Apatite as a tracer for magmatic-hydrothermal ore-forming processes

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Summary This project focuses on the trace element chemistry of igneous apatite in various magmatic systems with the use of *in situ* analytical techniques. The composition of apatite may possibly be used as a tracer for various magmatic-hydrothermal processes due to the breadth of chemical substitutions possible within the structure. Apatite is found in many mineralized layered intrusions as a minor phase. Apatite may be utilized in the tracking of metasomatic fluids in layered intrusions or in geochronological studies in the absence of other commonly used phases i.e. zircon. Apatite accumulations can be exploited economically for phosphorus and possibly for rare earth elements as well.

1. Introduction and background to current research

This contribution outlines a PhD project that investigates the trace element chemistry of igneous apatite. The project comprises three subprojects, each of which concentrates on a different type of magmatic system: 1) carbonatites, 2) massif-type anorthosites and layered intrusions, and 3) rapakivi granites. The aim of the study is to gain new insight into the substitution mechanisms of trace elements in these chemically different magmatic environments and to compile a chemical database of apatite compositions. The main analytical methods utilized are electron microprobe (EPMA) and laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) aided with cathodoluminescence (CL) and scanning electron microscopy (SEM) imaging techniques. These *in situ* methods allow the quantification of compositional differences (e.g. growth zonation, alteration) between and within individual grains of apatite in a single sample. The current stage of the project concentrates on the carbonatite subproject, in which the apatite compositions of the Archean Siilinjärvi glimmerite-carbonatite rocks are being studied. The sub-project on layered intrusions and massif-type anorthosites is planned to be launched during 2021.

2. Research questions at hand

The apparent compositional variability and geological ubiquity makes apatite a potential versatile tracer of numerous geochemical processes. Calcium-phosphate apatite minerals $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH},\text{Cl})_2]$ are the most common phosphate minerals in the Earth's crust and present as accessory or trace phases in most magmatic, metamorphic, and sedimentary rocks (e.g. Piccoli and Candela 2002, Hughes and Rakovan 2015). Magmatic apatite is typically fluorapatite in composition, with a varying hydroxyl component (Piccoli and Candela 2002). Chlorapatite is found in some mafic-ultramafic intrusions (e.g. Boudreau et al. 1986, discussed below) and in metasomatically altered rocks (Kusebauch et al. 2015). Bromine, I, S, C, and structural water can also be incorporated into the apatite structure to some extent. Sulphur is compatible in the apatite structure in many oxidation states ranging from reduced (S^{2-}) to oxidized (S^{4+}) (Konecke et al. 2017). The $\text{S}^{6+}/\Sigma\text{S}$ ratio can be used as an oxybarometer (Konecke et al. 2019).

The apatite structure can incorporate a range of elements to cation and anion sites, often with coupled substitutions to balance charges (Pan and Fleet 2002). Trace elements, such as

rare earth elements (REE) are strongly partitioned into apatite, with a preference of middle REE over heavy REE (e.g. Hughes et al. 1991, Pan and Fleet 2002). This enrichment in REE may lead to apatite accumulations being a potential source for REE (Emsbo et al. 2015). Economic apatite accumulations are typically exploited as raw material for phosphate fertilizers, with phosphorites (chemical sediments, Filippeli 2008) being the most voluminous rock type. Magmatic deposits are also exploited e.g. the Siilinjärvi glimmerite-carbonatite complex (O'Brien et al. 2015), which may be potentially be utilized for REE as well (Decrée et al. 2020). Besides alkali rock types and carbonatites, iron-oxide-apatite cumulates (Kiruna-type, nelsonites or oxide-apatite-gabbro-norites) are also exploited.

3. Future prospects

3.1. Chlorapatite in layered intrusions

Chlorine-bearing apatite is present in or near platinum group element (PGE) mineralized strata in many layered mafic-ultramafic intrusions, (e.g. Bushveld; JM and Merensky Reef; Boudreau, 1993; Great Dyke; Boudreau et al., 1986; Munni Munni; Boudreau et al., 1993; Stillwater; Boudreau and McCallum, 1989; Penikat; Halkoaho, 1994; Näränkäväära, Järvinen et al., 2020; Duluth Complex; Bathtub Intrusion; Raič et al., 2018; Norilsk; Serova and Spiridonov, 2018). The role of chlorine-bearing fluids in the metallogenesis of PGE reefs is controversial (cf. Godel 2015 and references therein). There are proponents of both orthomagmatic (Campbell et al. 1983) and magmatic-hydrothermal genetic models (Boudreau et al. 1986). Apatite compositions, textures, and inclusions (monazite, xenotime) can provide evidence of metasomatic events and the type of metasomatic fluid(s) involved in them (Harlov et al. 2002, Harlov and Förster 2003).

3.2. Apatite geochronology

Apatite can also be used in geochronological studies as uranium and thorium can be incorporated into the structure (Chew et al. 2011). Another suitable method for dating of mafic-ultramafic intrusions is the ^{176}Lu - ^{176}Hf isotope system (Chew and Spikings 2015, Scoates and Wall 2015). Apatite is a suitable mineral for this as well because Lu is readily incorporated ($K_d \gg 1$) into the apatite structure whereas Hf is not ($K_d < 1$).

3.3 Fennoscandian Fe-Ti(-V)-P mafic-ultramafic intrusions

In Finland, there are Paleoproterozoic (~1.88 Ga) Fe-Ti(-V)-P enriched mafic intrusions. These intrusions are typically composed of more fractionated mafic rocks than the Ni-Cu mineralized mafic-ultramafic Vammala and Kotalahti type intrusions of similar age (e.g. Makkonen 2017). These Fe-Ti(-V)-P intrusions are located within but near the periphery of the Central Finland Granitoid Complex, situated into two major areas with several small, gabbroic intrusions – Kauhajärvi (Kärkkäinen and Appleqvist 1999) and Koivusaarenneva (Kärkkäinen and Bornhorst 2003). The Kauhajärvi intrusion hosts Fe-Ti oxide (magnetite, ilmenite) and apatite rich layers which vary in thickness from 2 to 30 meters. The Koivusaarenneva gabbro has ilmenite and vanadiniferous magnetite layers (Kärkkäinen and Bornhorst 2003). The composition of apatite in these localities has not been investigated in detail. The trace element and halogen concentrations could possibly provide additional information about the conditions in which the mineralizations formed.

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