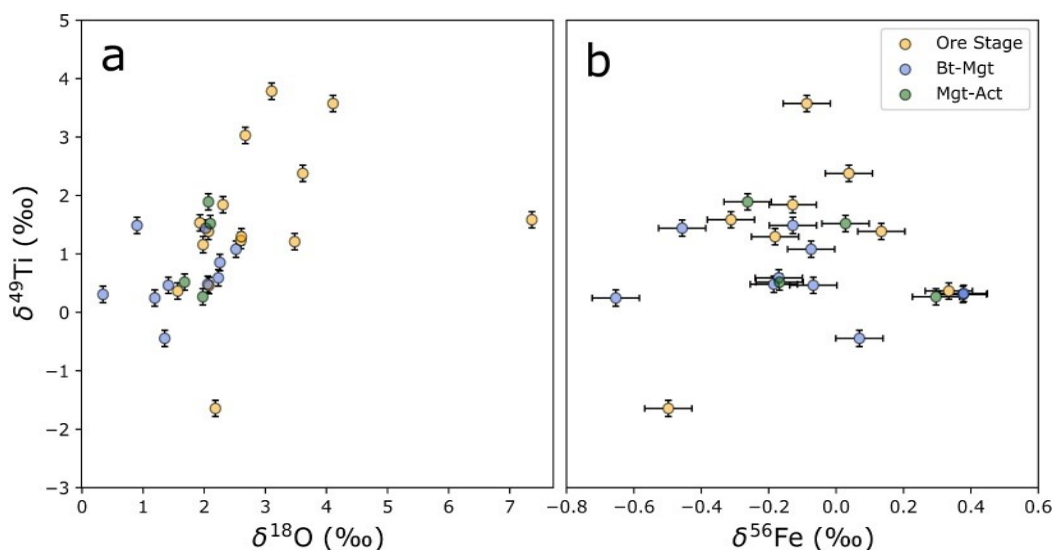


Fig. 7. Plots of $\delta^{49}\text{Ti}$ vs $\delta^{18}\text{O}$ (a) and $\delta^{56}\text{Fe}$ (b) for magnetite from each sample suite.

5.3. Fe isotopes

While the magnetite $\delta^{18}\text{O}$ values reported here are generally consistent with a silicate melt/uid source or the ore stage mineralization, $\delta^{56}\text{Fe}$ values for most magnetite samples are inconsistent with a silicate melt Fe source. Available Fe-O stable isotope data for magnetite from other IOCG systems (e.g., Candelaria and Mantoverde, Chile; Mina Justa, Peru) are broadly consistent with a silicate melt metal and uid source and do not exhibit a large (c. 1‰), principally non-magmatic $\delta^{56}\text{Fe}$ range (Fig. 3) (Childress et al., 2016; Rodriguez-Musta et al., 2020, 2022). Weathered and hydrothermally altered magnetite samples typically show shifts in either $\delta^{18}\text{O}$ or in both $\delta^{56}\text{Fe}$ and $\delta^{18}\text{O}$, whereas our data suggest that $\delta^{56}\text{Fe}$ and $\delta^{18}\text{O}$ variations are effectively decoupled for most samples across a wide range of $\delta^{56}\text{Fe}$ (Fig. 6) (Bilenker et al., 2016; Childress et al., 2020a; Troll et al., 2019; Rodriguez-Musta et al., 2020). A decoupling of Fe and O isotopic variation for most samples (other than the samples affected by carbonate assimilation as discussed above) is inconsistent with a model where the range in $\delta^{56}\text{Fe}$ may be entirely explained through contamination from crustal carbonates. Similarly, banded iron formations (BIFs) may exhibit low $\delta^{56}\text{Fe}$ values (e.g., -0.8‰), but typically have high $\delta^{18}\text{O}$ and, therefore, their contributions would be detectable in the $\delta^{18}\text{O}$ data at low uid-rock ratios (but may not be apparent at high uid-rock ratios) (Frost et al., 2007; Johnson et al., 2008; Konhauser et al., 2017).

