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Apatite in the Olympic Dam Fe-Oxide Cu-U-Au-Ag Deposit

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Abstract. Apatite from igneous rocks hosting the World-class Olympic Dam iron-oxide-copper-gold deposit, South Australia is characterized with respect to morphology, chemistry, mineral assemblage and grain-scale compositional zoning. In granites, apatite displays a characteristic core-to rim zonation due to REE content. Fields of dusty monazite as 'emulsion'-like cores or symplectite intergrowths with host apatite are recognized. Compositional data, and their correlation with textures, show a complexity but nevertheless, potential for characterizing the igneous-to-hydrothermal evolution at Olympic Dam. Knowledge of the evolution and geochemistry of apatite at Olympic Dam may offer insights into deposit formation and, potentially, be a tool to discriminate Cu-Au mineralized and barren Fe-oxide dominated hydrothermal systems.

Keywords. Olympic Dam, apatite, mineral chemistry

1 Introduction

The value of apatite in geological studies has long been known. Apatite can also contain high levels of rare earth elements (REE) and in many rocks it is their main host. Apatite can contain a large number of other elements, the incorporation of which is controlled by physiochemical parameters during crystallization. Due to the nature of hydrothermal systems where the precipitation of metals is often instigated by changes in parameters such as temperature, pressure and chemistry, the ability of apatite to record such changes, and its relatively resistant character to destruction by hydrothermal fluids gives it the potential to offer great insights into the formation history of ore deposits.

The Olympic Dam Cu-Au-U-Ag deposit (9840 Mt @ 0.78% Cu, 0.25kg/t U₃O₈, 0.3g/t Au, 2g/t Ag (BHP Billiton 2014) is the largest deposit in the Olympic Cu-Au province, South Australia, the World's premier Iron-Oxide-Copper-Gold (IOCG) province. At Olympic Dam, apatite is abundant throughout all igneous lithologies; lesser amounts are present in the hematite breccias hosting sulfide ore. Collectively, this apatite represents numerous generations that span the evolutionary history of the deposit, and thus offer insights into how the deposit formed.

Variation in apatite chemistry, particularly REE-fractionation trends, in the Hillside deposit, South Australia (Ismail et al. 2014) allowed a reconstruction of deposit evolution from magmatic to early hydrothermal to

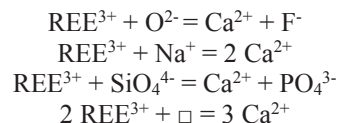
late-stage hydrothermal events. Similarly, in the Moonta-Wallaroo region, northwest of Hillside, Kontonikas-Charos et al. (2014) showed that the complex textures displayed by apatite backed up the interpreted changes in fluid characteristics during albitization and subsequent potassic alteration.

2 Background

2.1 Apatite chemistry

Minerals of the apatite supergroup (Pasero et al. 2010) have the general formula A₅(XO₄)₃Z, where the A site accommodates elements such as Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Cd²⁺, Na²⁺, Eu²⁺ and REE³⁺. The X site is occupied by P⁵⁺ as (PO₄)³⁺ but other small highly-charged cations (SiO₄⁴⁺, SO₄²⁻, AsO₄³⁻, VO₄³⁻ etc.) can occupy this structural position. Halogens, F⁻ and Cl⁻, occupy the Z site along with OH⁻.

REE substitution for Ca in apatite is controlled predominantly by the proximity principle whereby the REE with atomic radii most similar to that of the Ca position are most easily substituted. As a result most natural apatite REE contents peak in the area of Sm-Nd. Given the REE valence state of REE³⁺ with the exception of Eu²⁺ and Ce⁴⁺, coupled compensation mechanisms are necessary to maintain charge balance (Pan and Fleet 2002):



The atomic radius of Eu³⁺ is almost identical to that of Ca²⁺ and as such, apatite has a preference for Eu³⁺ over Eu²⁺. The Eu²⁺/Eu³⁺ ratio in melts is dependent on *f*O₂, bulk rock composition, temperature and, possibly, pressure. These parameters, particularly *f*O₂ exert a control on the substitution of Eu in magmatic apatite.

