Geochemical, geochronological, and textural relationships between magnetite-(apatite) and iron oxide-copper-gold mineralization,

Montecristo district, northern Chile

by

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Abstract

The genetic relationship, if one exists, between magnetite-(apatite) (MtAp) and iron oxidecopper-gold (IOCG) deposits has been debated for many years, and to this day, few representative places have been found where both types of mineralization occur. The Jurassic age Montecristo district in northern Chile is one of a few places in the world where both MtAp and IOCG mineralization occur with vertical and crosscutting relationships. Consequently, this is one of the best sites to better understand the possible relationship between these two types of mineralization and their formation, and is the main objective of this thesis project. For this project, the samples studied were selected from: (1) a MtAp vein (the San Juan vein), comprising magnetite, and pegmatite-like fluorapatite, and actinolite; (2) a vein with MtAp mineralization in the deeper parts of the system, and an overprinting IOCG assemblage of chalcopyrite, pyrite, magnetite, actinolite, quartz, gold, and molybdenite, in the shallower parts of the system (the Abundancia vein); and (3) the host rock that contains both types of mineralization.

The results of this study reveal that the host diorite, the MtAp mineralization in the Abundancia and San Juan veins, and the IOCG mineralization, are all coeval within error, and that their genetic relationship cannot be discriminated by geochronology alone. However, intermediate ϵ_{Ndi} values of the IOCG event suggest a mixing of Nd from the MtAp rocks and a deep magmatic-hydrothermal source. Hf, Sr–Nd, and sulfur isotopes support a model in which the IOCG mineralization was derived from magmatic-hydrothermal fluids. We propose that an ascending, immiscible iron-rich melt utilized structures of the Atacama fault system as pathways for the deposition of the MtAp mineralization, followed by precipitation of the IOCG sulfide-magnetite-actinolite-quartz-gold assemblage from magmatic-hydrothermal fluids that used the earlier MtAp rocks as a trap.

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General Summary

The iron oxide-copper-gold (IOCG) mineral deposits clan includes magnetite-(apatite) (MtAp) deposits (an iron-rich mineral deposit that also contains variable amounts of rare earth elements), and IOCG deposits (that are commonly mined for copper and gold, but can also contain variable amounts of cobalt, molybdenum, rare earth elements, or uranium, among others). Although formation of the MtAp deposits is a controversial topic, the possible existence of a genetic relationship between both types has been discussed for many years. The Montecristo district in northern Chile is among the best locations in the world to study this relationship because it is one of the few places where both types of mineralization occur in the same location. This district hosts MtAp and IOCG deposits with mutual vertical and crosscutting relationships. In this study we conclude, based on data from radiogenic isotopes, geochronology, mineral chemistry, and stable isotopes, that these two types of deposits at this location are not genetically related. We interpret the MtAp mineralization as having formed by an iron-rich melt that crystallized along the structures of the Atacama fault system, followed by crystallization from magmatic-hydrothermal fluids containing copper, gold, and molybdenum. The IOCG mineralization shows mixed ε_{Ndi} values, both from the MtAp rocks and a deep magmatichydrothermal source, probably an intrusion compositionally similar to the host diorite.

Co-authorship statement

Drs. J.M. Hanchar and F. Tornos obtained the funding for this research and supervised the whole project.

This master's thesis project was completed by the author of the thesis, Laura Mateo Ríos, which includes the research proposal, practical aspects of the research, data analysis, and initial preparation of the manuscript. Field work and sampling was done in Chile by Laura Mateo. Sample preparation was done by Laura Mateo and Dr. J.M. Hanchar; analyses were done by Laura Mateo and the co-authors of the manuscript. Subsequent data analysis, graphs, tables, and figures were done by Laura Mateo. The original draft was primarily written by the author of this thesis. The manuscript (Chapter 2), which has been submitted to an international peer-reviewed journal, was a collaborative effort with the co-authors, all of whom provided feedback and edits and did a critical review of the manuscript prior to submission.

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List of Abbreviations

- Act Actinolite
- AFS Atacama fault system
- **Ap** Apatite
- BSE imaging Back-scattered electron imaging
- CIB Chilean iron belt
- CL Cathodoluminescence
- Ccp Chalcopyrite
- EA-IRMS Elemental analyzer online with a Delta Plus XL mass spectrometer
- EDS Energy-dispersive spectroscopy
- EPMA Electron probe micro-analyzer
- FEG-SEM Field emission gun scanning electron microscope
- HR-ICPMS Double-focusing magnetic sector-inductively coupled-plasma mass spectrometer
- **ID-TIMS** Isotope dilution-thermal ionization mass spectrometry
- IOCG Iron oxide-copper-gold
- LA-ICPMS Laser ablation-inductively coupled plasma mass spectrometry
- LASS Laser ablation split stream
- LOD Limit of detection
- MAF Micro Analysis Facility
- MC-ICPMS Multi-collector inductively coupled plasma mass spectrometer
- MIC Matancilla intrusive complex
- Mol Molybdenite
- Mt Magnetite

MtAp - Magnetite-(apatite)

Py - Pyrite

Qt - Quartz

REE - Rare earth elements

Ttn - Titanite

- $\ensuremath{\textbf{UST}}$ Unidirectional solidification growth textures
- V-CDT Vienna-Canyon Diablo Troilite

Chapter 1

1.1. Introduction and Overview

The genetic relationship between iron oxide-copper-gold (IOCG) and magnetite-(apatite) (MtAp) deposits has been discussed and vigorously debated for several years. Due to their shared characteristics, such as the presence of iron oxides and the associated alkali-calcic-iron alteration zones, it has been suggested that these two deposit types are part of the same group (Williams et al., 2005), or are endmembers of a continuous spectrum of mineralization (Hitzman et al., 1992; Vivallo and Henríquez, 1997; Hitzman, 2000; Gandhi, 2003; Sillitoe, 2003; Knipping et al., 2015a, b; Corriveau et al., 2016; Simon et al., 2018).

The IOCG deposits sensu stricto contain Cu and Au minerals and low-Ti iron oxides (magnetite/hematite, or both), and have been attributed to two different hydrothermal processes: (a) a magmatic-hydrothermal origin associated with fluids derived from crystallizing intrusions (Vila et al., 1996; Vivallo and Henríquez, 1997, 1998; Pollard, 2000; Haynes 2000; Marschik and Fontboté, 2001; Trista and Kojima, 2003; Sillitoe, 2003; Williams et al., 2005; Pollard, 2006; Groves et al., 2010; Barton et al., 2011; Richards and Mumin, 2013; Tornos et al., 2010); and (b) a brine derived from the interaction of connate fluids with evaporitic deposits or fluids derived from them along with a heat source (magmatic or metamorphic) to provide the elevated temperatures to leach the metals (Hitzman, 2000; Barton and Johnson, 1996, 2000).

Alternatively, MtAp deposits are low-Ti magnetite deposits with variable amounts of apatite (commonly fluorapatite), actinolite/clinopyroxene, scapolite, and anhydrite (Nyström and Henríquez, 1994; Naslund et al., 2002; Valley et al., 2010; Day et al., 2016; Tornos et al., 2017; Liu et al., 2018; Heidarian et al., 2018). Some deposits contain anomalously high concentrations of rare earth elements (REE) and U (Hitzman, 2000; Naslund et al., 2000). They are also called

iron oxide-apatite (IOA), or Kiruna-type deposits (Geijer, 1931), which received its name from the type locality, the massive Kiirunavaara deposit in the Norrbotten region of northern Sweden. The origin of MtAp deposits has been controversial for decades, involving different proposed origins for this type of deposit: (a) a sedimentary-exhalative model involving deposition on the paleo seafloor (Parák, 1975); (b) direct crystallization from an immiscible Fe-rich melt (Henríquez and Martin, 1978; Frietsch, 1978; Philpotts, 1981, 1982; Nyström and Henríquez, 1994; Naslund et al., 2002; Lledó and Jenkins, 2008; Velasco et al., 2016; Nyström et al., 2016; Hou et al., 2018; Lledó et al., 2020), which follows with the exsolution of hydrothermal fluids (Tornos et al., 2016, 2017); (c) a hydrothermal model that involves the complete replacement of pre-existing rocks by dissolution of the contained minerals and precipitation of magnetite ± apatite from hydrothermal fluids of magmatic origin (Hildebrand, 1986; Ménard, 1995; Rhodes et al., 1999; Sillitoe and Burrows, 2002; Gandhi, 2003; Corriveau et al., 2016); (d) fluids of nonmagmatic origin (e.g., basinal brines; non-magmatic fluids equilibrated with evaporites) (Hitzman, 2000; Barton and Johnson, 1996, 2000; Rhodes and Oreskes, 1999); (e) crystallization of magnetite microlites from a silicate melt, followed by buoyant segregation and flotation of these early formed magmatic magnetite-bubble pairs then deposition of massive magnetite in regional-scale transcurrent faults, and eventual growth of hydrothermal magnetite during cooling (Knipping et al., 2015a, b; 2019); and (f) crystallization from an Fe-rich magma containing sulfate, the latter derived from the melting of marine sediments by andesite intrusion (Bain et al., 2020, 2021).

Despite the disagreements regarding the formation of MtAp deposits, the genetic relationship, if one exists, between MtAp and IOCG deposits remains unclear. To the author's knowledge, there are very few areas where both MtAp and IOCG mineralization occur in the same place. The Montecristo district in northern Chile hosts a vein-like mineralization with

IOCG deposits that transitions to MtAp mineralization at depth, showing vertical and crosscutting relationships between them. The district is located in the Chilean iron belt (CIB) (Espinoza, 1990), which hosts most of the MtAp and IOCG deposits in northern Chile (Vivallo et al., 2000; Maksaev et al., 2007). The district contains diorites of the Matancilla intrusive complex (MIC) (Middle Jurassic-Late Jurassic; ca. 168-154 Ma; Alvarez et al., 2016), which were produced through subduction-related volcanism and plutonism that formed the La Negra magmatic arc during the Early Jurassic to the Early Cretaceous. Deposits in the district are spatially controlled by secondary faults of the Atacama fault system (AFS) (Brown et al., 1993).

For this research project, two veins from the Montecristo district were selected: (1) the San Juan MtAp vein that contains magnetite, coarse-grained fluorapatite, and actinolite with pegmatitic textures; and (2) the Abundancia vein, which consists of MtAp mineralization at depth and IOCG mineralization in the shallower parts of the system. In order to understand the relationship between these two types of mineralization, isotopic, mineralogical, petrographic, geochemical, and geochronological analyses were done on the MtAp mineralization in the San Juan and Abundancia veins, and on the IOCG mineralization in the Abundancia vein.

1.2. Research Problem Statement

This study was undertaken to provide a better understanding of the relationship, if in fact one exists, between IOCG and MtAp deposits, with a focus on the Jurassic Montecristo district in northern Chile.

In the Coastal Cordillera of Chile several IOCG and MtAp deposits have been proposed to have temporal and spatial relationships (e.g., Naguayán district, Boric et al., 1990; Mantoverde deposit in the Los Pozos district, Vila et al., 1996; Dominga district, Arredondo et al., 2017), and elsewhere with different geological settings and formational ages (e.g., Norrbotten district in

Sweden, Martinsson et al., 2016; Missouri iron province in USA, Day et al., 2016; Great Bear Magmatic Zone in Canada, Ootes et al., 2017). Furthermore, several authors have proposed a continuum between both types of mineralization, involving the evolution from a deep magnetiterich system towards a Cu-Au-rich mineralization higher in the system (Hitzman et al., 1992; Sillitoe, 2003; Knipping et al., 2015a, b; Corriveau et al., 2016; Apukhtina et al, 2017; Simon et al., 2018; Verdugo-Ihl 2020). However, there is no clear evidence of a genetic relationship since this connection has been merely inferred. In a recent study by Rodriguez-Mustafa (2020), a continuum between both types of deposits was proposed, although the deposits are ~100 km apart with no direct geologic relationship. A set of geological, geochronological, mineralogical, and geochemical analyses done on each type of mineralization located spatially close to each other would help to better evaluate this possible link.

The Montecristo district in northern Chile is one of the best places to study the relationship between MtAp and IOCG mineralization, due to the occurrence of both mineralization types in close proximity and with crosscutting relationships. Findings of this study will be useful for future exploration programs in Chile and elsewhere in the world, as these will help address geological issues present within such deposit types and hopefully lead to the discovery of new deposits elsewhere.

1.3. Objectives of the research

This research project was undertaken in order to achieve the following two objectives: (1) to determine if a genetic relationship exists between the IOCG and MtAp mineralization;

(2) to constrain the origin and formation of the IOCG and MtAp mineralization in the Montecristo district, and their relationship with the host rocks.

To address these research objectives, several types of analyses were done that include: (a) chemical analyses of fluorapatite, magnetite, and actinolite from the IOCG and MtAp mineralization in the Abundancia and San Juan veins;(b) Rb–Sr and Sm–Nd whole-rock radiogenic tracer isotopes targeted on the IOCG mineralization, in order to compare these with previously published values for the MtAp mineralization and the host rocks; (c) ⁴⁰Ar–³⁹Ar geochronology of actinolite from the MtAp mineralization in the Abundancia and San Juan veins to date the MtAp event; (d) Re–Os geochronology of molybdenite to date the IOCG event; (e) U–Pb geochronology of zircon from the host rock in order to constrain its timing of emplacement; (f) Hf tracer isotopes on zircon from the host rock to better understand its origin; and (g) sulfur stable isotopes on sulfide minerals from the IOCG event to characterize the source of the fluids.

1.4. Project Overview

The findings of this research (Chapter 2) are presented as a manuscript that has been submitted to the journal *Mineralium Deposita*, followed by Chapter 3 that includes a summary of the conclusions of this research project.

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Chapter 2

The Montecristo mining district, northern Chile: genetic relationship between veinlike magnetite-(apatite) and iron oxide-copper-gold deposits

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2.1. Abstract

The Montecristo district, in the Atacama Desert region of northern Chile, is one of the few places worldwide where an obvious spatial relationship exists between magnetite-(apatite) (MtAp) mineralization and iron oxide-copper-gold (IOCG) mineralization. However, few geological studies have been done in this district. New field, geochronological, geochemical, and mineralogical data reported in this study provide insights about these types of mineralization and their mutual relationship. The deep MtAp mineralization at Montecristo comprises magnetite, fluorapatite, and actinolite with pegmatite-like textures that are cut and partially replaced by younger IOCG mineralization that includes a second generation of actinolite and magnetite together with chalcopyrite, pyrite, and molybdenite; this paragenetically later event is characterized by quartz inclusions in the magnetite and higher amounts of Cu. The MtAp stage is interpreted to be the product of immiscible iron-rich melts that used pre-existing structures of the Atacama fault system as conduits in which the magnetite-fluorapatite-actinolite mineralization crystallized, and the MtAp ore later acted as a trap for the magmatic-hydrothermal fluids that equilibrated with diorite and produced the IOCG mineralization. Geochronological data for Montecristo indicate that emplacement of the host diorite (U–Pb zircon 153.3 ± 1.8 Ma, 2-sigma) and formation of MtAp mineralization in the Abundancia vein (40 Ar $^{-39}$ Ar on actinolite, 154 ± 2 Ma, 2-sigma), and in the San Juan vein (${}^{40}Ar - {}^{39}Ar$ on actinolite, 153 ± 4 Ma, 2-sigma), and formation of the IOCG event (Re–Os on molybdenite, 151.8 ± 0.6 Ma, 2-sigma), are coeval within error and occurred within a time span of less than 8.0 m.y. The ε_{Hfi} and ε_{Ndi} values of the host diorite are +5.03 to +6.71 and +2.3 to +3.4, respectively. Whole-rock ⁸⁷Sr/⁸⁶Sr_i values of the IOCG mineralization (0.70425-0.70442) are similar to those of the MtAp mineralization (0.70426 and 0.70629; previous studies), whereas ε_{Ndi} values of the IOCG mineralization (+5.4 and +5.7) fall between those of the MtAp mineralization (+6.6 to +7.2) and the host diorite, suggesting that

the IOCG event was produced by the circulation of hydrothermal fluids having a more crustal Nd composition (ε_{Ndi} <+5.7) than the MtAp mineralization. This result likely reflects the mixing of Nd from the MtAp protolith and a deep magmatic-hydrothermal source, very likely an unexposed intrusion compositionally equivalent to the host diorite. Sulfur isotope compositions ($\delta^{34}S = +0.3$ to +3.4‰) are consistent with the IOCG mineralization being derived from a magmatic source. Although a spatial and temporal relationship between both mineralization types clearly exists, our data indicate that these formed from distinct, separate systems. The model presented herein provides a new framework for exploration purposes in targeting MtAp and IOCG deposits elsewhere.

