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Destabilisation of titanite in the Roxby Downs Granite surrounding the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit

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Abstract. Titanite textures and geochemistry have been investigated from the Roxby Downs Granite, host to the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, South Australia. Three textural subtypes of titanite are documented: primary magmatic (cores and rims); late/interstitial; and secondary (low T recrystallisation). Magmatic cores are defined by enrichment in LREE (~3 wt%), Nb (up to 1 wt%) and Zr relative to rims, which typically contain <1 wt% LREE and Nb, as well as greater concentrations of Al, Ca, Fe and F. Secondary titanite forms as a low temperature hydrothermal overprint on primary titanite, as well as an alteration product of chloritised phlogopite. Titanite breakdown is a ubiquitous feature of the RDG, and occurs through interaction with CO_2 - and F-rich fluids, forming REE-fluorocarbonates, which are subsequently overprinted by REE-phosphates with increased proximity to the Olympic Dam Breccia Complex. This change is related to interaction with fluids containing appreciable free PO_4^{2-} , liberated from local fluorapatite dissolution, and represents later/retrograde stages in the formation of the Olympic Dam deposit.

1 Introduction

Titanite is a common accessory mineral in intermediate-silicic igneous rocks and numerous studies have shown its potential to reflect bulk compositions of source rocks and track the physicochemical conditions of evolving magmatic-hydrothermal systems (Wones 1989; Nakada 1991; Piccoli et al. 2000; Frost et al. 2001; Mcleod et al. 2011). The applicability of titanite as a geochemical indicator mineral in magmatic-hydrothermal ore deposits and igneous-metamorphic terranes has also been documented (Buick et al. 2007; Storey et al. 2007; Smith et al. 2009; Ismail et al. 2014; Storey and Smith 2017). Here we report textures and geochemistry of titanite from the ~1595 Ma Roxby Downs Granite, host to the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, South Australia, in an attempt to further constrain hydrothermal stages preserved in the host rock and thus gain a greater understanding of fluid evolution and deposit genesis.

2 Geological background

The ~1595 Ma Roxby Downs Granite (RDG) hosts the world-class Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, which is located in the north of the Olympic Cu-Au Province on the eastern margin of the Gawler Craton. Rocks of the Hutchison Group (~2000-1860 Ma), Donington Suite (~1845-1810 Ma) and Wallaroo Group equivalents (~1750 Ma) form the Paleoproterozoic basement of the Olympic Dam region (Creaser 1989; Ferris et al. 2002; Jagodzinski 2005). These units are unconformably overlain and intruded by felsic and mafic-ultramafic lithologies of the Hiltaba Suite (HS) and Gawler Range Volcanics (GRV).

Deposition of Cu-U-Au-Ag mineralisation at Olympic Dam is considered to be contemporaneous with regional magmatism at ~1590 Ma (e.g. Johnson and Cross 1995; Jagodzinski 2005; Ciobanu et al. 2013; Courtney-Davies et al. 2016, 2019). Hydrothermal breccias of the Olympic Dam Breccia Complex (ODBC) host the Cu-U-Au-Ag mineralisation and are contained within the RDG. Compositions and textures within the ODBC are gradational, and comprise a continuum from sericite-hematite-altered granite through mineralised, hematite-rich breccias to barren hematite-quartz breccias in the deposit center (Ehrig et al. 2012).

The RDG is equigranular to porphyritic, medium-coarse grained and peraluminous to weakly metaluminous (Creaser 1989; Kontonikas-Charos et al. 2017). Dominant minerals are alkali feldspar (40-50%), plagioclase (20-25%), quartz (20-25%), with minor edenite and phlogopite (5-10%). Magmatic accessory minerals (~5%) include magnetite, titanite, ilmenite, fluorapatite, zircon and allanite. Other minor minerals include: fluorite, tourmaline, uranothorite, REE-fluorocarbonates (parisite, bastnäsite and the unnamed polytype B_2S) and sulphides (pyrite, chalcopyrite, galena, sphalerite and molybdenite) (Ehrig et al. 2012; Ciobanu et al. 2017; Kontonikas-Charos et al. 2017, 2018a, b).