A purely magmatic origin or the lowest $\delta^{56}\text{Fe}$ value observed in magnetite (EH187; -0.65‰; bt-mgt) would require a $\delta^{56}\text{Fe}_{\text{melt}}$ range of c. -0.77 to -0.74‰ or the temperature range of 1000 to 800 °C, assuming $\Delta^{56}\text{Fe}_{\text{mgt-melt}} = \text{c. } 0.2 \times 10^{-6}/T^{2/1.5}$ (Sossi et al., 2012; Bilenker et al., 2017). The 800 °C lower limit is derived from the ceiling of the IOA temperature range from Palma et al. (2020) and del Real et al. (2021) representing magnetite crystallizing from a silicate melt, whereas the upper limit is derived from temperature estimates of the Williams-Naraku suite reported in Wyborn (1998) and Creaser and White (1991). In a magmatic-hydrothermal model, a silicate melt would need a $\delta^{56}\text{Fe}$ of c. -0.63‰ to crystallize magnetite with a $\delta^{56}\text{Fe}$ of -0.65‰, assuming $\Delta^{56}\text{Fe}_{\text{melt-uid}} = 0.27\text{‰}$ and $\Delta^{56}\text{Fe}_{\text{uid-mgt}} = 0.25\text{‰}$ using fractionation factors reported in Schauble et al. (2001), Polyakov et al. (2007), and Sossi et al. (2012) or a silicate melt exsolving a $\text{Fe}^{2+}\text{Cl}_4$ -rich uid at 800 °C. Experimental studies of Fe speciation under hydrothermal conditions demonstrate that at lower Cl-Fe ratios below the magnetite-hematite buffer, octahedral $\text{Fe}^{2+}\text{Cl}_6(\text{H}_2\text{O})_6$ is most abundant, whereas at higher Cl-Fe ratios, tetrahedral $\text{Fe}^{2+}\text{Cl}_4$ is most abundant (Scholten et al., 2019). Light Fe isotopes prefer 6-fold

coordination complexes relative to 4-fold complexes, meaning that at lower Cl-Fe ratios, the uid will be more enriched in light Fe relative to uids with higher Cl-Fe ratios (Schauble et al., 2001). Therefore, using the $\text{Fe}^{2+}\text{Cl}_4$ fractionation factor instead of the $\text{Fe}^{2+}\text{Cl}_6(\text{H}_2\text{O})_6$ fractionation factor yields a more conservative estimate. Precipitation of magnetite from low $\delta^{56}\text{Fe}$ uids could result in magnetite with non-magmatic $\delta^{56}\text{Fe}$ values, as leaching of magnetite by Cl-rich uids would instead deplete magnetite in light Fe (Bilenker et al., 2016; Heilmann et al., 2008; Hill and Schauble, 2008). Because post-crystallization processes generally favor the depletion of light Fe isotopes in magnetite, magnetite most likely precipitated with $\delta^{56}\text{Fe}$ values similar to or lower than the measured values during at least the latest episode of major Fe input at Ernest Henry. Based on the reported $\delta^{56}\text{Fe}$ range for global igneous rocks (c. -0.1 to +0.5‰) and magmatic (hydrothermal) magnetite (c. 0 to +0.5‰), a purely magmatic Fe source for pre-ore and ore stage magnetite at Ernest Henry is unlikely (Bilenker et al., 2017; Troll et al., 2019; Foden et al., 2015; Xia et al., 2017).