Keywords: MtAp deposits, IOCG deposits, mineral chemistry, isotope geochemistry, geochronology, Montecristo district

2.2. Introduction

Iron oxide-copper-gold (IOCG) and magnetite-(apatite) (MtAp) mineralization are included in a controversial group of ore deposits that share some common characteristics, such as abundance of iron oxide minerals and associated calcic-iron-alkali alteration zones. The largest discovered deposit is the world-class Olympic Dam orebody, which is thought to be representative of the IOCG-MtAp system as a whole (Hitzman et al., 1992). IOCG sensu stricto mineralization consists of magnetite and/or hematite and chalcopyrite, with subordinate pyrite, pyrrhotite, and bornite, typically accompanied by actinolite and alkali feldspar. Ages of IOCG deposits range from the Late Archean (Carajás district in Brazil) to the Mesozoic (Chilean and Peruvian belts) (Hitzman et al., 1992; Williams et al., 2005); most deposits are replacive showing a space-time association with igneous rocks, from intrusions to volcanic rocks (Williams et al.,

2005). The IOCG sensu stricto mineralization is hydrothermal and has been explained by two contrasting models: (1) a magmatic-hydrothermal origin related to the exsolution of fluids derived from crystallizing intrusions (Vila et al., 1996; Vivallo and Henríquez 1997, 1998; Pollard, 2000; Haynes, 2000; Marschik and Fontboté 2001; Trista and Kojima 2003; Sillitoe, 2003; Williams et al., 2005; Pollard, 2006; Groves et al., 2010; Barton et al., 2011; Richards and Mumin 2013; Tornos et al., 2010); or (2) a brine derived from the interaction of connate fluids with evaporite deposits or fluids derived from them (Hitzman, 2000; Barton and Johnson 1996, 2000; Kirkham, 2001).

MtAp mineralization, sometimes referred to as Kiruna-type (Geijer, 1931), or iron oxide apatite (IOA), consist of massive, low-Ti magnetite ores with variable amounts of apatite (commonly fluorapatite), actinolite, or clinopyroxene (i.e., diopside), scapolite, and anhydrite (Nyström and Henríquez, 1994; Naslund et al., 2002; Valley et al., 2010; Day et al., 2016; Tornos et al., 2017; Liu et al., 2018; Heidarian et al., 2018); many contain anomalously high concentrations of REEs and U within the apatite (Hitzman, 2000; Naslund et al., 2000). The diagnostic feature is the presence of coarse-grained apatite and actinolite, which together locally show pegmatitic textures (Tornos et al., 2021). MtAp deposits are known to occur from the Early Proterozoic (e.g., Kiruna, Sweden; Geijer, 1931) to the Pliocene (El Laco, Chile; Park, 1961). These deposits are principally associated with calc-alkaline to alkaline volcanic or plutonic rocks (Naslund et al., 2000), and commonly have pervasive metasomatic alteration zones developed in the host rocks, characterized by calcic-iron-alkali zones (Hitzman, 2000) that may grade upward into hydrolytic altered zones (Hitzman et al., 1992).

Different hypotheses have been proposed for the origin of MtAp deposits including: (1) crystallization from an immiscible Fe-rich melt (Henríquez and Martin, 1978; Frietsch, 1978; Philpotts, 1981, 1982; Nyström and Henríquez, 1994; Naslund et al., 2002; Lledó and Jenkins,

2008; Velasco et al., 2016; Nyström et al., 2016; Hou et al., 2018; Lledó et al., 2020), coeval with the exsolution of large amounts of hydrothermal fluids equilibrated with these melts (Tornos et al., 2016, 2017); (2) hydrothermal fluids of magmatic derivation that completely replaced preexisting rocks by massive magnetite (Hildebrand, 1986; Ménard, 1995; Rhodes et al., 1999; Sillitoe and Burrows, 2002; Gandhi, 2003; Corriveau et al., 2016); (3) replacement of preexisting rocks by fluids of non-magmatic origin such as basinal brines, or by non-magmatic fluids that had equilibrated with evaporites (Hitzman, 2000; Barton and Johnson, 1996, 2000; Rhodes and Oreskes, 1999); (4) crystallization of magnetite microlites from a silicate melt followed by buoyant segregation and flotation of magmatic magnetite-bubble pairs, deposition of massive magnetite along faults, and posterior growth of hydrothermal magnetite (Knipping et al., 2015a, b; Ovalle et al., 2018; Salazar et al., 2019; Knipping et al., 2019); and (5) crystallization from a sulfate- and iron-rich magma, reflecting the product of melting and assimilation of shallow marine sediments by intruding andesite (Bain et al., 2020, 2021).

The relationship between both styles of mineralization is a controversial topic. Despite a wide range of interpretations, shared characteristics have led several authors to propose that these deposits are part of the same clan (Williams et al., 2005), or that they represent end members on a continuous spectrum of mineralization (Hitzman et al., 1992; Vivallo and Henríquez 1997; Hitzman, 2000; Gandhi, 2003; Sillitoe, 2003; Knipping et al., 2015a, b; Corriveau et al., 2016; Simon et al., 2018), evolving from a deep magnetite-rich system towards a more Cu-Au-rich shallow one. Several arguments have been discussed to support the incorporation of MtAp deposits as end members of the IOCG group (Hitzman et al., 1992), including a similar mineral association (i.e., iron oxides), hydrothermal alteration zones dominated by actinolite or clinopyroxene, and alkali feldspars, and their mutual spatial and temporal relationships.

This relationship is reinforced by the local occurrence of sparse, hydrothermal, late-stage Cu-Fe sulfides and gold overprinting some MtAp deposits or in the vicinity (e.g., Marcona in Peru, Chen et al., 2010a; Cerro Negro Norte in Chile, Vivallo et al., 1995, Salazar et al., 2019), or by the presence of mineralization ascribed to the IOCG group occurring near clusters of MtAp deposits (Norrbotten district in Sweden, Martinsson et al., 2016, Bauer et al., 2021; Missouri iron province in USA, Day et al., 2016; Great Bear Magmatic Zone in Canada, Ootes et al., 2017).

The characteristics of both styles of mineralization, however, are by some authors confused and intermixed despite the work of Groves et al. (2010) who emphasized that these are two separate types of mineralization. On a global scale, MtAp systems are much more abundant than IOCG systems and both only locally coexist, such as in the Carajás district in Brazil (Xavier et al., 2012; Schutesky and de Oliveira, 2020), at the Olympic Dam deposit in Australia (Ehrig et al., 2012; Apukhtina et al., 2017), and the Coastal Cordillera of the Andes (Espinoza, 1990; Sillitoe, 2003). The detailed structural studies of Bauer et al. (2018, 2021) in the Norrbotten region suggest that in many cases IOCG mineralization can be significantly younger and unrelated to the MtAp mineralization, and that the massive magnetite produced by the MtAp event acts as a trap for the later Cu-Au-rich event.

In the Coastal Cordillera, MtAp systems are dominantly vein-like with a few extrusive tops despite that locally hydrothermal replacive mineralization occurs where the subvertical veins, up to several tens of meters thick, cut rocks that are favorable for fluid-rock interactions (Espinoza, 1990; Henríquez et al., 1994; Travisany et al., 1995; Tornos et al., 2021). Most well-known IOCG deposits formed by replacement within favorable rocks such as andesite or carbonates (Mina Justa, Peru, Chen et al., 2010b; Punta del Cobre district, Chile, Marschik and Fontbote, 2001, Arevalo et al., 2006; Dominga, Chile, Arredondo et al., 2017). However, some smaller deposits occur within discordant veins in the basement or in the plutonic rocks that underlie the

Jurassic-Cretaceous mafic volcanic rocks (Boric et al., 1990; Sillitoe, 2003), and these are the few veins where the relationship between unambiguous MtAp and IOCG mineralization can be demonstrated. For these plutonic-hosted veins, Espinoza (1990) and Sillitoe (2003) proposed a vertical evolution from deep MtAp to shallower IOCG mineralization. This vertical zonation model has been expanded by Simon et al. (2018) to the giant IOCG deposits of Mantoverde and Punta del Cobre in Chile. At Mantoverde, the hematite-rich mineralization caps magnetite ore with no evidence of apatite (A. Sanguinetti, pers. commun., 2018) and in the similar and nearby mineralization at Carmen de Cobre; at the latter deposit, U–Pb dating of hematite suggests that the IOCG mineralization is ca. 10 m.y. younger than the MtAp of the nearby Carmen de Fierro deposit (Gelcich et al., 2005; Verdugo-Ihl et al., in press.). At the stratabound and discordant, magnetite-rich deposits in the Punta del Cobre district, there are no rocks with the pegmatitic magnetite-apatite-actinolite textures that can be assigned to a MtAp system (see Arevalo et al., 2006; Marschik et al., 2001; Del Real et al., 2018; J. Carriedo, pers. commun., 2020); thus, the link proposed by Simon et al. (2018) is based on the coexistence but unknown affiliation of massive magnetite with IOCG mineralization.

One of the best places for elucidating the genetic relationship between MtAp and IOCG systems is the group of vein-type deposits in the Montecristo and Tocopilla districts, where the veins display both styles of mineralization. These veins are representative of a large group of veins that extend from northern Chile into southern Peru (Sillitoe, 2003; Tornos et al., 2021). The absence of stratabound or shear-controlled replacive mineralization in the Montecristo and Tocopilla districts limits arguments for fluid-rock interactions. In the present study, new results from a detailed mineralogical, geochemical, and geochronological investigation of the Montecristo district reveal that although the IOCG and MtAp deposits are in close proximity, and

the radiometric ages are coeval within error, the data overall suggest that these deposits are not part of the same mineralizing system.

2.3. Geological Background

The Chilean iron belt (CIB) is situated along the Coastal Cordillera between 26° and 31°S and includes most of the IOCG and MtAp deposits in northern Chile, and other deposit types such as large porphyry copper deposits, Cu- and Au-bearing veins, and "manto-type" or stratabound Cu deposits (Vivallo et al., 2000; Maksaev et al., 2007). The CIB is underlain by up to a 10-km-thick sequence of Jurassic and Lower Cretaceous subaerial basaltic andesite to andesite of the La Negra Formation, and its stratigraphically equivalent subaqueous Punta del Cobre Formation to the south. Rocks of the La Negra Formation have predominantly high-K to calc-alkaline geochemical affinities (Buchelt and Tellez, 1988); however, rocks of tholeiitic compositions that formed during the initial stages of the magmatic arc also exist (Pichowiak et al., 1990; Lucassen and Franz, 1994). Plutonic rocks of Late Jurassic and Early Cretaceous age with similar geochemistry intrude these volcanic rocks (Espinoza, 1990), and together they represent the magmatism that marks the onset of the Andean arc.

The Andean magmatic arc formed in the Jurassic after the breakup of Gondwana as a consequence of the subduction of oceanic lithosphere under the South American plate in westernmost Chile, extending along the present-day Coastal Cordillera (Dalziel et al., 1987; Mpodozis and Ramos 1990; Charrier et al., 2007). Oblique subduction led to the formation of a large strike-slip structure, the Atacama fault system (AFS), which has a dominant sinistral component and extends along the Coastal Cordillera from ~20°30' to ~29°45'S (Hervé, 1987; Mpodozis and Ramos, 1990; Scheuber and Reutter, 1992; Brown et al., 1993; Cembrano et al., 2005).

During the Late Jurassic-Early Cretaceous, the AFS experienced both transtensional and transpressional movement (Cembrano et al., 1997, 2005; Grocott and Wilson, 1997). The main structure, and subsidiary faults, of the AFS also played an important role in the location of the IOCG and MtAp deposits (Boric et al., 1990; Freraut and Cuadra, 1994; Vila et al., 1996; Gelcich et al., 1998, Sillitoe, 2003; Vivallo et al., 2008; Tornos et al., 2021). Most of the mineralization is related to N-S and NW-SE structures, both having sinistral strike-slip and normal dip-slip extensional movements (Dallmeyer et al., 1996; Cembrano et al., 2005). These structures also controlled the emplacement of the plutonic rocks in the area (Grocott and Wilson, 1997).

Initial K–Ar, and later ⁴⁰Ar–³⁹Ar, dating of hydrothermal silicates (e.g., actinolite, Kfeldspar, biotite, white mica) indicate that most of the IOCG and MtAp deposits in the CIB formed during the Middle to Late Jurassic (~170-150 Ma) and Early Cretaceous (~130-110 Ma), but there are also some deposits that have Late Cretaceous or Paleocene ages (e.g., Dulcinea, La Africana, El Espino; Boric et al., 1990; Vila et al., 1996; Vivallo and Henríquez, 1998; Gelcich et al., 1998; Gelcich et al., 2003; Sillitoe, 2003; Vivallo et al., 2008; Arredondo et al., 2017). These diverse ages support the existence of discrete metallogenic sub-belts within the CIB.

The Montecristo district, the focus of the present study, is located in the Middle to Late Jurassic sub-belt (22-26°S) between Taltal and Antofagasta, Chile (Boric et al., 1990; Espinoza et al., 1996; Vivallo and Henríquez, 1998). Mineralized veins in this district are hosted by diorite of Middle to Late Jurassic age of the Matancilla intrusive complex (MIC) (~168-154 Ma; Naranjo and Puig, 1984; Escribano et al., 2013; Álvarez et al., 2016) (Fig. 1a). Overall, the plutonic rocks in this area have tholeiitic, to calc-alkaline, to high-K geochemical affinities, and are metaluminous (Álvarez et al., 2016). The host diorite contains amphibole and is phaneritic, hypidiomorphic, and inequigranular. This host rock has been pervasively metasomatically altered by hydrothermal fluids; original plagioclase has been replaced from the center to the edge of the grains by potassium feldspar, followed by low-temperature replacement by adularia, albite, or white mica, and a late calcite replacement; the amphiboles have been strongly chloritized (ESM Fig. 1, a-c).

The Montecristo district contains at least 12 mineralized veins that strike roughly NE-SW, are ~500 to ~5000 m long, and ~3 to ~30 m wide (Fig. 1b). The IOCG mineralization includes dominant magnetite, actinolite, chalcopyrite, pyrite, bornite, molybdenite, and minor titanite and quartz, plus small quantities of gold; some mineralized veins show a geochemical anomaly in Ag, Pb, Zn, and V (Espinoza et al., 1996). The oxidized zones contain atacamite, chrysocolla, antlerite, minor stringhamite [(CaCuSiO4•2(H₂O)] and chenevixite [Cu₂Fe³⁺₂(AsO4)₂(OH)₄], whereas the underlying supergene cementation is primarily composed of covellite and chalcocite (Espinoza et al., 1996). The veins show a restricted halo of calcic-iron-alkali alteration with albite, quartz, magnetite, chlorite, actinolite and sericite (Vivallo and Henríquez, 1998). Structural control of the veins is by tensional faults oblique to the main trend of the AFS (Tornos et al., 2021) in the Paposo segment, one of the three segments of the AFS between Antofagasta and Paposo (Brown et al., 1993).

The most well-known deposit in this district, the Montecristo vein, is a magnetite-rich vein striking N45-50°E and dipping 75-80°NW, with an average width of ~10 m but in places up to ~30 m in width, with a total vertical extent of ~400 m. This vein was discovered in 1850, and since then ~10 Mt or ore have been mined. However, the focus of this study is on the Abundancia and San Juan veins, due to their proximity and key geological characteristics. The Abundancia vein contains both MtAp and IOCG mineralization and despite its historic importance as a copper source in the region, this vein has not been studied comprehensively. The San Juan vein is part of the same vein system as Abundancia but differs from the others, being a classical MtAp vein composed of magnetite, fluorapatite, and actinolite.

2.3.1. The Abundancia MtAp-IOCG vein

The Abundancia vein trends N40°E and is ~4 m-wide with 1.4% Cu plus subordinate gold (0.4-0.5 g/t) and molybdenum (0.03%), and small concentrations of Co and Ni. The vein has been mined down to 940 m below the land surface. Several hypogene mineral assemblages are recognized, which are part of the following parageneses (Fig. 2): (1) an early MtAp stage that includes magnetite, fluorapatite, and actinolite predominantly arranged in parallel bands with cmsized crystals of fluorapatite that are perpendicular to the edge of the veins (Fig. 3a,b); (2) a second MtAp event having the same mineral assemblage but with decreasing grain size and more abundant magnetite occurring as crosscutting veins (Fig. 3a); (3) an IOCG stage that seems to dominate in the upper parts of the vein and clearly cuts the MtAp assemblages (Fig. 3a, b); Minerals of this stage include magnetite, actinolite, chalcopyrite, pyrite, quartz, titanite, gold, and pyrite that is replaced by later chalcopyrite; (4) a copper-rich event that produced massive chalcopyrite up to ~ 20 cm thick in quartz veins (Fig. 3c); and (5) a late stage that formed small veinlets of calcite and laminar molybdenite, which cut the earlier MtAp and IOCG mineralization. The halo of the calcic-iron-alkali metasomatic alteration zone is weak and seems to increase in size and intensity downwards.

In the deepest levels of the system (~940 to ~915 m) there is an altered and brecciated monzogabbro that is replaced by an andradite-diopside-magnetite assemblage. This Fe-rich silicate assemblage is coeval with albitization and shows replacement of pyroxene by actinolite and veinlets of actinolite and hydroxyapatite, together with minor biotite, quartz, chalcopyrite, and pyrite (Díaz et al., 2018).

2.3.2. The San Juan MtAp vein

The San Juan MtAp vein has a NE-SW strike, width of ~4 m, and ~600 m of inferred length. It contains massive magnetite in which subvertical bands are enriched in coarse-grained fluorapatite and actinolite (Fig. 2) that form pegmatite-like textures similar to those found in the Abundancia vein (Fig. 3d, e). Outcrops of this vein show a strong supergene alteration with replacement of the magnetite by hematite and late, cross-cutting calcite veinlets.