Several published studies have successfully used variations in apatite geochemistry to correlate certain intrusive rocks with particular styles of mineralization in large-scale mineralized belts (e.g. Cao et al. 2011). Other studies on the deposit scale (e.g. Harlov et al. 2002, Bonyadi et al. 2011) have successfully tracked changes in hydrothermal fluid chemistry by the evolution of apatite chemistry.

2.2 The Olympic Dam deposit

Olympic Dam is located in the north of the Olympic Cu-Au province, an elongate mineralized region on the eastern edge of the late Archean to Mesoproterozoic Gawler Craton. The deposit (Fig. 1) is hosted exclusively within the Olympic Dam Breccia Complex (ODBC) (Reeve et al. 1990), a term used to describe the mineralized breccias, felsic and mafic-ultramafic volcanic units and bedded clastic facies. In turn the ODBC is hosted within the Roxby Downs Granite (RDG), a member of the ~1590 Ma Hiltaba Suite (Creaser and White 1991). The RDG is an undeformed, medium- to coarse-grained granite consisting of alkali feldspar, quartz, sodic plagioclase, and minor biotite and amphibole with trace magnetite, titanite, fluorapatite, zircon and fluorite (Ehrig et al. 2012). Other granites, such as the Horn Ridge Granite (HG), dated at 1594.4 ± 3.4 Ma (Jagodzinski 2005), are also present. Mafic-ultramafic rocks occur as dikes, with ages spanning from ~1590 Ma (picrites) to ~800 Ma (Gairdner dolerite dykes) (e.g. Huang et al 2015). The RDG has experienced pervasive, texturally destructive hematite-sericite alteration and brecciation. Alteration and brecciation intensifies towards the deposit center with the granite-breccia contacts being largely gradational. The majority of the resource is hosted in hematite- or granite-rich breccias.

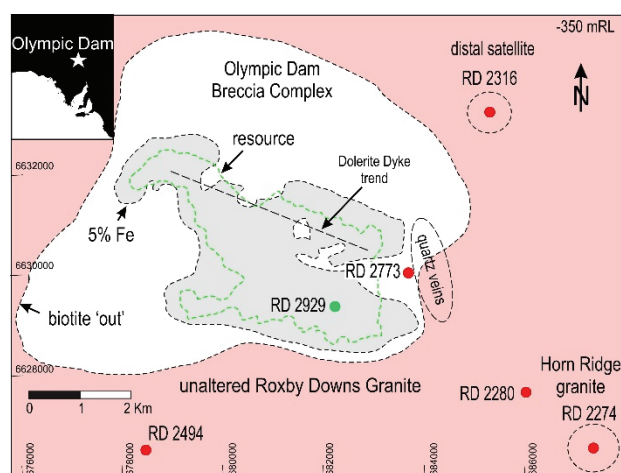


Figure 1. Sketch map of Olympic Dam, modified from Ehrig et al. (2012), showing the location of drillholes (circles in red for apatite in granite, and green for apatite in picrite). The trend of one of the ca. 800 Ma Gairdner dyke swarms is also shown.

Analyzed samples are from 5 drillholes intersecting granites outside, or at the immediate edge of the deposit, and from one of the highly altered picrites (Fig. 1). Granites intersected a few km outside the deposit outline are considered 'fresh' (biotite preserved), but are typically heterogeneous, altered on the m- to dm-scale, or include cm- to dm-sized mafic enclaves (e.g. RD2280; Fig. 2). Alteration correlates with hematite and sericite replacement of feldspars during albitization.

Distal and proximal satellites, i.e. weak chalcopyrite mineralization, associated with hematite $\pm$ magnetite alteration of variable intensity, are hosted in granites that were also sampled. In the distal satellite, intersected by drillhole RD2316, abundant, coarse molybdenite occurs at upper levels, whereas in the proximal satellite (drillhole

RD2773), mineralization increases at a depth of ~2000 m, and has a distinct base metal (sphalerite $\pm$ galena) signature.

Polished blocks and thin sections were analyzed by optical microscopy, scanning electron microscopy in back-scattered electron (BSE) mode and by electron microprobe (EPMA). The aim of the present, preliminary study is to texturally and geochemically characterize apatite from altered and unaltered intrusive rocks in an effort to identify whether apatite may be an effective pathfinder for magmatic and hydrothermal processes in the IOCG environment.