The oxidation of magnetite would not be expected to change bulk $\delta^{56}\text{Fe}$, as Fe is effectively retained in Fe oxides. Variably oxidized samples from the El Lago IOA deposit in Chile reported in Childress et al. (2020a) demonstrate that low-temperature alteration results in $\delta^{18}\text{O}$ values lower than the magmatic origin range, but does not appreciably change $\delta^{56}\text{Fe}$ in magnetite. Thus, the $\delta^{18}\text{O}$ data suggest that alteration by meteoric waters with or without the oxidative transformation of magnetite to ferric oxides is unlikely to be the cause of the $\delta^{56}\text{Fe}$ variation in Ernest Henry magnetite. Inter-mineral isotope fractionation between magnetite and ilmenite also fails to explain our $\delta^{56}\text{Fe}$ data, as $\Delta^{56}\text{Fe}_{\text{Mgt-Ilm}} = +0.18\text{‰}$ at 800 °C using $\ln \beta^{56/54}\text{Fe}$ factors from Polyakov et al. (2007) and Nie et al. (2021), meaning that exchange between magnetite and ilmenite should result in isotopically heavier magnetite, especially in the case of kinetic isotope fractionation (as has been proposed to explain extremely light Fe isotope compositions of pyrite) where light Fe is more likely to be mobilized in an exchange reaction due to the higher zero point energy of ^{54}Fe vs ^{56}Fe (Chen et al., 2014; Wei et al., 2020; Zhang et al., 2021). We cannot rule out inter-mineral isotopic exchange as an additional driver of Fe isotope variation, however, it is improbable that the lightest $\delta^{56}\text{Fe}$ values originated through this process acting upon magnetite with an initially magmatic (hydrothermal) Fe isotope composition (Chen et al., 2014; Wei et al., 2020).

An alternative hypothesis is that the Fe present in magnetite may have been partly or primarily scavenged from mafic rocks by intratelluric uids with a magmatic O isotope composition. Oliver et al.

(2008) proposed local mafic units as the Fe source based upon reported zoning and paragenetic observations suggesting that the Fe-Ba and Cu-Au-S fluids were distinct and mixed in the deposit. Leaching of igneous rocks by acidic fluids may result in isotopically light leachate—as light as c. 1.8‰ $\delta^{56}\text{Fe}$ for granite leached by HCl at 22 °C under laboratory conditions (Chapman et al., 2009). This effect has been observed in nature during the leaching of mafic rocks in submarine hydrothermal systems, resulting in fluids with reported $\delta^{56}\text{Fe}$ values c. 0.30 to 0.77‰ (Sharma et al., 2001; Dziony et al., 2014). Using the $\Delta^{56}\text{Fe}_{\text{fluid-mgt}} = 0.25\%$ fractionation factor for magnetite crystallizing from a hydrothermal $\text{Fe}^{2+}\text{Cl}_4$ -rich fluid at 800 °C, magnetite with a $\delta^{56}\text{Fe}$ value of 0.65‰ could result from a fluid with a $\delta^{56}\text{Fe}$ of 0.90‰. While not strictly within the known range of $\delta^{56}\text{Fe}$ in natural Fe leachate, this estimated fluid composition is closer to natural leachates than to projected magmatic hydrothermal fluid compositions (+0.17 to +0.77‰ using $\Delta^{56}\text{Fe}_{\text{melt-fluid}} = +0.27\%$ and the global igneous rock $\delta^{56}\text{Fe}$ range for a $\text{Fe}^{2+}\text{Cl}_4$ -rich fluid exsolved from a silicate melt at 800 °C).