2.4. Analytical Methods

2.4.1. Petrography

Samples for petrographic studies were selected from the IOCG and MtAp mineralization in the Abundancia and San Juan veins. Back-scattered electron (BSE) images were obtained on two 25-mm diameter x 6-mm tall, epoxy mounts containing several rock billets after polishing and carbon coating. The billets were examined with a JEOL 7100F field emission gun scanning electron microscope (FEG-SEM) at Memorial University of Newfoundland equipped with energy-dispersive spectroscopy (EDS) at 15 kV and 50 nA. The same epoxy mounts were used for further analysis by electron probe microanalysis (EPMA) and by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). Thin sections from the mineralized zones and the host rocks were used for reflected light microscopy, and for cathodoluminescence (CL) imaging on fluorapatite to reveal the distribution of metasomatic alteration.

2.4.2. Electron Probe Micro Analysis (EPMA) of minerals

EPMA traverses and spot analyses were done for major and minor elements on representative grains of actinolite, magnetite, and fluorapatite in the epoxy mounts (Fig. 4). Analyses were done for each type of mineralization in both deposits. Analyses include Ti, Mn, K, Ca, S, Na, Al, Si, Mg, Fe, F, and Cl for the actinolite samples. Special attention was devoted to the analysis of potassium because it is critical for ⁴⁰Ar–³⁹Ar geochronology that was done later (see below). Magnetite analyses include Cu, Ni, Mn, Ti, V, K, Ca, S, P, Na, Al, Si, Mg, Zn, Co, Fe, Cr, and Ba; fluorapatite was analyzed for F, Fe, Mn, As, Ca, Sr, S, Na, Si, Mg, Cl, Y, and P. EPMA traverses were done across mineral grains avoiding inclusions, cracks, and obvious altered zones.

The analyses were done using a JEOL JXA-8230 SuperProbe electron probe microanalyzer at Memorial University of Newfoundland. Details of the EPMA analyses are summarized in ESM Table 2A for actinolite, ESM Table 2C for magnetite, and ESM Table 2E for fluorapatite.

X-ray maps of actinolite were created by the EPMA in the same areas as the traverses and are based on analyses for Ti, Ca, Fe, Mg and K using the previous determinations of the actinolite compositions. Potassium was included in order to determine its distribution for later ⁴⁰Ar–³⁹Ar dating. For each X-ray map, an accelerating voltage of 15 kV, sample current of 200 nA, and a pixel dwell time of 100 ms were used. Each map took an average of 12 hr.

2.4.3. LA-ICPMS trace elements of actinolite

The same epoxy mounts containing actinolite from the Abundancia and San Juan veins were used for in situ LA-ICPMS trace-element analyses (Fig. 4a, c, d, f, g). The analyses were done on either the traverse or the spots where the EPMA analyses were acquired previously. Data for 43 trace elements were obtained by LA-ICPMS and are listed in ESM Table 2A.

The actinolite trace-element analyses were done at the Micro Analysis Facility (MAF) at Memorial University of Newfoundland, using a Thermo Finnigan Element XR high-resolution (HR), double-focusing magnetic sector-inductively coupled plasma mass spectrometer (HR-ICPMS), coupled to a GeoLas 193-nm Excimer laser system. Details of the LA-ICPMS analyses
are summarized in ESM Table 2A. The Ca concentration in the actinolite determined by EPMA was used as the internal standard for calibration of each LA-ICPMS analysis. Analyses were done using a pulse frequency of 10 Hz, energy density of 4 J/cm², and with a 40 µm diameter spot size. For each analysis, the background was measured for around 30 sec followed by 60 sec of laser ablation. NIST 610 was used as the primary standard, and USGS BCR-2G and NIST 612 were used as secondary standards, interspersed during the trace element analyses.

2.4.4. ⁴⁰Ar/³⁹Ar geochronology of actinolite

The study includes two ⁴⁰Ar/³⁹Ar dates on actinolite, one a fine-grained actinolite associated with the MtAp event in the Abundancia vein (MOC-18-09), and one coarse-grained actinolite with moderate chloritization from the San Juan vein (MOC-18-05). Actinolite grains were crushed using a steel Plattner mortar and pestle. Individual fragments were handpicked under a binocular microscope using tweezers, avoiding altered fragments and impurities, such as calcite in the San Juan actinolite. Both samples were crushed again using a Plattner mortar and pestle and sieved to a size of 90-150 μ m, to obtain a concentrate of visually pure actinolite. The amount of actinolite needed for each analysis was calculated based on the total K content of each sample, previously determined by the EPMA, in order to have >0.20 g total K present. The actinolite amount required for the Abundancia vein was 350 mg, and for the San Juan vein 880 mg.

Mineral separates were irradiated in the McMaster University nuclear reactor (Ontario, Canada) for 30 MWh, carefully avoiding Cd shielding. The age monitor was hornblende MMhb1 with an assumed age of 523.98 Ma (Schoene and Bowring, 2006). ⁴⁰Ar/³⁹Ar analyses by stepheating following the procedures described by Bosio et al. (2020) were done on the Nu Instruments Noblesse noble gas mass spectrometer at the University of Milano-Bicocca, Milan,

Italy, equipped with one Faraday cup having a $10^{11} \Omega$ resistor and two ion counters. Before each sample was analyzed, a blank measurement was followed by two successive measurements of atmospheric Ar delivered by a pipette system. The analytical protocol consisted of four measurement cycles to allow an in-run cross-calibration of the relative collector gains, F/IC0 and IC0/IC1, for each individual run under the (variable) mass spectrometer conditions. The four cycles were: (1) ⁴⁰Ar (F), ³⁸Ar (IC0), ³⁶Ar (IC1); (2) ³⁹Ar (F), ³⁷Ar (IC0), ³⁵Cl (IC1); (3) ⁴¹C₃H₅ (F), ³⁹Ar (IC0), ³⁷Ar (IC1); and (4) ³⁸Ar (F), ³⁶Ar (IC0). Each measurement consisted of 25 repetitions of the four cycles, so as to avoid artefacts due to ion counter nonlinearities (Barberini and Villa, 2015). The ion counter gains are similar, but not necessarily equal, to those determined from the atmospheric pipettes (which also independently quantify the mass fractionation originating in the source). The raw data from the mass spectrometer zero-time extrapolation were processed with an in-house Excel spreadsheet by correcting for mass spectrometer background, ion counter gains, blank measurements, source fractionation, and decay of ³⁷Ar since irradiation, as well as propagating all associated uncertainties. The total concentrations of ³⁹Ar, ³⁸Ar, and ³⁷Ar were converted to absolute concentrations of K, Cl, and Ca, respectively, so as to control stoichiometry, and to provide Ca/K and Cl/K ratios. Because the stoichiometry of the present samples was determined by EPMA, for the age calculation we consider only "isochemical steps" (Villa et al., 2006) with constant Ca/K and Cl/K ratios matching the EPMA measurements. The ⁴⁰K decay constant used for the age calculation was 5.543 x 10⁻⁴ Ma⁻¹ (Steiger and Jäger, 1977), even if this constant is very probably slightly inaccurate (Min et al., 2000; Naumenko-Dèzes et al., 2018); it was used, by convention, in order to facilitate inter-comparisons with literature data. Different levels of uncertainty must also be considered. The internal concordance/discordance of step ages is assessed based on in-run uncertainties only. The inter-comparison of samples analyzed in the same laboratory requires compounding the in-run uncertainty with that for the

neutron flux gradient. Finally, the inter-comparison of the present samples with those reported in the literature requires inclusion of the systematic uncertainties on the age of the irradiation monitor (if the information is provided at all) and of the uncertainty of the ⁴⁰K decay constant, where necessary.

2.4.5. LASS U-Pb geochronology and Hf tracer isotopes of zircon

Representative zircon crystals from the Abundancia host diorite (sample MOC-18-02) were analyzed in situ for U, Pb, and Lu–Hf isotopes. The diorite was processed using a jaw crusher, and a disc mill afterwards, retaining >90% of the crushed material between <500 µm and >63 µm. Magnetic separation and heavy liquids, bromoform and methylene iodide, were used to separate the zircon from the other minerals. The zircon grains were handpicked under a binocular microscope and mounted in epoxy. The mounts were polished to expose the crystal centers and carbon coated. Cathodoluminescence images were obtained at Memorial University of Newfoundland using a JEOL 7100F field emission gun scanning electron microscope (FEG-SEM) equipped with energy-dispersive spectroscopy (EDS) at operating conditions of 15 kV and 50 nA. The images were acquired in order to select the best zircon grains, and regions within zircon grains, for the in situ analyses, avoiding inclusions of other minerals, inherited cores, or cracks.

Lu–Hf isotopes, paired with U–Pb isotopes, were analyzed by laser ablation split stream (LASS) methods at the Micro Analysis Facility at Memorial University of Newfoundland. We followed the instrument configuration, operating parameters, and data reduction methods outlined by Fisher et al. (2011, 2014a, b), with the exception that N₂ was added to the Ar carrier gas introduced into both mass spectrometers for increased sensitivity.

The Lu–Hf analyses were done using a Thermo Finnigan Neptune multicollectorinductively coupled plasma mass spectrometer (MC-ICPMS). The U–Pb analyses were acquired using a Thermo Finnigan Element XR high resolution-magnetic-sector inductively coupled plasma mass spectrometer (HR-ICPMS). Both mass spectrometers were interfaced to a GeoLas Pro 193 nm Ar–F excimer laser, operated at 10Hz, 5 J/cm², and a 40 µm diameter spot size. After collecting background counts for 30 sec, the samples were ablated for 60 sec. The data were reduced using Iolite software (Paton et al., 2011).

The Lu–Hf analyses done on the Montecristo MOC-18-02 zircon crystals were interspersed with analyses of several zircon reference materials in order to assess accuracy, mass bias corrections, and external reproducibility. Whereas all of these reference materials listed below were analyzed during the LASS method, not all reference materials were used for both Hf–Lu and U–Pb data reduction schemes.

The zircon reference materials used in this study for the Lu–Hf LASS analyses (determined in previous studies by solution MC-ICP-MS), which covered the range of (Lu+Yb)/Hf of the MOC-18-02 zircon crystals, included MUNZirc-1 (B-140) (176 Hf/ 177 Hf = 0.282135 ± 7; Fisher et al., 2011), MUNZirc-4 (B-144) (176 Hf/ 177 Hf = 0.282135 ± 7; Fisher et al., 2011), Plešovice (176 Hf/ 177 Hf = 0.282482 ± 13; Sláma et al., 2008), FC-1 (176 Hf/ 177 Hf = 0.282182 ± 14; Fisher et al., 2014); and R33 (176 Hf/ 177 Hf = 0.282767 ± 18; Fisher et al., 2014).

The zircon reference materials used in this study for the U–Pb LASS analyses included 91500 (1065 Ma; Wiedenbeck et al., 2004) that was the primary U–Pb reference material, and Plešovice (337.13 Ma; Sláma et al., 2008); FC-1 (1099 Ma; Paces and Miller, 1993), R-33 (419 Ma; Black et al., 2004); Temora 2 (417 Ma; Black et al., 2004), and 02123 (295 Ma; Ketchum et al., 2001) were used as secondary reference materials.

Initial ϵ Hf_i values were calculated using a present-day CHUR value of ¹⁷⁶Hf/¹⁷⁷Hf = 0.282785, ¹⁷⁶Lu/¹⁷⁷Hf = 0.0336, as reported by Bouvier et al. (2008) and the ¹⁷⁶Lu decay constant of 1.867 x10⁻¹¹ yr⁻¹ from Söderlund et al. (2004).

The ²³⁸U counts acquired on the zircon grains from sample MOC-18-02 were anomalously high in the first batch of analyses (*n* = 41, individual analyses per grain) due to the anomalously high U concentrations in the zircon grains (920-7330 ppm). The in situ U–Pb analyses showed significant discordance caused by Pb loss, or radiation damage, or a combination of these two factors. A second batch of zircon grains (*n* = 27, analyses per grain) from sample MOC-18-02 were chemically abraded following, in general, the method in Mattinson (2005) prior to the LASS analyses for U–Pb and Hf isotopes. The zircon grains were annealed for 48 hr at 1100°C in air in a fused silica crucible. This annealing was followed by partial dissolution in concentrated HF (49%) sealed in a Parr bomb in an oven at 190°C for 2 hr (the Parr bomb was put into an oven at pre-set at 190°C, and then after two hr at 190°C the Parr bomb was removed from the oven and allowed to cool for 1 h to room temperature before opening). This procedure removes radiation-damaged, altered or metamict, zones in zircon that cannot be restored by annealing, thus virtually eliminating secondary lead loss; for simple grains of one age, concordant or near-concordant analyses are generally obtained.

Preliminary U–Pb data after the annealing process, however, produced similar results to the first batch of LASS analyses, likely because the uranium content in the zircon grains was still anomalously high (e.g., 560-5320 ppm). Thus, the accumulated radiation damage dose (i.e., alpha decay events per milligram) was calculated for each zircon using the equation from Murakami et al. (1991), in order to eliminate extensively radiation-damaged zircon grains in an attempt to obtain a concordant age. After the radiation damage calculations, zircon grains showing radiation damage in stages 2 and 3 (Nasdala et al., 2004; modified the damage stages initially reported by

Murakami et al., 1991) were removed, keeping 12 zircon grains in stage 1 for the final age calculation and those used for the ϵ Hf_i calculation.

2.4.6. Re–Os geochronology of molybdenite

Molybdenite has very high Re/Os ratios because during crystallization this mineral takes in almost no Os (Stein et al., 2001). Therefore, ¹⁸⁷Re–¹⁸⁷Os dating of molybdenite uses the following simplified equation: ¹⁸⁷Os_{measured} = ¹⁸⁷Re_{measured} × ($e^{\lambda t}$ - 1), where λ is the decay constant for ¹⁸⁷Re (1.666 × 10⁻¹¹ yr⁻¹; Smoliar et al., 1996).

Re–Os isotopic analyses were acquired on two molybdenite (MoS₂) samples from level 940 (m) of the Abundancia vein. Here, there is no evidence of supergene alteration; petrography shows that the molybdenite is pure and lacks mineral intergrowths. However, the samples belong to a zone of intense slickensides and shearing. Molybdenite separates were obtained using a small, hand-held drill that produced a molybdenite powder.

Re and Os isotopic concentrations were determined by isotope dilution using a Thermo Triton NTIMS (Negative Thermal Ionization Mass Spectrometry) machine at the AIRIE Program, Colorado State University, Fort Collins, Colorado. Precisely weighed samples were loaded into a Carius tube with 8 mL inverse aqua regia and Re–Os spikes for sample dissolution and sample-spike equilibration. A mixed Re-double Os spike (185 Re– 188 Os– 190 Os) permits a mass fractionation correction for Os and assessment of any common Os present in the molybdenite. Both samples had negligible common Os. All uncertainties are reported at 2-sigma (ESM Table 7), including the 187 Re decay constant uncertainty (λ). Re and Os blanks (Re blank = 11.77 ± 0.03 pg, Os blank = 0.130 ± 0.003 pg with 187 Os/ 188 Os = 0.350 ± 0.007) do not affect the calculated ages.

2.4.7. Whole-rock Rb–Sr and Sm–Nd radiogenic isotopes

Three whole-rock samples of the IOCG mineralization enriched in actinolite from the Abundancia vein were analyzed for bulk rock Sr and Nd radiogenic isotopic compositions. Samples were initially crushed using a Plattner mortar and pestle, then reduced to powder with an agate mortar and pestle. The samples might contain some minor contamination from the MtAp stage, as the fine-grained nature of the veinlets makes it difficult to physically separate the IOCG mineralization from the older MtAp event that was replaced.

Rb–Sr and Sm–Nd whole rock analyses were done at the Unidad de Geocronología (CAI de Ciencias de la Tierra y Arqueometría) of the Universidad Complutense de Madrid using isotope dilution-thermal ionization mass spectrometry (ID-TIMS) and an Isotopx Phoenix TIMS instrument. The samples were spiked with ⁸⁴Sr, ⁸⁷Rb, and a mix of ¹⁴⁹Sm–¹⁵⁰Nd, and digested using ultra-clean reagents. Samples were then processed using chromatography, where Rb, Sr, and rare earth elements (REEs), were separated in DOWEX AG (50W x 12 Resin, 200–400 mesh) columns. In order to isolate the Sm and Nd, REE fractions were separated in HDEHP-impregnated Teflon-powder columns. Instrumental fractionation effects were corrected using a normalization of ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The procedural blank was 0.5 ng for Sr and 0.1 ng for Nd. Standard materials used during the analyses were the following: Sr standard NBS-987 (0.710245 ± 0.000004; *n* = 58), and Nd standards La Jolla (0.511850 ± 0.000004, *n* = 36) and JNdi-1 (0.512108 ± 0.000003, *n* = 33).

2.4.8. δ^{34} S stable isotopes in sulfide minerals

Sulfur isotopic compositions were measured in fourteen samples of chalcopyrite and pyrite from the Abundancia vein. In four, two aliquots were taken for quality control to assess

repeatability. The sulfides were crushed in a stainless-steel mortar and handpicked under a binocular microscope using titanium tweezers, followed by magnetic separation to remove the magnetite. Visually pure sulfide grains were ground to $\sim 1 \mu m$ size in an agate mortar and pestle, obtaining a powder of ~ 0.5 g. Sulfides having other minerals attached to the surface were ground and sieved and retained to 63 µms, magnetite was removed with a magnet, and the sample was processed using heavy liquids, bromoform, and methylene iodide, in order to separate the sulfides from the other minerals.