4 Results

4.1 Apatite textures and petrographic context

Apatite from igneous rocks occurs as grains with morphologies ranging from equant (in granites) to elongate or bladed (in mafic enclaves in RDG and picrite), and of variable sizes (up to several hundred μ m). Apatite is characterized by chemical heterogeneity with variable complexity (e.g. Fig. 3). In the granites, apatite displays characteristic core-to rim zonation which is mostly due to REE content (REE-poor and REE-richer as darker cores and brighter rims on the BSE images; Fig. 3a). In both enclaves and host RDG, apatite (e.g. in drillhole RD2280) shows fields of dusty monazite as 'emulsion'-like cores or symplectite intergrowths with host apatite (Fig. 3a, b, respectively).

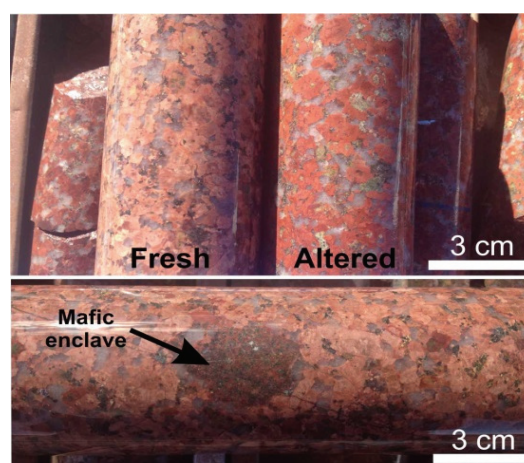


Figure 2. Drillcore photographs showing characteristics of RDG (drillhole RD2280).

Quartz cores are conspicuously seen in apatite from the mafic enclaves (Fig. 3c). Reworking of initial core-rim zonation patterns, mainly corresponding to REE-depletion, is seen as a darkening of apatite on the BSE images in and along fractures where sericite + hematite alteration occurs (Fig. 3d), as well as irregular inliers from margins towards the cores in equant grains (Fig. 3a).

Incipient development of porosity, microfracturing and coarsening of monazite from the areas of dusty inclusions are also observed. Advanced fracture- and pore-controlled replacement of apatite is seen in samples where sericite + hematite alteration is more prominent (Fig. 3e). In such cases, nucleation of coarser florencite is conspicuous.

Apatite from mineralized granites differs markedly in terms of appearance since it does not occur as single grains but rather as aggregates interstitial to other minerals, e.g. between pseudomorphically martitized magnetite (Fig. 3f). However, as in the case of apatite from the igneous rocks without any mineralization, it also shows strong chemical heterogeneity - corroded darker (early) cores and brighter (late) margins are evident on BSE images (Fig. 3f). Porosity, fracturing, and replacement of apatite are also associated with nucleation of discrete inclusions of REE-minerals.

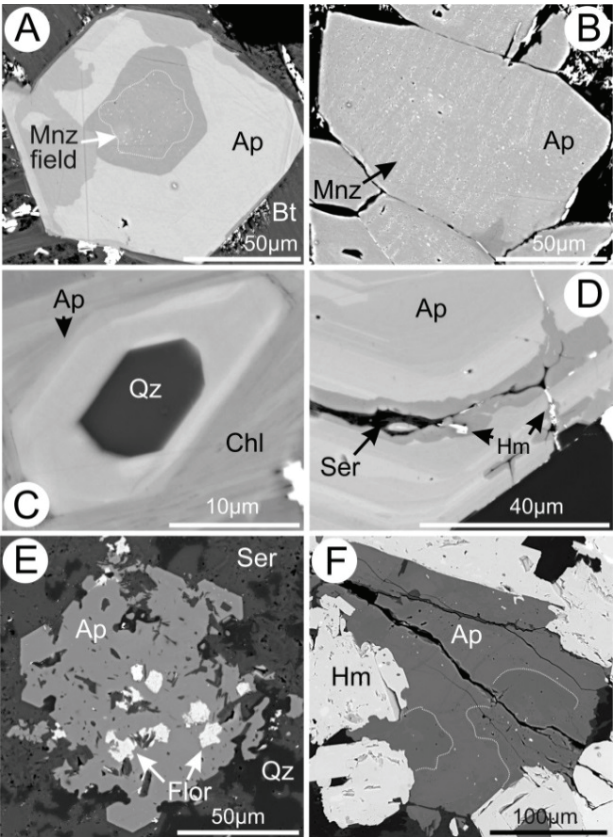


Figure 3. BSE images showing textures of apatite from RDG granite (a, d, e) and enclaves (b, c), and in mineralized granite (f) in sample from ~2,000m, drillhole RD2773. Abbreviations: Ab-albite; Ap-apatite; Bt-biotite; Chl-chlorite; Flor-fluorite; Hm-hematite; Mnz-monazite; Qz-quartz; Ser-sericite.