Most pre-ore samples plot outside of the magmatic $\delta^{56}\text{Fe}$ range while exhibiting magmatic $\delta^{18}\text{O}$ values, suggesting that the Cu-Au ore fluid was not the primary source of leached Fe. Debret et al. (2016) note that $\delta^{56}\text{Fe}$ increases with increasing metamorphic grade and attribute this to the loss of isotopically light Fe^{2+} during volatile release. Fluid contributions from rock-buffered metamorphic fluids may have introduced isotopically light Fe into the system and surrounding rocks during early magnetite mineralization (Fisher and Kendrick, 2008). Schlegel et al. report that magnetite (and hematite) in the albitites is generally in abundances of 0.1 to 5.3 vol%, which is consistent with an origin from the alteration-induced redistribution of Fe from primary Fe-bearing minerals including actinolite, hornblende, and biotite in the protolith metadiorite and not requiring additional Fe; this observation is consistent with our observations of magmatic $\delta^{56}\text{Fe}$ values in albitites in the shallow portion of the EH550 drill core. Occurrence within metamorphosed igneous rocks may be why some magnetite from Ernest Henry is isotopically lighter than magnetite from Candelaria, Mantoverde, and Mina Justa, which are hosted in undeformed volcanic units (Rodríguez-Mustafa et al., 2020, 2022; Childress et al., 2020b). It is also possible that the Andean IOA/IOCG deposits simply lack appreciable non-magmatic Fe contributions, which may not be required to form Fe oxide mineralization in IOA/IOCG systems.

5.4. Ti isotopes

This study is the first to investigate Ti isotope compositions in a mineralized system. Although previous studies have primarily focused on bulk Ti isotope compositions of igneous and metaigneous rocks, our work uses magnetite $\delta^{49}\text{Ti}$ values to track ore-forming processes, as Ti isotope compositions are proposed to withstand post-mineralization hydrothermal alteration (Millet et al., 2016; Hoare et al., 2020). The hypothesis that whole rock Ti isotope compositions are resilient to hydrothermal alteration is based on measurements of serpentinite and eclogite whole rock data reported in Millet et al. (2016), consistent with many studies that document the limited spatial mobility of Ti during metamorphism and metasomatism (Ryzhenko et al., 2006; Millet et al., 2016). However, these data: 1) are from systems that experienced metasomatism by fluids of very different chemistry than the ligand-rich brines interpreted to have driven alteration and mineralization at Ernest Henry and 2) are insensitive to the potential for inter-mineral isotope fractionation during regenerative mineral replacement, alteration, and exsolution reactions. Field and empirical observations have also demonstrated, at a minimum, local Ti mobility (Tanis et al., 2015, 2016; Brugger et al., 2016 and references therein). Recent work has further eroded confidence in the resistivity of Ti isotope signatures to secondary processes by demonstrating a c. 0.6‰ $\delta^{49}\text{Ti}$ difference between extracted Fe (oxy)hydroxide phases and refractory phases in a highly weathered basalt (He et al., 2022). The large (>5‰) range of magnetite

$\delta^{49}\text{Ti}$ throughout the orebody indicates that Ti isotope fractionation can also occur in hydrothermal systems and may additionally be driven by post- or non-magmatic processes.

In silicate magmas, Ti isotope fractionation is suggested to occur primarily due to the mass selectivity of precipitating Ti-bearing oxide phases, such as magnetite and ilmenite (Zhao et al., 2020). In magnetite, Ti primarily resides at the octahedral site through a dynamic coupled substitution where Fe^{2+} —rather than Fe^{3+} —occupies a nearby octahedral site at low Ti concentrations, transitioning to tetrahedral site Fe^{2+} accommodation at higher Ti concentrations (>0.4 apfu) (Pearce et al., 2010; Varshney and Yogi, 2012). Mass selectivity likely occurs due to coordination changes between common oxide minerals, where Ti is in 6-fold coordination, and silicate melts, where Ti may be 4-, 5-, or 6-fold coordinated as an inverse function of melt SiO_4^{4-} (Millet et al., 2016; Aarons et al., 2021). Heavier Ti isotopes prefer tighter coordination and are therefore underrepresented in the 5- and 6-fold Ti coordination complexes relative to lighter Ti isotopes (Millet et al., 2016). During oxide precipitation, 6-fold coordinated Ti is preferentially incorporated, leading to depletion in light Ti in the remaining melt and driving the $\delta^{49}\text{Ti}$ of the melt to higher (more positive) values (Millet et al., 2016). In silicate melts, $\Delta^{49}\text{Ti}_{\text{melt-oxide}}$ does not scale linearly with $1/T^2$ because Ti coordination is affected by SiO_4^{4-} activity in the melt—leading to a larger $\Delta^{49}\text{Ti}_{\text{melt-oxide}}$ at higher SiO_4^{4-} activity (Deng et al., 2019; Zhao et al., 2020).