The sulfur isotope measurements were done at the Stable Isotope Laboratory of the Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR, Granada, Spain). Samples were analyzed by combustion with V₂O₅ and O₂ at 1030°C in a Carlo Elba NC1500 elemental analyzer online with a Delta Plus XL mass spectrometer (EA-IRMS). The stable isotope compositions are reported as conventional δ per mil values, calculated using the $\delta = (R_{sample}/R_{standard} - 1)*1000$ equation, where R= ³⁴S/³²S for δ^{34} S. Commercial SO₂ was used as the internal standard for the sulfur isotopic analyses. For sulfur, five internal (organic and inorganic standards range in composition from –6.38 ‰ to +23.25 ‰, CDT), together with the IAEA international references IAEA-S1, IAEA-S2, IAEA-S3, NBS-127, and CP-1 were analyzed. For this study, three internal standards of +23.25 ‰, +6.03, and -6.38 ‰ (CDT) were used. The precision calculated, after correction of mass spectrometer daily drift, from standards systematically interspersed in analytical batches was better than ± 0.2‰. The standard material used for normalizing the sulfur isotope values is V-CDT (Vienna-Canyon Diablo Troilite).

2.5. Results

2.5.1. Mineral textures and chemical compositions

2.5.1.1. Actinolite

As mentioned above, two types of actinolite occur in the Montecristo system: (1) actinolite I, related to the MtAp event; and (2) actinolite II, associated with the later IOCG event.

Early actinolite I within the Abundancia vein forms unaltered, fine-grained (<500 µm long) euhedral crystals, arranged in thin aggregate bands hosted by magnetite. This actinolite also occurs disseminated in the magnetite or is enclosed by fluorapatite crystals in a "poikilitic" type texture (see ESM Fig. 1d, g, p) that is similar to those within cumulate rocks (Wager et al., 1960; McBirney and Noyes, 1979), and in chilled margins of mafic and ultramafic intrusions (Wager, 1961). Later crosscutting magnetite-rich mineralization also contains actinolite I with the same composition and characteristics but as smaller grains. Actinolite I in the San Juan MtAp vein is coarse-grained (up to 7 mm) and forms massive aggregates, some moderately altered to chlorite; it hosts magnetite as disseminated crystals or in fractures. BSE images show that the disseminated magnetite is made up of grains smaller than 100 µm and includes abundant exsolution of titanite (ESM Fig. 1v).

Actinolite II is fine-grained (<200 μ m) and occurs in veinlets paragenetically related to chalcopyrite, pyrite, quartz, and minor magnetite and titanite as part of the IOCG event. There are also abundant remnants of actinolite I within the IOCG zone (see ESM Fig. 1).

The chemical composition of the actinolite samples are available in ESM Table 2B and a representative oxide composition is shown in Figure 5b. All samples analyzed (I and II) are classified as actinolite (Fig. 5a) (Leake et al., 1997), with Mg# [molar (Mg/(Mg+Fe)] ranging from 0.67 to 0.79, and Si atoms per formula unit (a.p.f.u.) between 7.796 and 7.910. In general, the actinolite samples show the following compositional ranges for major elements: MgO (15.20-18.70 wt.%), CaO (12.20-12.60 wt.%) FeO (8.70-13.10 wt.%), Al₂O₃ (0.90-1.70 wt.%), Na₂O (0.10-0.20 wt.%), MnO (0.10-0.30 wt.%), TiO₂ (0.01-0.04 wt.%), SO₃ (0.01-0.02 wt.%), and

K₂O (0.02-0.10 wt.%). Concentrations of minor and trace elements are: Cl (190-940 ppm) and F (below LOD of 252 ppm).

The EPMA analyses show that actinolite I and II from Abundancia are more depleted in FeO (range of 8.70-9.10 wt.%), whereas actinolite I from San Juan is enriched in FeO (avg 13.05 wt.%). Actinolite I from San Juan is enriched in Mn (avg 2562 ppm) relative to actinolite I and II from Abundacia (range of Mn 430-525 ppm). Actinolite II in Abundancia has low average Cl (188 \pm 40 ppm), and K (197 \pm 40 ppm) compared to Actinolite I, which has on average 658 \pm 48 ppm, and 697 \pm 45 ppm, respectively. These average compositional differences are reinforced by Fe, Ca, Mg, K, and Ti X-ray maps (ESM Fig. 3). In contrast, San Juan actinolite I is enriched throughout all grains in Ti (253 \pm 90 ppm) relative to the other actinolite samples from Abundancia (I and II); X-ray maps show the presence of disseminated titanite crystals (ESM Fig. 3). The actinolite compositional data obtained in this study generally agree with other results published previously for actinolite in MtAp deposits of the Coastal Cordillera (Rojas et al., 2018).

LA-ICPMS trace element data for actinolite are presented in ESM Table 2B and are shown in Figure 5c normalized to continental crust (Rudnick and Gao, 2003). The data indicate that MtAp and IOCG-related actinolite, types I and II respectively, from Abundancia generally have the same trace element pattern. However, actinolite II has slightly higher Ba, Sr, and REE concentrations and lower Rb, K, and Ti. Actinolite I from the San Juan vein, on the other hand, shows a different trace element composition that is depleted in Nb, La, Ce, Nd, Sm, and Y, and slightly enriched in Hf, Zr, and Ti, relative to actinolite I and II from Abundancia.

2.5.1.2. Magnetite

Magnetite of the MtAp stage in the Abundancia and San Juan veins has similar textures and in both deposits is classified as magnetite type I. Magnetite I is massive, intergrown with actinolite and fluorapatite, inclusion-free, and lacks exsolution textures. Magnetite I from the Abundancia vein also hosts abundant acicular inclusions of actinolite. Magnetite II, only present as a product of the IOCG event, is relatively homogeneous and has quartz inclusions (See ESM Fig. 1). Major, minor, and trace elements data for both types I and II of magnetite are presented in ESM Table 2D; comparative plots of average oxide compositions are shown in Figure 5d.

All magnetite I samples have a nearly identical chemical composition, within analytical error. Ranges of concentrations for the most representative elements include: Ti (100-190 ppm), Cu (50-60 ppm), Ni (200-240 ppm), V (1420-3010 ppm), Cr (30-60 ppm), S (10-50 ppm), Si (1570-3510 ppm), Al (650-940 ppm), Mn (100-180 ppm), Mg (340-1610 ppm), Ca (710-1320 ppm), and Zn (130-160 ppm).

Magnetite II displays a similar composition but with an increase in Cu that is constant throughout the crystals. The average element composition for magnetite II include: Ti (282 ± 33 ppm), Cu (406 ± 46 ppm), Ni (150 ± 37 ppm), V ($6,193 \pm 56$ ppm), Cr (81 ± 10 ppm), S (162 ± 12 ppm), Si (871 ± 18 ppm), Al (730 ± 16 ppm), Mn (149 ± 33 ppm), Mg (211 ± 18 ppm), Ca (251 ± 11 ppm), and Zn (106 ± 62 ppm). Chemical compositions similar to magnetite I are reported in magnetite crystals from other MtAp deposits in the Coastal Cordillera of Chile (e.g., Knipping et al., 2015b, Los Colorados; Salazar et al., 2019, Cerro Negro).

2.5.1.3. Fluorapatite

Fluorapatite is abundant in the MtAp stage but has not been found fluorapatite in the IOCG stage. Fluorapatite crystals in MtAp mineralization of the Abundancia vein are generally euhedral, coarse-grained (up to 1 cm), and lack evidence in BSE or CL of superimposed

metasomatic alteration. The fluorapatite commonly encloses small (<250 μ m) actinolite crystals in a "poikilitic-like" texture and displays a yellow CL emission (caused by Mn²⁺) (see ESM Fig. 1e, h, n, t). Fluorapatite in the San Juan vein is also euhedral and coarse-grained (up to 2 cm). These fluorapatite crystals grew perpendicular to the actinolite-magnetite bands, in comb-like or unidirectional solidification growth textures (UST; Fig. 3a, b, e) that are identical to those described in the Carmen de Fierro and Fresia MtAp deposits (Tornos et al., 2021).

EPMA analyses of fluorapatite are provided in ESM Table 2F, and the average chemical composition for each crystal are plotted in Figure 5e. Our results are similar to published apatite compositional data for other MtAp deposits in the Coastal Cordillera (Treloar and Colley, 1996; La Cruz et al., 2019). All samples from Abundancia and San Juan correspond to fluorapatite (2.10-2.50 wt.% F) with a minor chlorapatite component (0.40-0.80 wt.% Cl) and includes Na (160-330 ppm), Mn (180-360 ppm), Mg (40-3,010 ppm), Fe (470-3,980 ppm), As (570-1,020 ppm), Sr (170-280 ppm), Y (140-200 ppm), Si (85-5,890 ppm), and S (50-110 ppm); however, there are some differences with respect to Fe, Si, and Mg. The greater variability in Fe, Si, and Mg concentrations relative to those of other elements is likely due to the presence of micro or nano inclusions of actinolite within the fluorapatite that were not visible with BSE or CL as imaged via SEM and EPMA.

2.5.2. Actinolite ⁴⁰Ar/³⁹Ar geochronology

 40 Ar/ 39 Ar data and related plots for the two actinolite samples are reported in Figure 6. The full data set is available in ESM Table 4. Actinolite MOC-18-09 from the Abundancia vein yielded a well-constrained plateau age of 154 ± 2 Ma (2-sigma), which represents 92.3 % of the 39 Ar released. This plateau age is indistinguishable from the 40 Ar/ 39 Ar isochron age (159 ± 17 Ma, 2-sigma). The three plateau steps show a constant Ca/K ratio, whereas the Ar-poor low-

temperature steps display lower ratios, indicating the presence of a contaminant phase with a higher amount of K or lower Ca content. Also shown are broadly constant Cl/K ratios, meaning that the sample is homogeneous and likely contains little if any hydrothermal component such as fluid inclusions. Coarse-grained actinolite MOC-18-05 from the San Juan vein yielded a plateau age of 153 ± 4 Ma (2-sigma), representing 76.2 % of the ³⁹Ar released, and has homogeneous Ca/K and Cl/K ratios within the plateau steps. The plateau age is indistinguishable at the 2-sigma level from the ⁴⁰Ar/³⁹Ar isochron age (160 ± 4 Ma).

A literature K–Ar age of actinolite associated with the alteration halo in the Mantos deposit in the Montecristo district yielded an age of 164 ± 11 Ma (JICA-MMAJ 1986). This age is consistent at the 1-sigma level with the present results.

2.5.3. Zircon U–Pb geochronology and Hf tracer isotopes from the host rock

The U–Pb data for zircon from the diorite host rock are reported in the ESM Table 5, and in Figures 7b to d. The Lu–Hf data are plotted in Figure 7e and all of the data and calculations are listed in ESM Table 6. Zircon grains are relatively small ($\leq 100 \mu m \log$), euhedral to subhedral, and inclusion-free; some show regular growth zoning, a characteristic of igneous zircon (Fig. 7a). No inherited cores were identified in any of the zircon analyses via the CL imaging and subsequent U-Pb analyses.

The Concordia diagram for sample MOC-18-02 shown in Figure 7b yields an age of 153.3 \pm 1.8 Ma (2-sigma; MSWD = 2.6; *n* = 12). This age overlaps with the weighted mean ²⁰⁶Pb/²³⁸U age of 152.1 \pm 2.6 Ma (2-sigma; MSWD = 1.3; *n* = 12), and with the inverse isochron age of 153.5 \pm 3.0 Ma (2-sigma; MSWD =15; *n* =12) obtained in this study. The Concordia age agrees with previously reported U–Pb dates for the latest crystallization stages of the Matancilla intrusive complex (Álvarez et al., 2016 and references therein). In situ initial Hf values obtained

from the above-mentioned 12 individual zircon grains, and calculated using the Concordia age, range from ε_{Hfi} of +5.0 (analysis 11a) to +6.7 (analysis 37a). These values together suggest a dominantly juvenile source, i.e., one produced in the primitive mantle but with some incorporation of less-radiogenic Hf inherited from continental crust through assimilation during emplacement (ε_{Hfi} = +10.6 to +16.6 for Mesozoic rocks of the Canadian Cordillera; Vervoort and Blichert-Toft, 1999).

2.5.4. Molybdenite Re–Os dates

The Re–Os dates for two molybdenite samples belonging to the IOCG stage are presented in ESM Table 7. The data show a significant age difference between the two samples: 162.4 ± 0.6 Ma (2-sigma) for MOC-18-07A, and 151.8 ± 0.6 Ma (2-sigma) for MOC-18-07G. Re concentrations are very different with sample 07A having 23.14 ppm whereas 07G has 369.7 ppm. The difference in the two Re–Os ages, with an unexpectedly older age obtained for sample MOC-18-07A, could reflect multiple molybdenite mineralizing events, or within-molybdenite mobility and redistribution of Re and Os associated with slickenside development, as proposed elsewhere (Stein et al., 2003). In an earlier study of a Chilean IOCG deposit at Raúl-Condestable (De Haller et al., 2006), two Re–Os ages several million years older than the associated intrusion were explained by Re loss. At Raúl-Condestable, however, molybdenite is markedly early in the paragenesis, preceding chalcopyrite and pyrite. In contrast, in our study molybdenite is paragenetically late (Fig. 2) and follows chalcopyrite ore mineralization, thus making direct analogy between these two deposits difficult. Given the association of our dated samples with a zone of intense slickenside and shearing, we suggest that redistribution of Re and of radiogenic Os within the molybdenite is a possibility.

2.5.5. Sr and Nd radiogenic isotopes

Whole rock Rb–Sr and Sm–Nd data are shown in Figure 8 and listed in Table 1. The approximate deposit formational age of 154 Ma determined by 40 Ar/ 39 Ar geochronology was used to calculate the initial 87 Sr/ 86 Sr and ϵ_{Ndi} values. For the IOCG event these calculations yield ϵ_{Ndi} values of +5.4 to +7.0 and 87 Sr/ 86 Sr_i compositions of 0.70425 to 0.70442, together suggesting a dominantly juvenile source. Other studies done on calcite in the Montecristo (87 Sr/ 86 Sr_i=~0.7058), Julia (87 Sr/ 86 Sr_i = ~0.7046 to ~0.7048), and Toldo-Velarde deposit in the Gatico district (87 Sr/ 86 Sr_i = ~0.7041 to ~0.7043) show similar 87 Sr/ 86 Sr_i values (Vivallo and Henríquez, 1998).

The ε_{Ndi} value of +7.0 is interpreted as inherited from the MtAp stage during the replacement of the MtAp assemblage by the IOCG mineralization, due to the higher ε_{Ndi} values of the MtAp stage (Tornos et al., 2021). One MtAp sample with a relatively low ε_{Ndi} value of +5.1 and high 87 Sr/ 86 Sr_i ratios (0.70629), from Tornos et al. (2021), is here interpreted as having been partially re-equilibrated with late IOCG-related fluids (see below).

2.5.6. δ^{34} S isotopes in sulfides

 δ^{34} S values of sulfides from the IOCG event are listed in Table 2 and plotted in Figure 9. Sulfur isotopes for 15 chalcopyrite and pyrite aliquots show a very restricted range between +0.3 to +3.4 per mil, with a mean of +1.8 ± 0.91 per mil. δ^{34} S values for the Abundancia IOCG event agree with previously published sulfur isotopic studies in the Montecristo deposit (0 to +5‰; Vivallo and Henríquez, 1998) and are similar to other sulfur isotopic compositions determined for IOCG deposits in the Coastal Cordillera of Chile (Tocopilla, -0.2 to +0.6‰, unpub. data, F. Tornos; Gatico district, 0 to +5‰, Vivallo and Henríquez, 1998; Naguayán-Desesperado, -1 to +1‰, Vivallo and Henríquez, 1998; Candelaria, 0.3 to +3.1‰, Marschik and Fontboté, 2001; Julia, -4 to +4‰, Vivallo and Henríquez, 1998) and to those reported for sparse sulfides in the MtAp mineralization such as at Los Colorados (-3.2 to +2‰; Tornos et al., 2021) (Fig. 9). Collectively, these data suggest that the sulfur is dominantly of juvenile magmatic derivation $(\delta^{34}S = -3 \text{ to } +2‰; Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997), with a minor$ contribution from either crustally contaminated igneous rocks or a sedimentary source (Poulsonet al., 2001).

However, hematite-rich IOCG deposits show a wider range of δ^{34} S values with a systematic displacement towards positive values, indicating a likely input of sulfur derived from abiogenic reduction of seawater sulfate or microbial reduction in a closed system but external to a magmatic-hydrothermal system, such as in Raul-Condestable (+1.0 to +26.3‰ main ore stage; De Haller and Fontboté, 2009), Teresa de Colmo (-5.5 to 18.2‰; Ledlie, 1998), and Mantoverde (-6.8 to +11.2 main ore stage, and +26.4 to +36.2 in later stages; Benavides et al., 2007; Rieger et al., 2010). This interpretation is consistent with the previous study of Chen (2013) that suggested external sulfur with δ^{34} S values > +10‰ was important in the ore-forming processes of hematite-rich IOCG systems.