3 Results

3.1 Petrography

For a comprehensive summary of primary magmatic titanite textures see Kontonikas-Charos et al. (*in review*). Secondary titanite appears green in plane-polarised light and is distinguished from primary titanite rims by its irregular zonation (Fig. 1a). It also occurs as an alteration product of phlogopite, forming fine-grained, cleavage-oriented lenticular inclusions enclosed within clinocllore (Fe# ~0.35-0.45), typically along rims and parallel to the basal plane (Fig. 1b).

Partial to complete breakdown of titanite is observed throughout the RDG. Initial dissolution occurs along the crystal face and produces a microporous phase at the reaction interface which propagates towards grain interiors (Fig. 1c). Further destabilisation of titanite produces coarser symplectites of a clinocllore (Fe# ~0.3) + calcite matrix intergrown with hetero-oriented Ti-oxide, Ce-dominant REE-fluorocarbonates (parisite and bastnäsite), and quartz. The predominance of chlorite over calcite in the alteration matrix decreases with sample depth. Most primary titanite shows evidence of such breakdown, and in many cases, large polyminerallc pseudomorphs are all that remain.

In granite samples affected by sericite-hematite alteration, titanite is no longer preserved. Rather, complete breakdown of titanite has produced euhedral pseudomorph grains of Ti-oxide and REE-phosphates (monazite, xenotime) + REE-fluorocarbonates within a dolomite and chamosite (Fe# ~0.65) matrix (Fig. 1d). With increased proximity to the ODBC and intensity in alteration, quartz + K-feldspar + sericite (Fe, Mg-rich) ± hematite predominate over chamosite and dolomite in the matrix, whereas REE-phosphates are the sole REE-minerals within the resultant pseudomorphs.

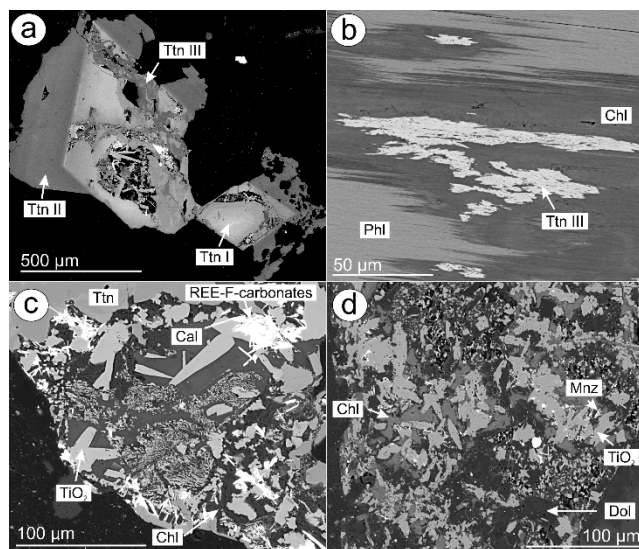


Figure 1. Back-scatter electron (BSE) images of titanite and its alteration products in the Roxby Downs Granite. Mineral abbreviations: Cal – calcite, Chl – chlorite, Dol – dolomite, Mnz – monazite, Phl – phlogopite, REE-F-carbonates – REE fluorocarbonates, TiO₂ – Ti oxide, Ttn – titanite.