The source of the Ti present in magnetite at Ernest Henry is of critical importance when interpreting our isotope data. The Ti isotope compositions of most pre-ore magnetite samples may have been inherited from primary minerals in the protolith, as the $\delta^{49}\text{Ti}$ range of these samples is largely consistent with primary magmatic Ti isotope ranges reported for bulk igneous rock samples (c. 0–2‰) (Millet et al., 2016; Zhao et al., 2020; Aarons et al., 2020). The redistribution of Ti or most pre-ore samples likely occurred during albitization of the metavolcanic rocks when primary ilmenite was consumed to produce rutile, titanite, and minor magnetite (Schlegel et al., 2021). However, magmatic Ti isotope fractionation is insufficient to explain the ore stage $\delta^{49}\text{Ti}$ data because such a model would require repeated or continuous sampling of magmatic magnetite throughout an extensive melt fractionation history and involve magmatic $\delta^{49}\text{Ti}$ values significantly (>2‰) higher than those that have been observed in nature (Deng et al., 2019; Johnson et al., 2019). Preservation of purely protolithic $\delta^{49}\text{Ti}$ is further inconsistent with our results as the ore stage magnetite exhibits $\delta^{49}\text{Ti}$ and $\delta^{56}\text{Fe}$ values that span a range eclipsing that of pre-ore magnetite.

Another source of fractionation may have been inter-mineral fractionation among Ti-bearing minerals. In hydrothermally altered magnetite, liberated Ti is typically locally retained in oxyexsolved ilmenite and/or localized ilmenite precipitation (Ovalle et al., 2018; Rojas et al., 2018). The close association of magnetite with Mn-rich ilmenite at Ernest Henry suggests that Ti in some ilmenite may have been sourced from precursor magnetite during regenerative mineral replacement. We observed no oxyexsolution lamellae preserved in Ernest Henry magnetite, so later re-equilibration among minerals would primarily be due to equilibrium inter-mineral isotope fractionation, represented by the $\Delta^{49}\text{Ti}_{\text{ilv-mineral}}$ given below. Inter-mineral fractionation factors between magnetite and ilmenite ($\alpha = 0.45$ to 0.47) and between magnetite and rutile ($\alpha = 0.39$ to 0.45) where $\Delta^{49}\text{Ti}_{\text{ilv-mineral}} = \alpha/(T/1000)^2$ predict that during inter-mineral fractionation between magnetite and either of these minerals, magnetite will be preferentially depleted in heavier Ti isotopes (Zhao et al., 2020). Similarly, magnetite inter-mineral fractionation with biotite should also result in depletion in heavier Ti isotopes in magnetite, as biotite and other minerals with Ti (at least partly) in 4-fold coordination prefer heavier Ti isotopes relative to minerals with Ti exclusively in 6-fold coordination (Greber et al., 2021). Inter-mineral fractionation during low temperature re-equilibration could potentially be responsible for the lowest $\delta^{49}\text{Ti}$ value observed (EH191: 1.64‰), as inter-mineral fractionation between magnetite and ilmenite at 200 °C results in a $\Delta^{49}\text{Ti}_{\text{ilv-ilim}}$ of c. 2.01‰ (Zhao et al.,

2020). Minor ilmenite and rutile are present in sample EH191 and magnetite is scarce in this sample. However, this mechanism does not explain the very high $\delta^{49}\text{Ti}$ values nor does it explain the overall $\delta^{49}\text{Ti}$ variation if the initial Ti isotope compositions are assumed to be initially homogeneous and/or similar to pre-ore magnetite. The variability of $\delta^{49}\text{Ti}$ within ore stage magnetite coupled with the uninherited $\delta^{49}\text{Ti}$ values indicates that Ti mobility may be affecting Ti isotope compositions of magnetite within the ore zone.