2.6. Discussion

2.6.1. Timing of mineralization

The U–Pb zircon crystallization age of 153.3 ± 1.8 Ma (2-sigma) obtained for the host diorite is consistent within error with the 40 Ar/ 39 Ar dates of the MtAp event (153 ± 4 Ma and 154 ± 2 Ma, 2-sigma) and the Re–Os molybdenite age of 151.8 ± 0.6 Ma (2-sigma), which suggests that the ore-forming events took place in a short time span that cannot be temporally resolved

with geochronology. The new dates obtained in the present study indicate that the MtAp and IOCG events, and crystallization of the host diorite, are coeval within error in a time span of ~3.4 m.y. The results further suggest, however, that the mineralization formed soon after the crystallization of the host diorite, especially given that the Ar cooling ages are younger than zircon dates (Renne et al., 1998; Min et al., 2000; Kuiper et al., 2008; Simon et al., 2008) and that on the basis of crosscutting relationships the IOCG mineralization is definitely younger than the MtAp event.

2.6.2. Evolution of the Montecristo system

The Montecristo vein system consists of multi-stage mineralization (Fig. 2) with an early MtAp stage (Events I and II) followed by an IOCG stage (Events III and IV). The magnetite, fluorapatite, and actinolite of the early MtAp stage show similar compositions (Figs. 5b, d, e), suggesting crystallization from a homogenous source. Textures of this stage are like those of the intrusive part of the El Laco MtAp deposit in Chile (Naslund et al., 2002), and the MtAp deposits of the Coastal Cordillera that include diagnostic, pegmatitic features including local banded, coarse-grained fluorapatite with UST textures coexisting with diopside or actinolite and magnetite (Tornos et al., 2017, 2021). The yellow CL emission of the fluorapatite (caused by Mn²⁺) is typical of magmatic apatite (Dempster et al., 2003), thus suggesting a magmatic origin (Bouzari et al., 2016). In the case of Abundancia, textures also include "poikilitic" fluorapatite enclosing well-formed acicular, mostly euhedral actinolite crystals. Some of these mineralized rocks likely represent the magmatic to hydrothermal transition in MtAp systems within a pulsating regime similar to that of granite-related pegmatite (Tornos et al., 2021).

Formation of the MtAp mineralization can be explained by the direct crystallization of immiscible melts. Geological (Chen et al., 2010a; Mungall et al., 2018), isotopic (Tornos et al.,

2016, 2017, 2021; Troll et al., 2019; Weis et al, 2021), experimental (e.g., Lledó 2005; Veksler et al., 2007; Hou et al., 2018; Mungall et al., 2018; Lledó et al., 2020), and melt inclusion data (Jacobsen et al., 2005; Naslund et al., 2009; Velasco et al., 2016; Bain et al., 2020, 2021) provide overwhelming evidence—often neglected by supporters of alternative models—that these rocks crystallized from iron-rich and silica-poor melts.

Overall, the compositions of magnetite and actinolite of the IOCG stage (Event III) are similar to that of the MtAp stage. The actinolite EPMA X-ray maps (ESM Fig. 3) show only slight chemical differences, suggesting that perhaps magnetite and actinolite compositions are not useful tracers for discriminating such types of mineralization within these vein-like systems. It is also possible that some actinolite and magnetite were assimilated and thus, they are geochemically equivalent. However, magnetite II is distinctive in containing abundant quartz inclusions that are not present in magnetite I. Furthermore, the higher amount of Cu present throughout magnetite type II crystals (406 ± 46 ppm) compared to magnetite type I (50-64 ppm) is consistent with the presence of higher Cu contents during the IOCG event.

2.6.3. Different sources for the IOCG and MtAp mineralization

The ⁸⁷Sr/⁸⁶Sr_i values of the IOCG mineralization at Abundancia (0.70425 to 0.70442) are indistinguishable from those of the MtAp event at San Juan (0.70466 and 0.70629) and the Abundancia veins (0.70422 and 0.70457; Tornos et al., 2021). These similarities suggest that in both cases the Sr was derived from reservoirs having a significant crustal inheritance and not wholly from primitive magmas produced during subduction-related melting of the mantle wedge. Sr isotope ratios as a whole likely reflect the interaction of these primitive melts either with continental crust of the hosting Antofalla terrane (see Ramos and Aleman, 2000; Lucassen et al., 2006; Parada et al., 2007), or an increase in ⁸⁷Sr/⁸⁶Sr_i ratios due to contamination of the mantle

wedge by fluids derived from dehydration of sediments or serpentinite within the subducted oceanic crust (Tornos et al., 2021). The fact that a similar Sr isotopic signature is present in most of the MtAp systems of the Coastal Cordillera, regardless of the primitive or continental nature of the underlying crust, supports the second alternative.

Nd isotopes are more robust and more difficult to reset than Sr isotopes and thus perhaps are a more reliable tracer of fluid sources. At Montecristo, the ε_{Ndi} values obtained for the IOCG event are significantly lower than those of the MtAp stage. Recalculated initial ε_{Nd} values of the MtAp mineralization at Montecristo for 154 Ma yield ε_{Ndi} of +6.7 and +7.5, which are similar to the values of +7.5, and +6.6 to +6.8, for nearby MtAp mineralization such as at the Jurassic Julia and Tocopilla vein deposits, respectively (Tornos et al., 2021). ε_{Ndi} values of the IOCG mineralized rocks at Abundancia are +5.4 to +5.7, implying that the Cu-Au mineralization cannot solely be derived from the same source as the MtAp mineralization or from fluids that had equilibrated with it. More negative ε_{Ndi} values of the IOCG mineralization record a significantly larger contribution of continental crust that do the values for the associated MtAp rocks.

 ϵ_{Ndi} values of the host diorite calculated from ϵ_{Hfi} of the zircon are between +2.3 and +3.4 (see ESM Table 8). These values were determined following the method of Vervoort et al. (2011), assuming no inheritance exists and that the zircon Hf value is representative of the bulk rock. Thus, the ϵ_{Ndi} values of the IOCG event likely track mixing between the replaced MtAp mineralization and the Nd inherited from the host diorite, or an unexposed underlying intrusion of equivalent isotopic composition.

The relatively low ε_{Ndi} values of the IOCG mineralization at Montecristo are broadly similar to those of the MtAp deposits located south of Taltal, as well as to the ε_{Ndi} values of several intrusions in the Coastal Batholith (Lucassen et al., 2006). In particular, the ε_{Ndi} values are like those of the Copiapó Plutonic Complex (CPC) of Early Cretaceous age (+4.7 to +5.8;

Marschik et al., 2003) that is thought to be the source of the ore-forming fluids of the IOCG mineralization in the Punta del Cobre deposits (Marschik and Fontboté, 2001; Arévalo et al., 2006).

Sulfur isotope values obtained in this study for both IOCG events III and IV are consistent with sulfur being derived from a H₂S-bearing, magmatic-hydrothermal fluid that transported the Cu, Mo, and Au (i.e., Rusk et al., 2004; Audetat et al., 2008, 2019; Kamenetsky and Kamenetsky, 2010). This fluid also likely precipitated magnetite II, actinolite II, and small amounts of quartz and sulfides by cooling and interaction with the older MtAp mineralized rocks. Thus, the MtAp rocks only acted as structural and geochemical traps for the later IOCG mineralizing fluids, due to the brittle and oxidized nature of the magnetite. Such fluid-rock interactions would also create the calcic-iron-alkali alteration observed in the deeper parts of the system.

In the Coastal Cordillera, the formation of iron-rich melts during the Middle-Late Jurassic appears to be controlled by contamination of the mantle wedge via slab-derived dehydration fluids. This process would promote partial melting of the mantle wedge, triggering in the most contaminated zones the separation of iron-rich melts from a parental mafic melt (Tornos et al., 2021). In this model, after emplacement and crystallization of the MIC, iron-rich melts ascended along the transcrustal faults of the AFS due to a drop in pressure, followed by crystallization of magnetite I, actinolite I, and fluorapatite (Fig. 10); this event was accompanied by the crystallization at ca. 800-1200°C (Bain et al., 2021 and references therein) of the pegmatite in a pulsating regime of dewatering. High temperatures and the oxidized nature of these iron-rich melts—uniformly enriched in anhydrite (Tornos et al., 2017; Tornos et al., 2021) —together with the likely low Cu contents of the magnetite, inhibited the formation of significant sulfides. The small amounts of available reduced sulfur allowed precipitation below ca. 700°C of the sparse sulfides typically found in MtAp systems. The homogeneous structures found within the MtAp

veins of the study area, and the lack of explosion breccias, suggest that these veins crystallized below the two-phase boundary surface, at ca. 0.2 GPa fluid pressure.

Geologic features, Hf, Sr–Nd, and S isotopic signatures are consistent with the IOCG mineralization at Montecristo being deposited from magmatic-hydrothermal fluids derived from crustally contaminated primitive intrusions of likely dioritic composition. In this model, upwelling fluids derived from the crystallization of the diorite react with the earlier MtAp mineralization, promoting the neoformation of large amounts of magnetite II together with minor actinolite and sulfides. Chalcopyrite and pyrite precipitate due to increases in pH and oxidation state of the fluids owing to reaction with magnetite I, a classical mechanism for destabilizing the chloride complexes that transport Cu at high temperatures (Liu and McPhail, 2005). Decrease in aH_2S_{aq} due to sulfide precipitation in turn destabilize the HS⁻ complexes that control gold solubility (Shenberger and Barnes, 1989; Loucks and Mavrovenges, 1999; Zezin et al., 2007; Pokrovski et al., 2014), leading to its precipitation. Later collapse of the hydrothermal system should promote quartz saturation and precipitation of the observed quartz-chalcopyrite assemblage and later calcite veins. Again, we have not found any evidence suggesting that the IOCG mineralization precipitated above the two-phase boundary, hence these veins also probably formed at relatively deep levels.

In this scenario, the brecciated monzogabbro beneath the Abundancia vein as recorded by Díaz et al. (2018) may represent the upper part of a crystallizing subvolcanic cupola that served as the deep magmatic-hydrothermal root of the IOCG mineralizing system. Equivalent related breccias with Cu-Mo-(Au) mineralization hosted by diorite have previously been described by Tornos et al. (2010) a few kilometers from the Montecristo district, in the Tropezón IOCG deposit; there, breccia pipes containing tourmaline or quartz grade into IOCG-type mineralization containing magnetite, sulfides, and actinolite that replace mafic plutonic rocks. A direct link

between the IOCG mineralization and the nearby silicate intrusions has been proposed previously for other IOCG deposits in the Coastal Cordillera (Boric et al., 1990; Vila et al., 1996; Hopper and Correa, 2000; Marschik and Fontboté, 2001; Ray and Dick, 2002; Gelcich et al., 2003; Sillitoe, 2003).

Erosion prevents our knowledge of mineralization that may have originally overlain these vein-like deposits. However, despite the difference in ages, these veins probably represent the roots of the abundant stratabound IOCG deposits in the Coastal Cordillera such as in the Punta del Cobre district. There, the IOCG mineralization replaces favorable horizons within Late Jurassic-Early Cretaceous andesite (Marschik and Fontboté, 2001), but is rooted in large NNW-SSE to WNW-ESE tensional, sub-vertical structures that are infilled with an assemblage very similar to that of the IOCG stage at Montecristo. In fact, the late calcite veins at Montecristo are texturally identical to the uppermost part of the feeder structures in the Punta del Cobre district (N. Pop, pers. commun., 2015).

In summary, our data provide evidence of the superposition of genetically unrelated MtAp and IOCG systems that were channelized along deep-rooted tensional structures. The isotopic data presented herein for independent sources of components within these MtAp and IOCG systems probably explains why, on a global scale, they are only rarely juxtaposed. Whereas MtAp systems are rather abundant, only a very few host superimposed Cu-Au IOCG mineralization. Importantly, however, the large size of some IOCG deposits is likely due to the fact that magnetite is an excellent geochemical trap, and that the Cu-rich event can be several m.y. younger than the host magnetite-rich rock (Rotherham, 1997; Bauer et al., 2018).

2.7. Conclusions

Mineralization in the Montecristo vein system involved the formation at ca. 154 Ma of a MtAp assemblage of magnetite, fluorapatite, and actinolite having rather high ε_{Ndi} values and initial ⁸⁷Sr/⁸⁶Sr ratios, emplaced within secondary structures of the transcrustal Atacama fault system. This early event was followed by the circulation of magmatic-hydrothermal fluids along the same secondary structures, and by partial replacement of the earlier MtAp mineralization by an IOCG assemblage derived from a more crustally contaminated source likely equivalent to the host Jurassic diorite. All mineralizing events took place within a relatively short time span of less than ~8.0 m.y.

Although the genetic relationship between MtAp and IOCG deposits remains debatable, geochemical, mineralogical, geochronological, and field data presented in this study suggest that the IOCG and MtAp mineralization in the Montecristo district are genetically independent and formed at different times. The MtAp mineralization derived via the crystallization of an iron-rich melt, whereas the IOCG mineralization has a magmatic-hydrothermal origin most likely related to the crystallization of an underlying diorite.

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Figure 1. (a) Location map and simplified regional geological formations in Montecristo mining district (modified from Escribano et al., 2013; Alvarez et al., 2016). (b) Location of IOCG and MtAp veins and simplified geological map of Montecristo district (modified from Álvarez et al., 2016).

	SAN JUAN				ABUNDANC	IA		
	М	tAp ST	4 <i>GE</i>			IOCG STAGE		SUPERGENE STAGE
MINERALOGY	Ever	ntl		Event II	Event III	Event IV	Event V	
Magnetite	m	 <i>m</i>	I	m	<u>v</u> II			
Pyrite		1			v,d	mv		
Chalcopyrite		1			v,d	mv		<u>v,d</u>
Chalcocite		1 						v,d
Molybdenite		 					v	
Apatite	peg,b	ib,d		d				
Actinolite	peg	b,d,i	Ι	d, i	<u>v</u> II			
Gold		 						
Titanite	<u>d</u>	1						
Quartz		 ,			<u>v</u>	mv		
Calcite		1 					<i>v</i>	V
Abundant Moderate								

Figure 2. Mineral assemblages of MtAp and IOCG mineralization stages in San Juan and Abundancia veins. Mineral textures and structures: b: banded; d: disseminated; i: inclusions; m: massive; mv: massive veins; peg: pegmatite; v: veinlets



Figure 3. (a) Mineralized sample from Abundancia vein showing MtAp and IOCG events (MOC-18-09). **(b)** Banded MtAp actinolite with perpendicular grows of coarse-grained fluorapatite and magnetite at Abundancia (MOC-18-09), overprinted by IOCG event. **(c)** Massive chalcopyrite vein with quartz at Abundancia (MOC-18-11a). **(d)** San Juan MtAp vein, with coarse-grained actinolite rock as shown. **(e)** Magnetite from San Juan vein with banded coarse-grained fluorapatite.



Figure 4. BSE images showing EPMA analysis traverses on actinolite (red), magnetite (green), and fluorapatite (blue), and spots of LA-ICPMS trace element analyses of actinolite (yellow; crosses are failed analyses). (a), (b) MtAp mineralization in Abundancia vein. (c) Mt-rich mineralization in Abundancia vein. (d), (e) IOCG mineralization in Abundancia vein. (f) MtAp mineralization remnants in IOCG zone. (g), (h) Coarse-grained actinolite and magnetite and fluorapatite in San Juan vein. act: actinolite; ap: apatite; cal: calcite; ccp: chalcopyrite; ilm: ilmenite; mt: magnetite; py: pyrite; qz: quartz







(*Previous pages*) Figure 5. Results and error bars of all the traverses analyzed and spots of actinolite, magnetite, and fluorapatite from Abundancia and San Juan deposits. Plots show average composition of each mineral. (a) Classification chart for calcic amphiboles (after Leake et al., 1997) for actinolite analyzed in this study. (b) EPMA actinolite data. (c) LA-ICPMS trace element data on actinolite, normalized to continental crust (Rudnick and Gao, 2003). (d) EPMA magnetite data. (e) EPMA fluorapatite data.



Figure 6. 40 Ar/ 39 Ar dating results. (a) Plateau age, isochron age, and Ca/K ratios for sample MOC-18-09. (b) Plateau age, isochron age, and Ca/K ratios for sample MOC-18-05.



Figure 7. U–Pb and Hf isotope results on zircon from sample MOC-18-02. (a) CL images of representative zircon grains from host rock diorite after annealing process. (b) Concordia diagram. (c) Tera-Wasserburg diagram. (d) Weighted mean age plot. (e) $\varepsilon_{\rm Hfi}$ vs age plot.



Figure 8. Initial Sr and Nd isotope compositions of Cretaceous and Jurassic MtAp deposits in Coastal Cordillera, including for MtAp mineralization in Abundancia and San Juan deposits recalculated for 154 Ma, compared to those of volcanic and plutonic rocks of La Negra Formation, together with isotopic data from this study for IOCG event in Abundancia IOCG deposit (diagram modified from Tornos et al., 2021). N zone: vein-like MtAp deposits hosted by Jurassic diorite; S zone: MtAp ore lenses hosted by coeval (sub-)volcanic intermediate rocks



Figure 9. δ^{34} S sulfide mineral compositions for MtAp and IOCG deposits in Chile and Peru.