4.2 Compositional patterns

EPMA data was collected on grains with various textural complexities as described above. Results show that, for zones of apatite that display no textural evidence of overprinting (termed ‘unaltered’ on Fig. 4a), there is a strong correlation between the type of igneous rock and halogen content. Both are fluorapatite but whereas those in the RDG are end-member fluorapatite, apatite in the picrite is characterized by marked Cl-enrichment.

Apatite from the HG contains both F and Cl, and plots half way along the line between Cl- and F-rich groups on Fig. 4a. Both types of Cl-bearing fluorapatite show a decrease in Cl-content in areas where there is evidence of alteration (porosity, fractures, inclusions, etc). Calculated formulae show full occupancy of the Z site by (F+Cl), implying negligible OH component. Analyzed apatites display varying REE contents, up to > 5 wt% REE₂O₃

(Fig. 4b) concordant with zoning (Fig. 3a). REE content correlates with (Na₂O+SiO₂), indicating coupled substitution(s) to maintain charge balance.

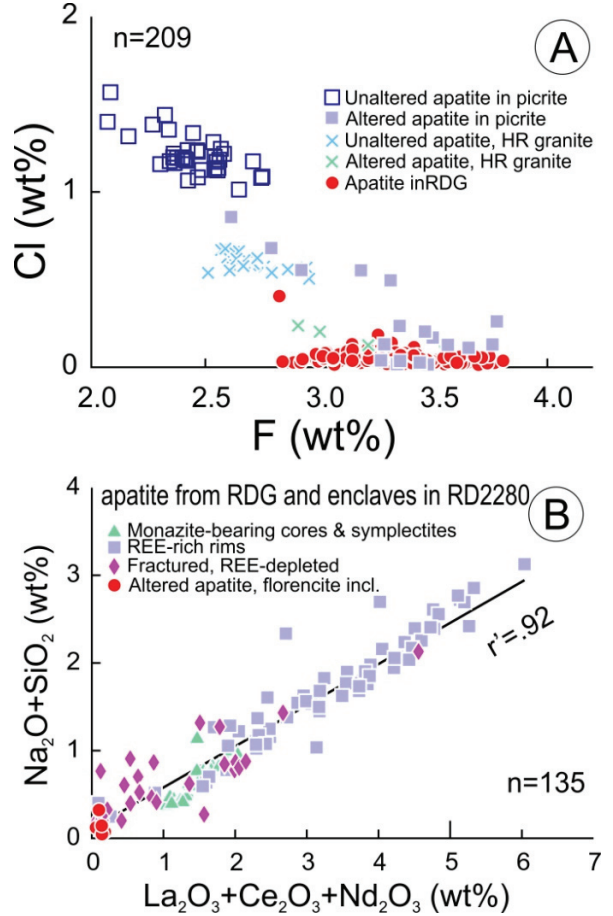


Figure 4. A. Plot of Cl (wt.%) vs. F (wt.%), and B. Na₂O+SiO₂ (wt.%) vs. La₂O₃+Ce₂O₃+Nd₂O₃ (wt.%) for apatite from igneous rocks. r²-Spearman rank correlation coefficient.

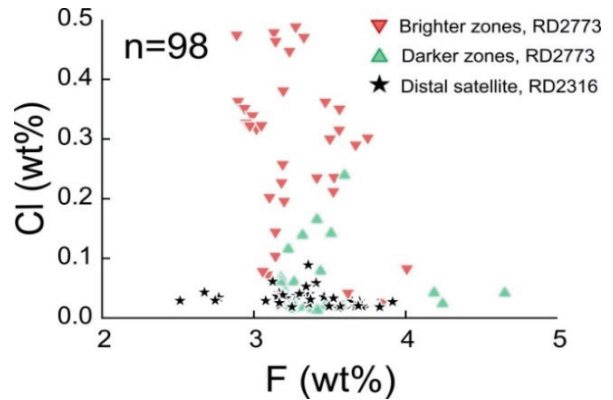


Figure 5. Plot of Cl (wt.%) vs. F (wt.%) for apatite from granites containing sulfide mineralization.