The introduction of a high $\delta^{49}\text{Ti}$ magmatic-hydrothermal fluid may explain the loose correlation between $\delta^{49}\text{Ti}$ and $\delta^{18}\text{O}$ as a mixing relationship between Ti in the pre-ore rock and Ti carried in the ore fluid. Because $\delta^{49}\text{Ti}$ correlates with silica content, a highly evolved granitic magma may have a bulk $\delta^{49}\text{Ti}$ of c. +1.5 to +2.0‰ (Greber et al., 2017; Aarons et al., 2020). However, the bulk transfer of Ti from a magma with a $\delta^{49}\text{Ti}$ of c. +1.5 to +2.0‰ into the Ernest Henry ore zone fails to explain $\delta^{49}\text{Ti}$ values higher than c. +2.0‰ assuming no additional fractionation. Available Ti data are exclusively from non-mineralized systems, so it is possible that extensive oxide fractionation may have resulted in a higher degree of light Ti depletion in the magma prior to volatile release and/or that fractionation between the melt and fluid resulted in an isotopically light fluid relative to the melt. Post-magmatic fractionation is likely required to achieve fluid Ti isotope compositions compatible with an overprinting model, unless $\Delta^{49}\text{Ti}_{\text{fluid-mgt}} - \Delta^{49}\text{Ti}_{\text{melt-fluid}}$ or their sum $\leq 0\text{‰}$. If $\Delta^{49}\text{Ti}_{\text{fluid-mgt}} > 0\text{‰}$, then the data may be explained by a very high $\delta^{49}\text{Ti}$ fluid precipitating and/or exchanging with magnetite. A high $\delta^{49}\text{Ti}$ fluid could be derived by selective leaching of heavy Ti isotopes by a ligand-rich brine. If $\Delta^{49}\text{Ti}_{\text{fluid-mgt}} < 0\text{‰}$, then the data may be explained by fluid leaching light Ti from magnetite during regenerative mineral replacement.

Titanium in aqueous halide solutions is mostly present as $[\text{TiH}_6]^{2+}$, where H₂ is most typically F, Cl, or OH in geologic systems (Ryzhenko et al., 2006). Empirical studies of Ti solubility in CO_3 , SO_4 , F⁻, and Cl⁻ rich fluids demonstrate that F-rich, acidic solutions are most effective at mobilizing Ti; however, mobility from Ti oxides (e.g., rutile) still remains low at < c. 1 ppm in aqueous solutions at low temperatures (Agapova et al., 1989; Ryzhenko et al., 2006; Van Baalen, 1993; Brugger et al., 2016). The presence of fluorite and near-endmember fluorapatite at Ernest Henry favors the presence of at least one phase of F-rich fluids, whereas hydrolytic alteration involved acidic fluids (Schlegel et al., 2020, 2021). The transport and precipitation of Fe (and Cu) most likely involved Cl-rich brines (Simon et al., 2004; Knipping et al., 2015; Simon et al., 2018). Thus, conditions favorable to Ti mobility may have occurred during one or more alteration events throughout the formation of the deposit. The larger range of Ti isotope compositions in ore stage magnetite implies that the most significant Ti isotope fractionation occurred during ore stage mineralization. The solubility of Ti in hot, briny fluids is mostly unknown, and experiments investigating Ti solubility in aqueous solutions are unlikely to be representative of conditions at Ernest Henry during ore formation (Brugger et al., 2016). However, brannerite (UTi_2O_6) at the Olympic Dam IOCG deposit is evidenced to have formed from in-situ alteration of rutile pseudomorphs after ilmenite, arguing against late-stage Ti mobility in at least some IOCG systems (Macmillan et al., 2017). If Ti was indeed mobile under ore-forming conditions, then fractionation may have been enhanced by lower (c. 520 °C) temperatures. The two lowest ore stage $\delta^{49}\text{Ti}$ values occur within the shallow portion of the EH435 drillhole, whereas the deeper portions of the deposit generally display higher $\delta^{49}\text{Ti}$ values. Regenerative mineral replacement of magnetite may have preferentially liberated light Ti, after which the light Ti-laden fluid may have then percolated up to shallower levels of the deposit where it either exchanged with magnetite or was unable to effectively leach and transport Ti due to lower temperatures or dilution with less acidic (or F-poor) fluids. Interaction with carbonate rocks (as inferred from $\delta^{18}\text{O}$ data) or dilution through mixing may have served to locally neutralize acidic fluids or otherwise alter their composition sufficiently to lower Ti solubility. The data demonstrate that Ti mobility and isotope