Figure 10. Genetic model for formation of San Juan-Abundancia system in Montecristo district. (a) Immiscible iron-rich melts ascend after separating from silicate melt and crystallize within tensional faults related to the Atacama fault system, after emplacement and crystallization of Matancilla intrusive complex. (b) Younger magmatic-hydrothermal fluids channelize along the structures and equilibrate with silicate igneous intrusions of Coastal Batholith and react with previous MtAp rocks, promoting the precipitation of an IOCG-like assemblage. (c) Replacement of favorable units by IOCG mineralization, forming stratabound deposits. Note that thicknesses shown are estimates.

		StdErr*10 ⁻⁶								StdErr*10 ⁻⁶			
Sample	Description	Rb	Sr	⁸⁷ Sr/ ⁸⁶ Sr	(2σ)	⁸⁷ Sr/ ⁸⁶ Sr _i	Sm	Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	(2σ)	εNdi		
MOC-18-06b	Magnetite- actinolite-sulfides	0.6	12.4	0.704556	2.8	0.704249294	2.17	14.9	0.512822	1.5	5.7		
MOC-18-09b	Magnetite- actinolite-sulfides	0.6	6.7	0.704935	3.8	0.704367326	0.54	5.2	0.512781	3.6	5.4		
MOC-18-12	Magnetite- actinolite-sulfides	0.5	5	0.705051	6.5	0.704417625	0.42	4.5	0.512858	1.9	7.0		

 Table 1. Whole-rock Rb–Sr and Sm–Nd isotopic data for Abundancia IOCG mineralization.

Sample	Mineral	Sample description	δ ³⁴ S ‰ (CDT)
MOC-18-6-1	Сср	Magnetite, sulfides disseminated and in veinlets (ccp, py), fine-grained actinolite, fluorapatite (915m)	1.9
MOC-18-6-2	Сср	Magnetite, sulfides disseminated and in veinlets (ccp, py), fine-grained actinolite, fluorapatite (915m)	2.0
MOC-18-9-1	Сср	Magnetite, fluorapatite, fine-grained actinolite, sulfides, disseminated and in veinlets (py, ccp) (940m)	0.6
MOC-18-9-2	Ру	Magnetite, fluorapatite, fine-grained actinolite, sulfides, disseminated and in veinlets (py, ccp) (940m)	0.3
MOC-18-11-a-1	Ccp	Late massive chalcopyrite vein with quartz (940m)	3.1
MOC-18-11-a-2	Ccp	Late massive chalcopyrite vein with quartz (940m)	3.1
MOC-18-11-b-1	Ccp	Magnetite, sulfides disseminated and in veinlets (ccp, py) (940m)	1.2
MOC-18-11-b-2	Ccp	Magnetite, sulfides disseminated and in veinlets (ccp, py) (940m)	1.2
ABU-3	Ру	Magnetite, sulfides disseminated and in veinlets (ccp, py), fine-grained actinolite, fluorapatite (915m)	3.4
ABU-4	Ру	Magnetite, sulfides disseminated and in veinlets (ccp, py), fine-grained actinolite, fluorapatite (915m)	1.8
ABU-5	Ру	Magnetite, sulfides disseminated and in veinlets (ccp, py), fine-grained actinolite, fluorapatite (915m)	0.5
MOC-18-12	Сср	Magnetite, fine-grained actinolite, and sulfides (ccp, py)	2.0
MOC-18-12	Ccp	Magnetite, fine-grained actinolite, and sulfides (ccp, py)	1.6
MOC-18-06b	Ccp	Magnetite, fluorapatite, fine-grained actinolite, and sulfides (ccp, py)	2.0
MOC-18-06c	Сср	Magnetite, fluorapatite, fine-grained actinolite, and sulfides (ccp, py)	2.4

Table 2. δ^{34} S results for Abundancia IOCG mineralization.

CDT: Canyon Diablo Troilite (CDT) standard

Chapter 3

3.1. Conclusions

The genetic relationship between MtAp and IOCG mineralization has been a controversial topic for many years. The key question has been whether these two types are end-members of the same mineralizing system, or form independently with no genetic relationship.

The results from this research project contribute to a better understanding of the relationship, or lack thereof, between these two types of mineralization in a magmatic arc environment within the Chilean iron belt of northern Chile. The Montecristo district hosts IOCG veins that in the deepest parts are rich in magnetite, and coarse-grained pegmatitic fluorapatite and actinolite, and thus are classified as MtAp mineralization. These veins are hosted by a Jurassic diorite (U–Pb zircon date of 153.3 \pm 1.8 Ma) and are spatially controlled by secondary structures of the Atacama fault system.

The following conclusions are drawn from this study:

- Field data, such as the presence of massive magnetite bodies, coarse-grained pegmatitic fluorapatite and actinolite, and fluorapatite with comb-like textures or UST within the MtAp mineralization, strongly suggest that MtAp mineralization in the Montecristo district is of magmatic origin.
- 2) Mineralogical studies of both the MtAp and IOCG mineralization show differences between minerals in both systems. Yellow CL emission of fluorapatite crystals, together with "poikilitic" fluorapatite hosting acicular actinolite crystals in the MtAp mineralization, are consistent with being crystallized from a melt. The fact that magnetite from the IOCG stage hosts quartz inclusions indicates deposition from hydrothermal fluids.

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- 3) Mineral chemical data show that actinolite from both events is compositionally similar within error, suggesting that actinolite chemistry is not a successful tool for differentiating the two types of mineralization. However, magnetite from the IOCG event is enriched in Cu compared to that from the MtAp event, indicating a higher amount of Cu in the system during the IOCG event.
- 4) The geochronological results suggest an early formation at ca. 154 Ma of the MtAp assemblage in the Montecristo district that includes magnetite, fluorapatite, and actinolite. This mineralization is characterized by higher ε_{Ndi} values (+6.6 to +7.2) relative to the IOCG mineralization, and variable initial ⁸⁷Sr/⁸⁶Sr ratios (0.70426 and 0.70629). Formation of the MtAp mineralization is explained by ascending, immiscible iron-rich melts that intruded along secondary structures of the transcrustal Atacama fault system.
- 5) At ~154-152 Ma, magmatic-hydrothermal fluids partially replaced the early MtAp mineralization by an IOCG assemblage that comprises chalcopyrite, pyrite, magnetite, actinolite, quartz, and gold, with the latest molybdenite crystallization at 151.8 ± 0.6 Ma. The IOCG mineralization has ε_{Ndi} values of +5.4 and +5.7, and whole rock ${}^{87}Sr/{}^{86}Sr_i$ values of 0.70425 to 0.70442; the MtAp mineralization has similar ${}^{87}Sr/{}^{86}Sr_i$ ratios but higher ε_{Ndi} values. Hf (ε_{Hfi} = 5.0 to 6.7), Sr–Nd, and S isotopes (+0.3 to +3.4‰) support a magmatic-hydrothermal source of components in the IOCG mineralization. Fluids that deposited this mineralization, equivalent to the host Jurassic diorite. These magmatic-hydrothermal fluids used the MtAp rocks as a trap, owing to their oxidizing and brittle characteristics, as a means to deposit the Cu-Au IOCG mineralization.
- 6) ϵ_{Ndi} values of the host diorite vary from +2.3 to +3.4, which are significantly lower than those of either the MtAp or the IOCG mineralizations.

7) Differences in the ε_{Ndi} values can be explained by the magmatic-hydrothermal fluids of the IOCG system being a mixture of the higher ε_{Ndi} values of the MtAp rocks, and the lower values of the host diorite, or of an unexposed and unidentified intrusion compositionally similar to the host diorite. These fluids likely were exsolved from the monzogabbro magma at deeper levels of the system.

In summary, geochemical, mineralogical, geochronological, and field data obtained in this study suggest that the IOCG and the MtAp mineralization events in the Montecristo district are genetically independent, each having formed from fluids with different sources.

3.2. References

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Appendices

APPENDIX 1



(*Previous page*) Figure 1. Photomicrographs of Abundancia and San Juan veins. (a) Dioritic host rock; XPL. (b) Plagioclase crystal in diorite; XPL. (c) CL image of plagioclase in diorite replaced by potassic feldspar and late calcite veinlets. (d) MtAp mineralization in Abundancia, with poikilitic euhedral fluorapatite and acicular fine-grained actinolite crystals, also disseminated in surrounding magnetite; XPL. (e) CL image of (d) showing yellowish color of fluorapatite. (f) Contact between MtAp and Mt-rich zones in Abundancia vein, the Mt-rich event being later; XPL. (g) Mt-rich mineralization with poikilitic fluorapatite and acicular fine-grained actinolite, surrounded by magnetite; XPL. (h) CL image of (g). (i), (i) IOCG event in Abundancia, with MtAp mineralization cut by ccp-py-qt-act-mt veinlets; XPL. (k), (l) BSE images of ccp-py-qz-act-mt IOCG veinlets. (m) Remnants of MtAp mineralization in IOCG zone, with coarse-grained poikilitic fluorapatite enclosing acicular actinolite crystals. (n) CL image of previous fluorapatite. (o) Bands of acicular, fine-grained actinolite within magnetite from MtAp mineralization in Abundancia. (p) BSE image of remnants of MtAp mineralization in IOCG zone. (q) Secondary electron image of laminar molybdenite with minor calcite. (r) BSE image of molybdenite crystals encrusted in open spaces of magnetite. (s) Coarse-grained fluorapatite and massive magnetite in San Juan vein; XPL. (t) CL image showing magmatic fluorapatite and late calcite veinlets in San Juan vein. (u) Coarse-grained actinolite with weak to moderate chloritization, and late calcite veinlets in San Juan vein; XPL. (v) BSE images showing crystals of magnetite and titanite with exsolution textures disseminated in actinolite in San Juan vein. Act: actinolite; amp: amphibole; ap: apatite; cal: calcite; chl: chlorite; ccp: chalcopyrite; kfs: potassic feldspar; mol: molybdenite, mt: magnetite; pl: plagioclase; qt: quartz; ttn: titanite.

APPENDIX 2

Table 2A. Summary methods for EPMA analyses and LA-ICPMS trace element analyses of actinolite.

EPMA												
Model	JEOL JXA-8230 Superpro	obe										
Voltage	15 kV											
Current	20 nA											
Spot size	3µm											
Secondary standard	Kaersutite											
	F	Ti	Mn	Cl	К	Ca	S	Na	Al	Si	Mg	Fe
Peak counting time (s)	10	40	40	20	20	40	40	20	20	20	20	40
Background counting												
time (s)	5	20	20	10	10	20	20	10	10	10	10	20
Element X-ray line	K_{α}	K _α	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	LDE1	LIFL	LIFL	PETL	PETL	PETL	PETL	ТАР	ТАР	ТАР	ТАР	LIFH
Primary Standard Avg limit of detection (ppm)	JMH_fluorapatite_319 252	rutile 63	rhodenite 47	tugtupite 18	orthoclase 21	diopside 18	sphalerite 31	albite 48	albite 40	diopside 77	diopside 41	almandine_garnet 54
LA-ICP-MS												
Model	Thermo-Finnigan ELEME	NT XR c	oupled with a	GeoLas 19	3 nm Excime	r laser syste	m					
Pulse frequency	10 Hz											
Energy density	4 J/cm ²											
Spot size	40 µm											
Gas blank	30s											
Signal	60s											
Internal standard	Ca (from EPMA)											
Primary reference material	NIST-610											
Secondary reference material	NIST-612; BCR-2G ⁷ Li, ²⁵ Mg, ²⁷ Al, ²⁹ Si, ³¹ P, ³	⁹ K, ⁴⁵ Sc, ⁴	⁴⁹ Ti, ⁵¹ V, ⁵³ C	r, ⁵⁵ Mn, ⁵⁷ Fe	e, ⁵⁹ Co, ⁶⁰ Ni, ⁶	⁵⁵ Cu, ⁶⁶ Zn, ⁷	⁷¹ Ga, ⁷⁵ As, ⁷⁷	Se, ⁸⁵ Rb,	⁸⁸ Sr, ⁸⁹ Y	7, ⁹⁰ Zr, ⁹³ Nb	, ⁹⁵ Mo,	
Elements/isotopes	¹⁰⁷ Ag, ¹¹¹ Cd, ¹¹⁸ Sn, ¹²¹ Sb, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ¹⁴⁶ Nd, ¹¹ ¹⁹⁷ Au, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi, ²⁰	¹³⁷ Ba, ⁴⁷ Sm, ¹⁵³ I ³² Th, ²³⁸ U	Eu, ¹⁵⁷ Gd, ¹⁵⁹	Гb, ¹⁶³ Dy, ¹⁶	⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹	⁷⁷² Tm, ¹⁷² Yb,	¹⁷⁵ Lu, ¹⁷⁸ Hf,	¹⁸¹ Ta, ¹⁹	⁵ Pt,	, ,	, -,	

	MOC-18-05	sd	MOC-18-09C1	sd	MOC-18-09C2	sd	MOC-18-09C3_1	sd	MOC-18-09C3_2	sd
	San Juan MtAp vein	<i>n</i> = 40	Abundancia MtAp zone	<i>n</i> = 10	Abundancia mt- rich zone	<i>n</i> = 20	Abundancia IOCG zone	n = 15	Abundancia MtAp remnants in IOCG zone	<i>n</i> = 3
EPMA (wt. %)										
F	<lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>		<lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td></lod<></td></lod<></td></lod<></td></lod<>		<lod< td=""><td></td><td><lod< td=""><td></td><td><lod< td=""><td></td></lod<></td></lod<></td></lod<>		<lod< td=""><td></td><td><lod< td=""><td></td></lod<></td></lod<>		<lod< td=""><td></td></lod<>	
TiO ₂	0.04	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01
MnO	0.33	0.01	0.07	0.01	0.06	0.01	0.06	0.01	0.06	0.01
Cl	0.04	0.00	0.05	0.00	0.05	0.00	0.02	0.00	0.09	0.01
K ₂ O	0.04	0.00	0.10	0.01	0.06	0.01	0.02	0.00	0.09	0.01
CaO	12.48	0.03	12.43	0.03	12.15	0.03	12.34	0.03	12.64	0.03
SO ₃	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Na ₂ O	0.11	0.01	0.24	0.02	0.22	0.02	0.24	0.02	0.22	0.02
Al ₂ O ₃	0.86	0.02	1.66	0.02	1.63	0.02	1.66	0.02	1.50	0.02
SiO ₂	53.91	0.12	54.42	0.12	54.08	0.12	55.14	0.12	54.97	0.12
MgO	15.20	0.08	18.63	0.08	18.01	0.08	18.70	0.08	18.59	0.08
FeO	13.05	0.06	8.73	0.05	9.05	0.05	9.09	0.05	9.04	0.05
Total recalculated	96.08	-	96.35	-	95.33	-	97.30	-	97.24	-
Total(Mass%)	95.75	-	96.09	-	95.05	-	97.03	-	96.96	-
LA-ICPMS (ppm)	n = 3		n = 3		n = 4		n = 3		n=3	
⁷ Li	<lod< td=""><td>_</td><td>1.36</td><td>0.62</td><td>2.11</td><td>0.74</td><td>2.17</td><td>0.66</td><td>3.80</td><td>1.40</td></lod<>	_	1.36	0.62	2.11	0.74	2.17	0.66	3.80	1.40
²⁵ Mg	101,700	2,600	118,733	1,833	115,450	2,725	120,067	2,700	117,300	6,467
²⁷ Al	3,832	122	9,557	193	9,545	380	15,323	690	10,807	990
²⁹ Si	293,567	10,600	293,300	8,167	285,000	11,475	290,967	9,467	252,333	15,000
³¹ P	11.07	3.33	21.83	4.67	13.90	4.28	16.63	4.50	<lod< td=""><td>_</td></lod<>	_
³⁹ K	218	7.30	1054	50.00	612	34.75	282	13.67	896	43.33
⁴⁵ Sc	292	11.13	2.67	0.27	3.99	0.32	1.42	0.17	1.32	0.31
⁴⁹ Ti	194	11.17	68.73	7.00	77.35	11.25	19.33	2.57	106	15.37

Table 2B. Actinolite average results for oxides (EPMA; wt. %) and trace elements (LA-ICP-MS; ppm) in Abundancia and San Juan veins. Minimum limits of detection (LOD) calculated by Iolite.