3.2 Geochemistry

Electron microprobe analyses reveal intracrystalline variation in major and minor elements of titanite cores and rims, as well as between late/interstitial and secondary titanite. Brighter BSE cores are markedly enriched in LREE (~3 wt%), Nb (up to 1 wt%) and Zr relative to darker BSE rims. In contrast, rims typically contain <1 wt% LREE (La, Ce, Nd) and Nb, however they are richer in Al, Ca, Fe, F and calculated OH than cores. Binary plots in Figure 2 illustrate these characteristics and show strong correlations consistent with the coupled substitutions at the octahedral Ti site and 7-fold polyhedral Ca site: (Al, Fe)³⁺ ↔ Ti⁴⁺ + (OH, F); and Ca²⁺ + Ti⁴⁺ ↔ REE³⁺ + (Al, Fe)³⁺. Late and secondary titanite are also distinguished by major and minor element variation, defined by progressive increases in F, Al and Fe accompanied by depletion in LREE (La, Ce, Nd), Nb and Y (Fig. 2).

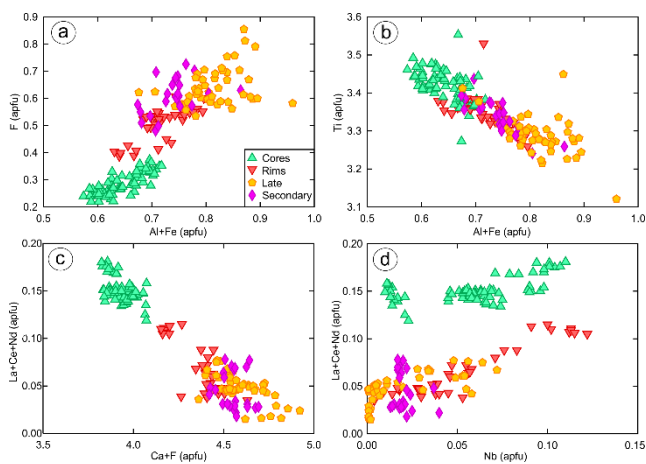


Figure 2. EPMA data binary plots of titanite textural subtypes in the Roxby Downs Granite. Data presented as atoms per formula unit based on 20(O,OH) for titanite. (a) (Al+Fe) vs F, (b) (Al+Fe) vs Ti, (c) (Ca+F) vs (La+Ce+Nd), (d) Nb vs (La+Ce+Nd).

Laser Ablation ICP-MS maps provide a visual insight into the spatial distribution of elements in titanite, either in the crystal lattice (solid solution) or as inclusions. Selected elemental maps are shown for primary, late and secondary titanite (Fig. 3). Zirconium (not shown), REE (Ce, Eu) and Y are strongly correlated and show high concentrations within primary titanite cores. All these elements are significantly depleted in recrystallised and late titanite. Minor dissolution of primary titanite has resulted in the redistribution of REE in irregular inclusions, identified as REE-fluorocarbonates within the REE-poor calcite ± clinocllore and Ti-oxide matrix. Interestingly, some zones within late titanite and recrystallised primary titanite show decoupling of Eu from other REE. Uranium and ²⁰⁶Pb (not shown) are negatively correlated with Th, and generally concentrate along rims and within late titanite. Recrystallised titanite is almost devoid of Nb and Ta (not shown), however they appear to preferentially partition into newly formed Ti-oxide. Tin and Sc (not shown) show a consistently low abundance within titanite cores, which steadily increases towards grain

rims. They also strongly correlate with areas of recrystallised titanite. Vanadium (not shown) has a preference for certain zones towards grain boundaries and, like Sc, is concentrated in recrystallised titanite.