fractionation can occur in hydrothermal systems associated with the transport and deposition of Cu and Au. Further investigation of Ti solubility in hydrothermal systems as well as experimental investigation of Ti behavior in hydrothermal brines similar to those involved in the formation of IOCG deposits are required to more confidently interpret the $\delta^{49}\text{Ti}$ data presented here.

5.5. Deposit formation model

Combined with data and interpretations from previous studies, our results are consistent with an episodic, two-stage hydrothermal model for the formation of the Fe oxide and Cu-Au mineralization at Ernest Henry involving at least two different intratelluric fluid sources and a basinal brine. Pre-ore mineralization consisted of localized Na-Ca alteration followed by later bt-mgt, K-feldspar, and mgt-act alteration at c. 1530 Ma that directly preceded ore mineralization and apparently involved Fe leached from local crustal units by magmatic and/or mantle-derived fluids (Cave et al., 2018; Schlegel et al., 2021). Local reorganization of less mobile elements resulted in magnetite inheriting the Ti isotope composition of the protolith prior to ore mineralization. The second pulse of cooler (c. 200–520 °C) Cu-Au-rich fluids associated with the emplacement of the nearby Williams-Naraku suite may have mixed with evaporitic or other non-magmatic fluids resulting in heterogeneous $\delta^{18}\text{O}$ compositions in bt-mgt and ore stage magnetite and $\Delta^{17}\text{O}$ indicative of mixing with non-magmatic sources (Baker et al., 2008; Rusk et al., 2010; Cave et al., 2018). Local carbonate assimilation may have also contributed to variably increasing magnetite $\delta^{18}\text{O}$ values. This interpretation is similar to that presented in Cave et al. (2018) to resolve apatite geochronological and geochemical data—however, those authors attributed the first hydrothermal event to crustally-derived Ca-Cl-rich brines circulating at c. 1580 Ma at peak metamorphic conditions during the Isan Orogeny. If crustally-derived brines had extensively altered the host rocks at Ernest Henry, then their O isotope compositions are not preserved in later generations of magnetite. Similar models are proposed for other IOCG deposits to explain geothermometry data suggesting episodic heating and cooling recorded in actinolite (del Real et al., 2021). Those authors present a two-stage model to explain actinolite zoning in Andean IOCG deposits, wherein magnetite-actinolite-apatite mineralization was the result of an initial magmatic-hydrothermal event at temperatures ranging from c. 675–800 °C and Cu-Au-magnetite-actinolite-apatite mineralization resulted from a younger magmatic-hydrothermal event at temperatures of c. 550–700 °C (del Real et al., 2021). In IOCG systems, these two hydrothermal pulses may occur millions of years apart—explaining age discrepancies and radiogenic isotope resetting in IOCG systems (Cave et al., 2018; del Real et al., 2021).