⁵¹ V	188	6.47	282	12.30	213	10.70	81.57	7.23	327	31.67
⁵³ Cr	327	15.00	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
⁵⁵ Mn	3308	111	524	20.33	570	31.00	715	40.33	532	46.33
⁵⁷ Fe	121,967	3,667	77,433	1,700	83,900	3,025	88,067	3,033	84,167	12,000
⁵⁹ Co	86.53	4.97	60.00	1.73	64.63	2.25	78.40	2.50	65.57	9.33
⁶⁰ Ni	55.87	2.20	201	8.87	232	11.83	177	10.17	259	35.00
⁶⁵ Cu	81.00	14.00	2.11	0.68	34.41	36.57	74.48	17.04	1.45	1.15
⁶⁶ Zn	102	4.80	30.47	2.47	33.00	3.58	33.40	2.40	38.17	6.40
⁷¹ Ga	4.22	0.22	8.13	0.41	7.97	0.81	6.33	0.42	10.20	1.77
⁷⁵ As	4.58	0.49	5.89	0.62	3.66	0.66	6.90	0.75	3.56	1.32
⁷⁷ Se	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
⁸⁵ Rb	0.14	0.05	0.39	0.09	0.19	0.05	0.08	0.04	0.32	0.13
⁸⁸ Sr	3.31	0.27	5.16	0.29	4.91	0.43	10.16	1.80	4.90	0.70
⁸⁹ Y	1.75	0.16	9.39	0.33	10.24	0.82	28.43	1.93	7.37	1.03
⁹⁰ Zr	1.81	0.19	0.73	0.18	1.00	0.20	0.73	0.15	0.34	0.13
⁹³ Nb	0.01	0.01	0.94	0.13	0.46	0.10	0.59	0.10	0.60	0.17
⁹⁵ Mo	0.08	0.05	0.01	0.02	0.05	0.06	0.05	0.04	0.26	0.52
¹⁰⁷ Ag	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
¹¹¹ Cd	<lod< td=""><td>_</td><td>0.16</td><td>0.13</td><td><lod< td=""><td>_</td><td>0.12</td><td>0.11</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	0.16	0.13	<lod< td=""><td>_</td><td>0.12</td><td>0.11</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	0.12	0.11	<lod< td=""><td>_</td></lod<>	_
¹¹⁸ Sn	0.31	0.12	1.34	0.22	1.19	0.25	0.73	0.18	1.25	0.25
¹²¹ Sb	0.66	0.11	0.10	0.04	0.10	0.05	0.11	0.05	0.09	0.01
¹³⁷ Ba	0.34	0.17	0.41	0.15	0.40	0.18	1.00	0.48	0.45	0.53
¹³⁹ La	0.03	0.01	1.14	0.11	0.89	0.12	3.72	0.34	0.95	0.24
¹⁴⁰ Ce	0.12	0.03	4.46	0.24	3.43	0.28	14.06	1.00	3.54	0.49
¹⁴¹ Pr	0.03	0.01	0.66	0.06	0.54	0.07	2.26	0.18	0.57	0.16
¹⁴⁶ Nd	0.19	0.07	4.00	0.42	3.49	0.53	13.50	1.07	3.56	1.78
¹⁴⁷ Sm	0.12	0.07	1.17	0.21	1.19	0.23	4.13	0.48	0.82	0.33
¹⁵³ Eu	0.03	0.02	0.18	0.04	0.19	0.06	0.57	0.09	0.16	0.15
¹⁵⁷ Gd	0.18	0.09	1.35	0.24	1.58	0.33	5.63	0.66	1.15	0.52

¹⁵⁹ Tb	0.03	0.01	0.21	0.02	0.24	0.04	0.75	0.07	0.20	0.08
¹⁶³ Dy	0.21	0.06	1.48	0.18	1.74	0.29	4.96	0.39	1.42	0.37
¹⁶⁵ Ho	0.05	0.01	0.30	0.04	0.35	0.06	1.05	0.10	0.20	0.08
¹⁶⁶ Er	0.18	0.04	0.90	0.12	1.02	0.15	3.06	0.30	0.81	0.50
¹⁶⁹ Tm	0.02	0.01	0.13	0.02	0.13	0.03	0.42	0.05	0.09	0.06
¹⁷² Yb	0.28	0.06	1.00	0.16	1.02	0.22	3.28	0.35	0.96	0.50
¹⁷⁵ Lu	0.09	0.02	0.15	0.02	0.16	0.03	0.64	0.07	0.17	0.05
$^{178}\mathrm{Hf}$	0.06	0.03	0.02	0.02	0.03	0.03	0.03	0.02	0.03	0.06
¹⁸¹ Ta	0.00	0.00	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.02
¹⁹⁵ Pt	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
¹⁹⁷ Au	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
²⁰⁵ Tl	<lod< td=""><td>_</td><td>0.01</td><td>0.02</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<></td></lod<>	_	0.01	0.02	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td><lod< td=""><td>_</td></lod<></td></lod<>	_	<lod< td=""><td>_</td></lod<>	_
²⁰⁸ Pb	0.40	0.08	0.29	0.06	0.23	0.08	0.30	0.07	0.14	0.07
²⁰⁹ Bi	0.01	0.00	0.01	0.01	0.02	0.01	0.02	0.01	<lod< td=""><td>_</td></lod<>	_
²³² Th	0.25	0.06	0.31	0.08	0.42	0.08	0.11	0.03	0.20	0.10
²³⁸ U	0.11	0.03	0.03	0.01	0.07	0.02	0.04	0.02	0.17	0.09

Note: n = number of analyses; sd = standard deviation; <LOD = below limit of detection

Table 2C. Summary methods for EPMA magnetite analyses.

Model	JEOL JXA-8 Superprobe	230								
Voltage	15 kV									
Current	100 nA									
Spot size	1µm									
Secondary standard	KRN-10-02									
	Cu	Ni	Mn	Ti	V	K	Ca	S	Р	Na
Peak counting time (s)	60	60	60	60	60	60	60	60	60	20
Background counting time (s)	30	30	30	30	30	30	30	30	30	10
Element X-ray line	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}
Analyzing crystal	LIFL	LIFL	LIFL	LIFL	LIFL	PETL	PETL	PETL	PETL JMH fluorap	TAF
Primary Standard Avg limit of detection (ppm)	cuprite 26	pentlandite 23	rhodenite 23	rutile 30	V metal 22	orthoclase 10	diopside 8	pyrite 13	atite_319 14	Albit 42
		Al	Si	Mg	Zn	Co	Fe		Cr	Ba
		60	60	60	60	60	20		60	60
		30	30	30	30	30	10		30	30
		K_{α}	K_{α}	K_{α}	K_{α}	K_{α}	K_{α}		K_{α}	L_{α}
		TAP	TAP	TAP	LIFH	LIFH	LIFH	Ι	JIFH	LIFE
		albite d	opside	diopside	willemite	Co metal	magnetite	chrom	ium_oxide	barite

	MOC-18-03	sd	MOC-18-09C1	sd	MOC-18-09C2	sd	MOC-18-09C3_1	sd	MOC-18-09C3_2	sd
	San Juan MtAp vein	n = 20	Abundancia MtAp zone	n = 20	Abundancia mt- rich zone	n = 20	Abundancia IOCG zone	<i>n</i> = 10	Abundancia MtAp remnants in IOCG zone	<i>n</i> = 20
EPMA (wt. % oxide)										
SiO ₂	0.56	0.00	0.75	0.00	0.34	0.00	0.19	0.00	0.74	0.00
TiO ₂	0.03	0.01	0.02	0.01	0.03	0.01	0.05	0.01	0.02	0.01
Al_2O_3	0.15	0.00	0.18	0.00	0.12	0.00	0.14	0.00	0.16	0.00
Cr_2O_3	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
V_2O_3	0.21	0.01	0.35	0.01	0.44	0.01	0.91	0.01	0.26	0.01
CaO	0.11	0.00	0.18	0.00	0.10	0.00	0.04	0.00	0.18	0.00
FeO	90.16	0.09	90.73	0.09	91.42	0.09	90.19	0.09	89.34	0.09
Na ₂ O	0.05	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.04	0.01
P_2O_5	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00
K ₂ O	0.02	0.00	0.07	0.00	0.01	0.00	0.06	0.00	0.02	0.00
CuO	0.01	0.00	0.01	0.00	0.01	0.01	0.05	0.01	0.01	0.01
MnO	0.02	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.01	0.00
MgO	0.06	0.00	0.27	0.00	0.14	0.00	0.03	0.00	0.32	0.00
ZnO	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01
NiO	0.03	0.00	0.03	0.00	0.03	0.00	0.02	0.00	0.03	0.00
BaO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
CoO	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00
SO_3	0.01	0.00	0.01	0.00	0.00	0.00	0.04	0.00	0.01	0.00
Total recalculated	91.46	-	92.70	-	92.75	-		-	91.20	-
Total(Mass%)	91.41	-	92.66	-	92.71	-	91.75	-	91.14	-

Table 2D. Magnetite average results from EPMA (wt. % oxide) for oxides in the Abundancia and San Juan veins.

Note: n = number of analyses, sd = standard deviation

EPMA													
Model	JEOL JXA-82	.30											
Voltage	Superprobe 15 kV												
Current	20 nA												
Spot size	20 µm												
Secondary standard	JMH fluorapatite 347												
	F	Fe	Mn	As	Ca	Sr	S	Na	Si	Mg	Cl	Y	Р
Peak counting time (s)	20	40	40	40	20	40	40	20	20	40	20	40	20
Background counting time (s)	10	20	20	20	10	20	20	10	10	20	10	20	10
Element X-ray line	Kα	Kα	K_{α}	Kα	Κα	Lα	Kα	Kα	K_{α}	Kα	K_{α}	La	Κα
Analyzing crystal	LDE1	LIFL	LIFL	LIFL	PETL	PETL	PETL	TAP	TAP	TAP	PETH	PETH	PETH
Primary Standard Avg limit of detection (ppm)	JMH_fluor apatite_319 114	arseno pyrite 41	rhodenite 49	arseno pyrite 273	JMH_fluor apatite_319 30	celestite 71	sphalerite 34	albite 43	albite 51	diopside 30	JMH_chlor apatite_346 19	YP5O14 69	JMH_fluor apatite_319 55

Table 2E. Summary methods for EPMA fluorapatite analyses.

	MOC-18-03	sd	MOC-18-09C1	sd	MOC-18-09C2	sd	MOC-18-09C3_2	sd
	San Juan MtAp vein	<i>n</i> = 20	Abundancia MtAp zone	<i>n</i> = 20	Abundancia mt- rich zone	<i>n</i> = 20	Abundancia MtAp remnants in IOCG zone	<i>n</i> = 20
EPMA (wt. %)								
F	2.49	0.04	2.26	0.04	2.14	0.04	2.19	0.04
FeO	0.06	0.01	0.12	0.01	0.26	0.01	0.51	0.02
MnO	0.02	0.01	0.04	0.01	0.04	0.01	0.05	0.01
As ₂ O ₅	0.09	0.06	0.10	0.06	0.16	0.06	0.13	0.07
CaO	55.41	0.08	55.18	0.08	55.14	0.08	54.14	0.08
SrO	0.02	0.01	0.03	0.02	0.03	0.02	0.03	0.02
SO ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01
Na ₂ O	0.02	0.01	0.02	0.01	0.03	0.01	0.04	0.01
SiO ₂	0.02	0.01	0.30	0.01	0.07	0.01	1.26	0.02
MgO	0.01	0.01	0.18	0.01	0.03	0.01	0.50	0.01
Cl	0.58	0.01	0.76	0.01	0.79	0.01	0.44	0.01
Y ₂ O ₃	0.03	0.01	0.02	0.01	0.02	0.01	0.02	0.01
P ₂ O ₅	42.32	0.16	41.99	0.16	42.01	0.16	41.09	0.16
Total recalculated	101.08	-	101.02	-	100.74	-	100.44	-
Total(Mass%)	99.80	-	99.63	-	99.57	-	99.35	-

Table 2F. Fluorapatite average results from EPMA (wt. %) for oxides in Abundancia and San Juan veins.

Note: n = number of analyses, sd = standard deviation

APPENDIX 3







d. Abundancia remnants of the MtAp stage in the IOCG zone, MOC-18-09C3_2



e. San Juan MtAp deposit, MOC-18-05



(previous pages) Figure 3. EPMA X-ray maps of actinolite from samples from Abundancia and San Juan deposits. (a) Sample MOC-18-09C1. (b) Sample MOC-18-09C2. (c) Sample MOC-18-09C3_1. (d) Sample MOC-18-09C3_2. (e) Sample MOC-18-05.

APPENDIX 4

Table 4. ⁴⁰Ar-³⁹Ar results.

⁴⁰ Ar Total	Err. ⁴⁰ Ar	⁴⁰ Ar*	Err. ⁴⁰ Ar *	³⁹ Ar	Err. ³⁹ Ar	% ³⁹ Ar	³⁸ Ar	Err. ³⁸ Ar	³⁸ ArCl	Err. ³⁸ Cl	³⁷ Ar	Err. ³⁷ Ar
MOC 18-05												
Concentrations (g/g)	K=	3.19 E-04	Cl=	2.86 E-04	Ca=	1.02 E-01						
wt (g)	0.01467											
J	0.0011642											
3.745 E-08	8.51E-12	4.005 E-10	1.11 E-10	3.219 E-12	2.66E-14	7.61	3.252 E-11	5.47 E-14	8.802 E-12	8.66 E-14	1.088 E-09	2.52E-12
1.166 E-08	2.10E-12	3.409 E-10	3.44 E-11	5.195 E-12	1.97E-14	12.28	2.600 E-11	4.35 E-14	1.863 E-11	5.53 E-14	6.335 E-10	1.53E-12
4.535 E-09	1.01E-12	1.248 E-09	1.11 E-11	1.720 E-11	2.08E-14	40.64	9.293 E-11	1.47 E-13	9.011 E-11	4.86 E-14	2.143 E-09	4.86E-12
3.722 E-09	8.85E-13	6.877 E-10	9.90 E-12	9.838 E-12	1.69E-14	23.25	4.942 E-11	7.82 E-14	4.702 E-11	4.85 E-14	1.460 E-09	3.34E-12
3.725 E-09	7.94E-13	2.274 E-10	1.12 E-11	4.692 E-12	1.27E-14	11.09	2.103 E-11	3.60 E-14	1.861 E-11	5.25 E-14	6.372 E-10	1.54E-12
1.073 E-08	2.46E-12	1.649 E-10	3.20 E-11	2.174 E-12	1.34E-14	5.14	1.517 E-11	2.79 E-14	8.397 E-12	5.95 E-14	3.040 E-10	8.64E-13

³⁶ Ar	Err. ³⁶ Ar	Age	1 sigma Err Age	Age +2sigma	Age - 2sigma	Ca/K	Error Ca/K	Cl/K	Error Cl/K	39/40	error 39/40	36/40	error 36/40
1.244 E-10	3.71E-13	309.65	85.90	481.44	137.86	847.789	9.992	0.48667	0.00739	6.650 E-05	7.687 E-07	3.314 E-03	9.929 E-06
3.806 E-11	1.15E-13	144.15	14.57	173.30	115.01	257.614	1.279	0.63841	0.00336	4.093 E-04	1.779 E-06	3.251 E-03	9.893 E-06
1.156 E-11	3.59E-14	159.07	1.44	161.95	156.19	263.755	0.783	0.93266	0.00185	3.475 E-03	6.692 E-06	2.428 E-03	8.150 E-06
1.053 E-11	3.25E-14	156.08	2.28	160.65	151.52	319.793	1.093	0.85079	0.00233	2.380 E-03	6.067 E-06	2.731 E-03	8.900 E-06
1.188 E-11	3.74E-14	108.63	5.37	119.38	97.88	289.834	1.198	0.70583	0.00309	1.145 E-03	3.848 E-06	3.145 E-03	1.009 E-05
3.545 E-11	1.07E-13	167.74	32.54	232.83	102.65	299.330	2.252	0.68764	0.00683	1.837 E-04	1.280 E-06	3.298 E-03	9.982 E-06
(continued)

⁴⁰ Ar Total	Err. ⁴⁰ Ar	⁴⁰ Ar*	Err. ⁴⁰ Ar*	³⁹ Ar	Err. ³⁹ Ar	% ³⁹ Ar	³⁸ Ar	Err. ³⁸ Ar	³⁸ ArCl	Err. ³⁸ Cl	³⁷ Ar	Err. ³⁷ Ar
MOC 18-09												
Concentrations (g/g)	K=	5.57 E-04	Cl=	4.31 E-04	Ca=	6.17 E-02						
wt (g)	0.01794											
J	0.0011644											
2.552 E-08	5.80E-12	3.904 E-10	7.53 E-11	1.426 E-12	1.72E-14	1.69	2.115 E-11	3.76 E-14	5.253 E-12	7.01 E-14	3.691 E-11	3.78E-13
4.006 E-09	6.13E-13	1.138 E-10	1.21 E-11	7.948 E-13	1.20E-14	0.94	4.890 E-12	1.22 E-14	2.415 E-12	7.28 E-14	3.203 E-11	3.75E-13
3.610 E-09	8.44E-13	4.126 E-10	1.03 E-11	4.298 E-12	1.27E-14	5.09	2.612 E-11	4.55 E-14	2.398 E-11	5.09 E-14	2.771 E-10	7.53E-13
1.836 E-08	4.64E-12	3.457 E-09	4.55 E-11	4.501 E-11	4.47E-14	53.32	2.000 E-10	3.16 E-13	1.895 E-10	5.40 E-14	2.352 E-09	5.28E-12
6.985 E-09	1.45E-12	1.981 E-09	1.61 E-11	2.703 E-11	2.98E-14	32.01	1.106 E-10	1.72 E-13	1.068 E-10	4.63 E-14	1.561 E-09	3.53E-12
5.381 E-09	1.28E-12	3.706 E-10	1.56 E-11	5.868 E-12	1.43E-14	6.95	2.886 E-11	4.88 E-14	2.553 E-11	5.00 E-14	3.882 E-10	9.61E-13

³⁶ Ar	Err. ³⁶ Ar	Age	1 sigma Err Age	Age +2sigma	Age - 2sigma	Ca/K	Error Ca/K	Cl/K	Error Cl/K	39/40	error 39/40	36/40	error 36/40
8.419 E-11	2.51E-13	506.97	97.98	702.93	311.01	51.105	0.817	0.65580	0.01188	5.489 E-05	6.729 E-07	3.298 E-03	9.881 E-06
1.304 E-11	4.06E-14	285.22	30.77	346.77	223.68	80.350	1.566	0.54096	0.01836	1.930 E-04	3.008 E-06	3.254 E-03	1.015 E-05
1.078 E-11	3.43E-14	199.34	5.01	209.36	189.31	130.721	0.546	0.99324	0.00379	1.139 E-03	3.624 E-06	2.967 E-03	9.539 E-06
5.050 E-11	1.51E-13	159.88	2.11	164.10	155.66	105.043	0.266	0.74934	0.00090	2.366 E-03	2.824 E-06	2.719 E-03	8.283 E-06
1.716 E-11	5.34E-14	153.43	1.26	155.96	150.90	116.523	0.304	0.70308	0.00096	3.719 E-03	4.897 E-06	2.400 E-03	7.711 E-06
1.688 E-11	5.21E-14	133.75	5.65	145.04	122.46	134.297	0.486	0.77450	0.00255	1.042 E-03	2.764 E-06	3.119 E-03	9.715 E-06

APPENDIX 5

Table 5. Geochronology results for zircon from host diorite (MOC-18-02): U-Pb-Th LA-ICPMS analytical data. Zircon grains from stag	es
2 and 3 with radiation damage were ignored for final age calculations.	

