

## Geochemistry and geochronology of Apatite and Zircon from MTAP and IOCG deposits, Atacama Desert, Chile

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Abstract: The Chilean Iron Belt in the Atacama Desert offers a unique opportunity to investigate both Iron Oxide Copper Gold (IOCG) and Magnetite Apatite (MtAp) deposits in a geographically concentrated setting. This unique setting allows for the comparison of apatite and zircon between MtAp and IOCG deposits to better constrain differences and similarities between age, magma source, and fluid composition associated with the different deposits types. Zircon from the Cenozoic El Laco and apatite from El Laco and Incahuasi MtAp deposit in the Central Volcanic Zone are also included for comparison. Major and minor elements in both minerals were analyzed in situ by EPMA, while trace element compositions and U-Pb ratios were measured in situ by LA-ICPMS. Sm-Nd and Lu-Hf isotopes were measured in situ by LA-MC-ICPMS in the same regions as the trace elements and U-Pb. U-Pb geochronology of the El Laco zircon samples were done by SIMS due to their young age and their high U/Pb ratios. Ore apatites from the MtAp deposits contain 0.3-3 REE wt%, multiple phases of Cl-fluid alteration coupled with S and REE enrichment, and a general enrichment in LREE and HREE compared to their respective host.  $\boldsymbol{\epsilon}_{_{Nd}}$ values are negative with respect to the Cenozoic MtAp deposits and positive with respect to the Cretaceous MtAp deposits, indicating that crustal contamination may not be a necessary process in the formation of MtAp deposits. Future zircon analysis will better constrain age, magma source, and oxidation state of host and ore samples in both deposit types.

Keywords: MtAp, IOCG, apatite, zircon, Sm-Nd, U-Pb, Lu-Hf, trace elements

1. Introduction ron oxide-bearing deposits under the "IOCG clan" classification can contain economically significant amounts of iron +/copper +/- gold +/- uranium +/- rare earth elements, making these systems a priority research topic. However, differing mineralogy and deposit types have rendered an all-encompassing genetic model implausible. The Atacama Desert in northern Chile boasts varying types of IOCG clan deposit types including Paleocene to Miocene Cu- +/- Au +/- Mo porphyry systems (e.g., Chuquicamata, La Escondida (Charrier et al., 2007 and references therein) many of which are associated with the Domeyko fault system, Cretaceous IOCG sensu stricto deposits (Punta del Cobre district) associated with the Atacama fault system (AFS), and MtAp deposits of Cenozoic age and ~50 MtAp deposits containing >100 Mt Fe in the Cretaceous Iron Belt (CIB), occurring on the peripheries of the AFS, making Chile an ideal location for studies involving iron- +/- apatite +/- copper- +/gold-bearing systems. IOCG deposits sensu stricto occur globally in varying crustal settings, with fluid type/metal source generating the most discussion. Three main fluid type/metal source models exist: 1) magmatic fluids/metals are released from a magma body; 2) basinal fluids/metals are leached from wallrock; or 3) metamorphic fluids (expelled during pluton emplacement)/metals sourced from wall rock (Williams et al., 2005; Porter, 2010; Barton, 2014). Magnetite-apatite (MtAp) deposits, the copper-poor end member of the IOCG clan, are also highly debated with three different formation hypotheses: 1) complete metasomatic replacement of host rocks by hydrothermal fluids of magmatic or connate derivation (e.g., Sillitoe and Burrows (2002); 2) coalescence of buoyant microphenocrysts of magnetite and later cementation by hydrothermal magnetite (e.g., Knipping et al., 2015); or, 3) crystallization of Fe-P-rich immiscible melts in a magmatichydrothermal environment (e.g., Tornos et al., 2017).

2. Objectives and Samples The objectives of this study are twofold; firstly, to broadly interpret the formation of MtAp deposits using apatite trace element geochemistry and Sm-Nd isotopes and to draw comparisons within the MtAp deposit class, and secondly, to use zircon U-Pb geochronology to constrain ore emplacement, and to use zircon trace element geochemistry and Lu-Hf isotopes to distinguish MtAp deposits from IOCG deposits. Four MtAp deposits, and one apatite-only deposit (for comparison) were sampled for the apatite study, including El Laco and Incahuasi in the Cenozoic Central Volcanic Zone, the most modern analogues of these systems. These MtAp deposits are generally hosted in andesite and contain massive magnetite + apatite +/- actinolite and are pervasively altered by alkali-calcic +/- sodic +/- steam alteration. The main objective of the present study are: 1) to use the geochemical data of the apatites from the unaltered host rock (where possible), altered host rock, and ore, from Cenozoic and Cretaceous MtAp, paired with Sm-Nd isotopes to understand: a) crustal contamination; b) fluid composition; and c) mobilization of cations and REEs in the transporting fluids, leading to a broad interpretation of MtAp deposit formation and comparison of these deposits through time; 2) U-Pb geochronology on the El Laco host rock zircon crystals will constrain the age of the MtAp deposit, while Lu-Hf isotopes and trace elements will provide insight into source and oxidation state of host (Ballard et al., 2002; Banik et al., 2017). Additionally, one IOCG deposit (Tropezon) was sampled for the zircon study. Within the Cerro del Pingo plutonic complex, Tropezon is hosted in andesitic rock showing, fault controlled, chlorite-sericite-epidote-calcic alteration. Cu-Mo-Au mineralization is associated with pervasive Ca-Fe-K alteration of a host quartz diorite (Tornos et al., 2010). U-Pb geochronology of zircon from both the host quartz diorite and the Cu-Mo-Au mineralized ore will better constrain ore mineralization, while Hf isotopes and trace elements analysis will be used to see a difference between the ore and host within the deposit. Zircon analysis of El Laco and Tropezon will allow for a direct comparison between MtAp and IOCG deposits.