Our data support the interpretations from previous studies (e.g., Kendrick et al., 2007 and Baker et al., 2008) proposing a fluid mixing model where magmatic-hydrothermal fluids exsolved from A-type granitic magmas contemporaneous with the Williams-Naraku batholiths and mixed with shallow Cu-poor, evaporite-derived fluids—explaining the diversity of salinities and presence of fluid inclusions with magmatic and evaporitic halogen contents, respectively (Fisher and Kendrick, 2008; Kendrick et al., 2007; Mark et al., 2006b). The model of Kendrick et al. (2007) is more complex than that favored by Baker et al. (2008) and proposes a three-fluid model where Cu-Au mineralization originated from magmatic-hydrothermal fluid(s) mixed with evaporite-derived brine(s); this solution was diluted by less saline surficial fluids. Our $\Delta^{17}\text{O}$ data support the mixing of evaporitic brines with the ore fluid, however, a deposit-scale dilution of the ore fluid is not readily apparent in the $\delta^{18}\text{O}$ data. The mixing of magmatic-hydrothermal fluids and basinal brines in some IOCG deposits has also been supported by $\delta^{34}\text{S}$ and Se/S evidence in pyrite from the Candelaria-Punta del Cobre IOCG district in Chile, emphasizing the potential for fluid mixing as an important factor in the formation of some—but not all—IOCG deposits (del Real et al., 2020). Oliver et al. (2008) also included fluid mixing in

their model or an explosive breccia origin whereby mixing between mafic and felsic melts resulted in the rapid evolution of a CO_2 -rich fluid from the roof of the felsic magma chamber during the late stage of emplacement. Paragenetic and fluid inclusion evidence suggest that the fluids responsible for transporting Fe and Ba were not the same as those transporting S during Cu-Au mineralization (Fisher and Kendrick, 2008; Kendrick et al., 2007; Mark et al., 2006b; Oliver et al., 2008). This interpretation is consistent with our data suggesting a non-magmatic Fe source, but magmatic O source as well as with literature data indicating a magmatic S source for IOCG deposits in the Cloncurry District (Davidson and Dixon, 1992; Rotherham et al., 1998; Mark et al., 2006b). The O isotope data presented here are also consistent with that of Twyerould (1997) and Oliver et al. (2008) constraining a magmatic fluid source and are therefore incompatible with the suggestion of Kendrick et al. (2007) that crustal carbonates were a major CO_2 source, as more widespread crustal carbonate contributions would be resolvable in the O isotope data rather than occurring in localized portions of the deposit, as observed in our data.

6. Conclusions

Integrated isotopic analysis indicates multiple metal and fluid sources contributed components to form magnetite at Ernest Henry. The O isotope data largely fingerprint a magmatic fluid source, but also demonstrate localized contamination from carbonate wall rocks. However, Fe isotope compositions suggest that much of the Fe in the deposit was not directly sourced from a magma and was instead leached from crustal rocks by magmatic-hydrothermal fluids prior to Cu-Au mineralization. These results differ from those of previous studies using Fe-O stable isotope pairs to fingerprint a magmatic-hydrothermal metal and fluid source for Andean IOA and IOCG deposits and demonstrate that the fluids and metals involved in IOCG formation for some deposits may be polygenetic—involving both magmatic fluids as well as crustally-derived metals. Ernest Henry is the first known IOCG deposit to exhibit a major non-magmatic Fe input as determined via Fe stable isotope geochemistry. However, the results are broadly consistent with previous models for Cloncurry IOCG deposits invoking fluid mixing between magmatic-hydrothermal and evaporitic fluids. Despite evidence for non-magmatic metal and fluid input, these findings still advocate for a direct link between IOCG mineralization and magmatic-hydrothermal fluids. Additionally, Ti isotope variations observed in the Ernest Henry deposit demonstrate for the first time that Ti isotope fractionation can occur in hydrothermal systems, although more data are needed to understand the mechanisms behind this.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge funding from the University of Michigan Rackham Graduate School, the University of Michigan Department of Earth and Environmental Sciences Mitchell Fund, and from the NSF EAR grant #1924142. We are grateful to Catherine Miller, Jensen Delawder, and Sarah Purdom for their assistance with sample preparation. We thank the two anonymous reviewers for their helpful comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2022.105170>.

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