				Isotopic ratios											
Sample MOC-18-02	U approx.	Th approx.		²⁰⁷ Pb		²⁰⁶ Pb			²³⁸ U		²⁰⁷ Pb			²⁰⁸ Pb	
spot #	[ppm]	[ppm]	U/th	²³⁵ U	2SE	²³⁸ U	2SE	rho	²⁰⁶ Pb	2SE	²⁰⁶ Pb	2SE	rho	²³² Th	2SE
01a	3080	5400	0.938	0.1533	0.009	0.02297	0.0014	0.43549	43.53505	2.65342	0.0496	0.0024	0.33989	0.00592	0.00053
03a	2200	4630	0.848	0.1615	0.0064	0.0234	0.0012	0.39051	42.73504	2.191541	0.05	0.0016	0.16524	0.00641	0.00047
06a	5720	26300	0.4904	0.1582	0.0042	0.02332	0.0011	0.53561	4 2.88165	2.022719	0.04931	0.00063	0.22631	0.00643	0.00042
07a	3470	11060	0.836	0.1592	0.0049	0.02331	0.0011	0.27556	42.90004	2.024455	0.0496	0.0011	0.34411	0.00646	0.00044
08a	1484	6090	0.801	0.1601	0.0053	0.02363	0.0011	0.35949	42.31909	1.969996	0.0495	0.0012	0.16461	0.00634	0.00044
11a	2583	1060	4.66	0.167	0.0048	0.02421	0.0012	0.46667	41.30525	2.047348	0.05049	0.0009	0.19352	0.00667	0.0005
12a	3380	19700	0.412	0.1459	0.0045	0.02147	0.001	0.40153	4 6.57662	2.169381	0.0496	0.001	0.20506	0.00583	0.00039
18a	2664	22370	0.5327	0.1609	0.0052	0.02339	0.0011	0.45802	4 2.75331	2.01063	0.0505	0.0011	0.14338	0.00635	0.00043
19a	2083	20320	0.592	0.1689	0.0069	0.02245	0.0011	0.21911	44.54343	2.182529	0.0551	0.0021	0.36546	0.00612	0.00044
21a	1747	19410	0.709	0.1494	0.005	0.02221	0.0011	0.12929	4 5.02476	2.229952	0.0491	0.0012	0.16562	0.00583	0.0004
22a	5320	118000	0.448	0.1502	0.0056	0.02209	0.0011	0.44179	4 5.26935	2.254246	0.0497	0.0014	0.1861	0.00576	0.00042
23a	562	11350	0.547	0.1739	0.0096	0.02503	0.0013	0.33742	39.95206	2.075017	0.0514	0.0025	0.16474	0.00576	0.00056
28a	1197	697	2.93	0.1609	0.0053	0.0237	0.0011	0.37217	42.19409	1.958376	0.0496	0.0012	0.16404	0.00666	0.00049
30a	1427	1179	1.191	0.1612	0.0058	0.02422	0.0012	0.2985	41.28819	2.045658	0.0486	0.0014	0.23245	0.00664	0.00045
31a	1750	1795	0.861	0.1608	0.0054	0.02388	0.0012	0.46649	41.87605	2.104324	0.0487	0.0011	0.09649	0.00653	0.00045
32a	3590	1478	2.011	0.1664	0.0053	0.0239	0.0012	0.62178	41.841	2.100804	0.05047	0.00095	0.015	0.00627	0.00043
33a	1773	1940	0.817	0.1603	0.0071	0.02295	0.0012	0.43364	43.57298	2.278326	0.0507	0.0018	0.1331	0.00609	0.00045
35a	5000	7550	0.5963	0.1577	0.0043	0.02325	0.0011	0.58177	4 3.01075	2.034917	0.04942	0.0007	0.10043	0.00644	0.00042
36a	1930	1360	1.442	0.1548	0.006	0.02247	0.0012	0.41036	44.50378	2.376704	0.0505	0.0015	0.26325	0.00634	0.00048
37a	1690	1460	1.101	0.173	0.0075	0.02483	0.0013	0.46883	40.27386	2.108579	0.051	0.0017	0.11887	0.00634	0.00049
38a	3200	3210	0.92	0.1602	0.0045	0.02362	0.0011	0.42706	42.337	1.971664	0.04974	0.00079	0.19957	0.00635	0.00042
41a	1463	1270	1.228	0.1687	0.0054	0.02416	0.0012	0.43084	41.39073	2.055831	0.0504	0.0011	0.09644	0.00643	0.00045
42a	462	523.7	0.962	0.1663	0.0076	0.02472	0.0012	0.19023	40.45307	1.963741	0.0486	0.0018	0.07031	0.00678	0.0005
43a	1352	1291	1.16	0.1644	0.0052	0.02402	0.0011	0.27313	41.63197	1.906543	0.0499	0.0012	0.28616	0.00646	0.00045
44a	1118	802	3.61	0.1649	0.0057	0.02387	0.0011	0.3096	41.89359	1.93058	0.0502	0.0013	0.16209	0.00698	0.00055
45a	4360	7690	0.606	0.1582	0.0044	0.02265	0.0011	0.52757	44.15011	2.144155	0.05045	0.00078	0.15947	0.00627	0.00041
47a	3852	5890	0.705	- 0.1579	0.0043	0.02275	0.0011	0.53644	43.95604	2.125347	0.0501	0.00071	0.19161	0.0064	0.00042

(cont)	
(0000.)	

Ages (Ma)									Zircon radiation damage			
	²⁰⁷ Pb		²⁰⁶ Pb		²⁰⁷ Pb		²⁰⁸ Pb		D	Radiation damage stage		
spot #	²³⁵ U	2SE	²³⁸ U	2SE	²⁰⁶ Pb	2SE	²³² Th	2SE	(Murakami et al., 1991)	(Nasdala et al., 2004)		
01a	145	8	146	9	160	110	119	-11	2.08854E+15	2		
03a	152	6	149	8	179	69	129	10	1.61186E+15	2		
06a	149	4	149	7	155	29	130	9	5.83405E+15	3		
07a	150	4	149	7	176	49	130	9	2.97523E+15	2		
08a	150	5	151	7	153	52	128	9	1.44846E+15	1		
11a	157	4	154	7	200	39	134	10	1.4355E+15	1		
12a	138	4	137	7	163	46	118	8	3.60799E+15	2		
18a	151	5	149	7	203	48	128	9	3.88325E+15	2		
19a	159	6	143	7	377	82	123	9	3.22597E+15	2		
21a	141	4	142	7	130	52	118	8	2.9465E+15	2		
22a	142	5	141	7	186	67	116	9	1.5329E+16	3		
23a	162	8	159	8	220	110	116	11	1.69008E+15	2		
28a	151	5	151	7	154	49	134	10	6.76127E+14	1		
30a	152	5	154	7	110	59	134	9	8.63726E+14	1		
31a	151	5	152	7	121	49	132	9	1.08634E+15	1		
32a	156	5	152	7	201	41	126	9	1.96944E+15	2		
33a	151	6	146	7	202	76	123	9	1.07036E+15	1		
35a	149	4	148	7	158	31	130	9	3.29826E+15	2		
36a	146	5	143	7	216	70	128	10	1.0578E+15	1		
37a	162	7	158	8	224	74	128	10	1.05872E+15	1		
38a	151	4	151	7	171	35	128	9	1.96477E+15	2		
41a	158	5	154	7	199	47	130	9	8.92812E+14	1		
42a	155	7	157	8	95	76	137	10	3.02398E+14	1		
43a	154	5	153	7	168	51	130	9	8.33532E+14	1		
44a	155	5	152	7	177	56	141	11	6.5349E+14	1		
45a	149	4	144	7	202	35	126	8	2.92067E+15	2		
47a	149	4	145	7	195	33	129	9	2.49714E+15	2		

APPENDIX 6

Table 6. Hf results for zircon grains from LASS, and calculation of ε_{Ndi} for host diorite.

Lu-Hf Parameters (Bouvier et al., 2008)	
1.867E-11	Lu 176 decay constant*
0.0336	¹⁷⁶ Lu/ ¹⁷⁷ Hf CHUR present day
0.282785	¹⁷⁶ Hf/ ¹⁷⁷ Hf CHUR present day
*Söderlund et al., 2004	

(Vervoort et al., 2017)							
Depleted Mantle Parameters							
0.039760	¹⁷⁶ Lu/ ¹⁷⁷ Hf						
0.283238	¹⁷⁶ Hf/ ¹⁷⁷ Hf						

CHUR today	
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.282785
¹⁷⁶ Lu/ ¹⁷⁷ Hf	0.0336
decay*	1.867E-11

$e_{Hf(t)} = 1.50 * e_{Nd(t)} + 1.57$ (Vervoort et al., 2011).
Rearranged for $\varepsilon_{Nd(t)}$
$e_{Nd(t)} = (e_{Hf(t)} - 1.57) / 1.50$ (Vervoort et al., 2011).

MOC-18-02 zircon crystals @ ~153 Ma

Analysis #	Today	Age (Ma)	Sample	Age (a)	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	CHUR at age m	Sample at age m	єНf today	єНf @ 153 Ма	εNd today	εNd @ 153 Ma
8a	0	150.5	0.15050	1.505E+07	0.000631	0.282924	0.282776	0.282924	4.92	5.24	2.23	2.44
11a	0	154.2	0.15420	1.542E+07	0.001109	0.282918	0.282775	0.282918	4.70	5.03	2.09	2.30
28a	0	151	0.15100	1.510E+07	0.000546	0.282930	0.282776	0.282930	5.13	5.46	2.37	2.58
30a	0	154.2	0.15420	1.542E+07	0.000886	0.282949	0.282775	0.282949	5.80	6.13	2.82	3.03
31a	0	152.1	0.15210	1.521E+07	0.001189	0.282935	0.282775	0.282935	5.30	5.63	2.49	2.70
37a	0	158.1	0.15810	1.581E+07	0.000927	0.282965	0.282775	0.282965	6.37	6.71	3.20	3.41
41a	0	153.9	0.15390	1.539E+07	0.000694	0.282923	0.282775	0.282923	4.88	5.21	2.21	2.42
42a	0	157.4	0.15740	1.574E+07	0.000928	0.282929	0.282775	0.282929	5.09	5.43	2.35	2.56
43a	0	153	0.15300	1.530E+07	0.000696	0.282944	0.282775	0.282944	5.62	5.96	2.70	2.91
44a	0	152.1	0.15210	1.521E+07	0.000768	0.282928	0.282775	0.282928	5.06	5.39	2.32	2.53

(cont.)

			εHf		
Time	Time (Ga)	DM	DM	CHUR	CHUR
0	0	0.283238	16.01924	0.282785	0.000000
100	0.1	0.283164	15.61563	0.282722	0.000000
200	0.2	0.283089	15.21109	0.282659	0.000000
300	0.3	0.283015	14.80561	0.282596	0.000000
400	0.4	0.282940	14.39919	0.282533	0.000000
500	0.5	0.282865	13.99183	0.282470	0.000000
600	0.6	0.282790	13.58353	0.282406	0.000000
700	0.7	0.282715	13.17428	0.282343	0.000000
800	0.8	0.282640	12.76408	0.282279	0.000000
900	0.9	0.282564	12.35293	0.282216	0.000000
1000	1	0.282489	11.94082	0.282152	0.000000
1100	1.1	0.282413	11.52776	0.282088	0.000000
1200	1.2	0.282337	11.11374	0.282024	0.000000
1300	1.3	0.282261	10.69875	0.281960	0.000000
1400	1.4	0.282185	10.28280	0.281895	0.000000
1500	1.5	0.282109	9.86588	0.281831	0.000000
1600	1.6	0.282032	9.44799	0.281766	0.000000
1700	1.7	0.281956	9.02913	0.281701	0.000000
1800	1.8	0.281879	8.60930	0.281637	0.000000
1900	1.9	0.281802	8.18848	0.281572	0.000000
2000	2	0.281725	7.76668	0.281507	0.000000
2100	2.1	0.281648	7.34390	0.281441	0.000000
2200	2.2	0.281571	6.92013	0.281376	0.000000
2300	2.3	0.281493	6.49538	0.281311	0.000000
2400	2.4	0.281416	6.06963	0.281245	0.000000
2500	2.5	0.281338	5.64289	0.281180	0.000000
2600	2.6	0.281260	5.21515	0.281114	0.000000
2700	2.7	0.281182	4.78641	0.281048	0.000000
2800	2.8	0.281104	4.35666	0.280982	0.000000
2900	2.9	0.281026	3.92591	0.280916	0.000000
3000	3	0.280947	3.49415	0.280849	0.000000
3100	3.1	0.280869	3.06139	0.280783	0.000000
3200	3.2	0.280790	2.62760	0.280716	0.000000
3300	3.3	0.280711	2.19280	0.280650	0.000000
3400	3.4	0.280632	1.75698	0.280583	0.000000
3500	3.5	0.280553	1.32014	0.280516	0.000000
3600	3.6	0.280474	0.88227	0.280449	0.000000
3700	3.7	0.280394	0.44338	0.280382	0.000000
3800	3.8	0.280315	0.00345	0.280315	0.000000
3900	3.9	0.280247	0.00000	0.280247	0.000000
4000	4	0.280180	0.00000	0.280180	0.000000
4100	4.1	0.280112	0.00000	0.280112	0.000000
4200	4.2	0.280044	0.00000	0.280044	0.000000
4300	4.3	0.279976	0.00000	0.279976	0.000000
4400	4.4	0.279908	0.00000	0.279908	0.000000
4500	4.5	0.279840	0.00000	0.279840	0.000000
4560	4.56	0.279799	0.00000	0.279799	0.000000

APPENDIX 7

Table 7. Re–Os dates for two samples with slickenside fractures coated with molybdenite from Abundancia vein.

AIRIE Run #	Sample Name	Re, ppm	Re err, abs (ppm)	¹⁸⁷ Os, ppb	¹⁸⁷ Os err, abs (ppb)	Os _{Common,} ppb	Os _{Common} , err, abs (ppb)	Age, Ma	abs err, ± in Ma, with λ	Sample weight, g
MD-1869	MOC 18-07G	316	926	559.8	3.1	0.03542	0.00051	169	494	0.1062
MD-1870	MOC 18-07A	19.85	0.63	34.01	0.19	0.00238	0.00031	163.4	5.3	0.1596
MD-1886	MOC 18-07A (b, same sep)	23.138	0.042	39.395	0.015	0.00000	0.00040	162.38	0.60	0.0533
MD-1887	MOC 18-07G (b, same sep)	369.72	0.60	588.38	0.20	0.02151	0.00506	151.79	0.55	0.0217

Re-Os determinations used Carius tube dissolution with mixed double-Os spike (Markey et al., 2003).

Isotopic measurements were made using Triton TIMS instrument, AIRIE Program, Colorado State University.

Designation of (b, same sep) indicates that same mineral separate was used for second analysis.

Runs MD-1869 and MD-1870 were both underspiked, and data should not be used except for illustrative purposes.

Runs MD-1886 and MD-1887 should be used because spiking was corrected for these runs, as seen in normal uncertainties for molybdenite ages.

All data reported at 2-sigma uncertainty, inclusive of 187 Re decay constant uncertainty (l); decay constant of Smoliar et al. (1996) was used for age calculations; assumed Os initial ratio = 0.2.

For MD-1869 and MD-1870, Re blank = 2.13 ± 0.06 pg, Os blank = 0.099 ± 0.008 pg with ${}^{187}\text{Os}/{}^{188}\text{Os} = 0.350 \pm 0.023$ For MD-1886 and MD-1887, Re blank = 11.77 ± 0.03 pg, Os blank = 0.130 ± 0.003 pg with ${}^{187}\text{Os}/{}^{188}\text{Os} = 0.350 \pm 0.007$ Blanks and common Os present are both insignificant to Re–Os age calculations.