A plot of Cl vs. F in apatite from the drillcores intersecting satellite mineralization (Fig. 5) also shows that deeper mineralization in drillhole RD2773 is also characterized by modest enrichment in Cl in parts of the grains that do not show evidence of alteration. The same analyses (and also those from RD2316) also show the presence of both sulfur and silica (Fig. 6), even if REE are only present at concentrations around the detection limit as measured by EPMA.

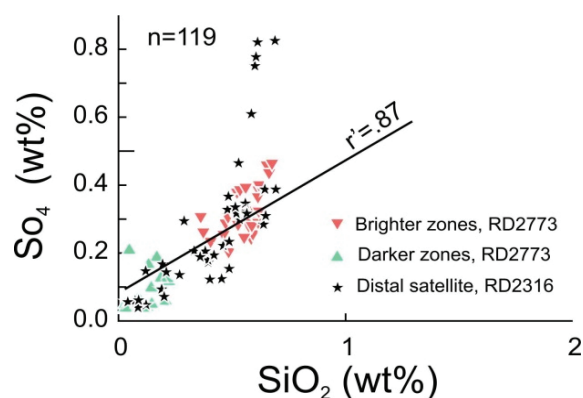


Fig. 6. Plot of SO_4 (wt.%) vs. SiO_2 (wt.%) for apatite from granites containing sulfide mineralization.

5 Discussion and concluding remarks

The presence of numerous small monazite inclusions in apatite has been observed in magmatic, metamorphic and hydrothermal systems, including the Kiirunavaara magnetite-apatite ore, northern Sweden (Harlov et al. 2002). The range of apatite-monazite relationships shown here, i.e. from emulsion-like and symplectites to pore-attached and coarsening of monazite, are of particular interest as such features have not been seen elsewhere in the Olympic IOCG Province.

The emulsion-like and symplectite intergrowths are indicative of exsolution from a higher-temperature, homogenous phase. However, no such field of immiscibility is known between the two phosphates. Experiments (Wolf and London 1995) show that monazite formation could be due to partial incongruent dissolution of early-formed apatite grains in peraluminous granitic melts. Such apatite-monazite relationships thus indicate that pristine, magmatic apatite is preserved in our samples. Porosity development, fracturing and inclusion coarsening are features that can all be attributed to progressive hydrothermal alteration leading to depletion of the overall REE concentration in apatite, as seen in the present samples. Hydrothermal experiments (e.g. Harlov et al. 2005) show that growth of monazite inclusions can be induced by reaction with KCl-rich fluids, removing Si+Na from apatite, thus destabilizing the coupled substitution, releasing REE and forming monazite. This argument could apply here but as a hydrothermal overprint on primary igneous apatite.

The difference in grain habit of apatite in the RDG and the mafic enclaves hosted within it can be explained by variable rates of cooling. Wyllie et al. (1962) found that at a near equilibrium cooling rate, small equant apatite grains are formed whereas conditions of significant undercooling lead to skeletal acicular grains often with central cavities. In the case of the RDG enclaves, these central cavities appear to have been subsequently filled with quartz. Other studies (e.g. Holden et al. 1987) used observations of acicular grains in and around mafic enclaves to imply rapid cooling of the mafic component upon emplacement into a felsic magma.

The compositional data, and their correlation with textures, show a complexity but nevertheless, potential for characterizing the igneous-to-hydrothermal evolution at Olympic Dam. The Cl component of magmatic apatite from granite and picrite differs. Taken together with S, the

Cl component of apatite also appears to be a tracer for the magmatic-to-hydrothermal evolution of the deposit and may also assist understanding subsequent reworking of primary mineral generations.

Further work will focus on determining the REY (REE+Y) fractionation trends of different textural categories of apatite in and surrounding the Olympic Dam deposit, including apatite within sulfide-hosting hematite breccias of the deposit itself. We will also compare and contrast the textural and chemical signature of apatite with that in other IOCG systems in the Gawler Craton, including those with both comparable and distinct alteration features, as well as worldwide.

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