**3. Analytical Methods** Epoxy mounts of apatite and zircon separates were examined with cathodoluminescence to reveal internal structures

and zoning before both EPMA, LA-ICPMS, and LA-MC-ICPMS analysis at Memorial University. Heavy minerals were separated using standard techniques, including heavy liquid separation and a Frantz magnetic separator. Major and minor element compositions of apatite crystals were measured using a JEOL JXA-8230 SuperProbe electron probe microanalyzer (EPMA), trace elements were measured using a Finnigan Element XR high-resolution, double-focusing magnet sector-inductively coupled-plasma mass spectrometer (HR-ICP-MS), coupled to a GeoLas 193 nm Excimer laser system, and Sm-Nd isotope compositions were obtained by a ThermoFinnigan Neptune MC-ICPMS, coupled to the same laser. Zircon mounts were dated and analyzed for trace elements by LA-ICPMS and Hf isotope ratios were measured using LA-MC-ICPMS at the same facility. Due to the young age and high U-Pb ratios in the Cenozoic zircon samples, a Cameca ims1280 large-format, high mass resolution ion microprobe at the Swedish Museum of Natural History (NordSIM Facility) was used for U-Pb geochronology.

4. Results and Discussion Preliminary results indicate ore apatites containing up to 0.3-3 wt% REE, are evidence of one to four growth/ fluid alteration events, which varies depending on the deposit, and an enrichment in REE and S in Clrich zones leading to the interpretation that Clrich fluids can mobilize and carry REE and S (Fig. 1). Ores are enriched in both LREE and HREE when compared to their host rock and there are consistently geochemical differences between the Cenozoic- deposits and the Cretaceous-aged deposits.  $\varepsilon_{Nd}$  values for El Laco and Incahuasi are -4 to -5, and -2 to -3 respectively, while  $\varepsilon_{Nd}$  values for Los Colorados and Carmen di Fierro are +3 to +5 and +3 to +6 respectively, indicating a greater degree of crustal contamination in the Cenozoicaged MtAp deposits and a greater mantle contribution in the Cretaceous deposits. Apatite discrimination plots from the literature, most notably those by Belousova et al. (2002) do not constrain the ore apatites from this study to strictly the "iron ores" fields. In addition, the Mn-V-Mg ternary discriminant plot from Mao et al. (2016) used to distinguish IOCG and Kiruna-type (aka MtAp) deposits displays a lack of conformity to the Kiruna-type field. U-Pb zircon geochronology by SIMS from the El Laco host rock gave an age of  $\sim 2$  Ma, constraining the age of the deposit to 2 Ma or younger.



Figure 1. CL image of grain 33 from sample INC-15-01 (Incahuasi ore) and X-ray maps of the same grain for elements Cl, F, Fe, Nd, La, and S. Blue areas indicate areas of relative low concentrations and warmer colours (red, pink) indicate areas of relative high concentrations. Green and blue circles indicate where analysed by LA-ICPMS. The darker grey zone is enriched in Cl, Nd, La, and S as displayed by the X-ray maps and enriched in all LREE and MREE, concentrations of HREE are similar, as displayed by the REE diagram normalized to chrondrite values of Anders and Grevesse (1989). The  $\sum$ REE concentration between the two zones differs by ~1 wt% (2.81(dark zone) vs. 1.82 (light zone)  $\sum$ REE wt%.

**5. Conclusions** Preliminary apatite results suggest that a complex fluid alteration history plays a significant role to the formation of REE-enriched MtAp deposits and that sulphur is present but is not able to form sulphides.  $\varepsilon$ Nd values suggest that magma source environments have evolved through time from a mantle source to a continental crust source. Future work will include zircon geochronology, trace element analysis, and Hf isotopes. The zircon data along with additional apatite geochemistry and Sm-Nd isotope concentrations will aid in the discussion and the implications for a genetic model for MtAp

formation and comparisons with other deposits within the IOCG clan.

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