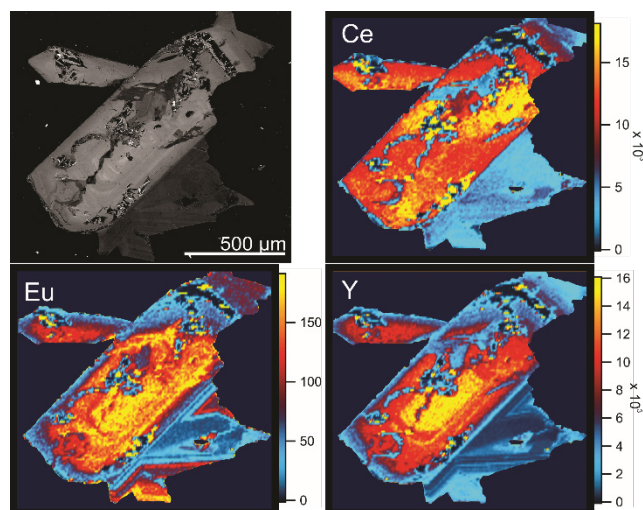


Figure 3. BSE image and selected LA-ICP-MS element maps for primary, late and secondary titanite. Scale bar is in ppm.

4 Discussion

Titanite breakdown is a ubiquitous feature of the RDG. Textural observations support initial fluid permeation along grain boundaries and microfractures at the titanite crystal interface. The microporous matrix represents the first stage in the dissolution process. As the reaction progresses, the chemical components of titanite mix with percolating fluids (likely introducing additional Fe, Al and Mg) and eventually precipitate as pseudomorphs comprising a fine-grained calcite + clinochlore matrix with coarser Ti-oxide + REE-fluorocarbonates (parisite and bastnäsite) + quartz. Although the overall precursor grain shape is retained (e.g. pseudomorphic), neither calcite nor clinochlore (the dominant matrix minerals) share any structural similarity with titanite. This explains the extremely fine crystalline nature of the initial matrix, which would be a consequence of complete breakdown of titanite structural bonds. Primary titanite rims are relatively unaffected by dissolution in comparison to cores, indicating hydrothermal fluids were in disequilibrium with the F-poor, REE-Ti-rich cores, and that F and REE contents may influence titanite stability under certain physicochemical conditions.

Fluids responsible were likely rich in CO_2 and F, based on the presence of fluorocarbonates and calcite as alteration products. Similar alteration assemblages in corroded titanite grains have been reported from numerous other granitic rocks (Pan et al. 1993; Morad et al. 2009; Middleton et al. 2013), with inferences for interaction with hydrothermal fluids characterised by high CO_2 and HF activity levels. This is also supported by experimental studies, which indicate that both CO_2 and F promote titanite destabilisation (Hunt and Kerrick 1977; Troitzsch and Ellis 2002).

Suitable element sources in the RDG include the

chloritisation of phlogopite (~3 wt% F) which likely produced FCO_3 -bearing fluids and released Fe, Al and/or Mg, which can account for the presence of chlorite in the resultant alteration assemblage. A similar source of F has been suggested in other altered granitic rocks (e.g. Förster 2000; Middleton et al. 2013). In addition to phlogopite, albitisation of adjacent and local plagioclase could also be a suitable source of Al for alteration pseudomorphs which contain chlorite.

The prevalence of REE-phosphates over REE-fluorocarbonates in pseudomorphs, observed in sericite-hematite-altered RDG, would require a change in physicochemical conditions that promotes the availability of free phosphate anions. In the case of the RDG, fluorapatite is the main carrier of PO_4^{2-} and would thus be the most likely source. Previous mineralogical and geochemical studies on these samples (Krneta et al. 2016, 2017) provide substantial evidence for multistage dissolution of fluorapatite and eventual replacement by quartz through interaction with highly acidic, CO_2 -rich fluids. The initial dissolution of fluorapatite would thus release PO_4^{2-} , as well as Ca^{2+} and F⁻, to the fluid, allowing for precipitation of monazite and xenotime. At this later stage, low temperature and high acidity (low pH) would likely buffer F⁻ in the fluids as HF (e.g. Migdisov et al. 2016). Florencite may also form on behalf of fluorapatite at this stage (Krneta et al. 2016, 2017). The observation of early REE-fluorocarbonate and later REE-phosphate crystallisation is consistent with REE-mineral speciation within the Olympic Dam Breccia Complex (Schmandt et al. 2017, 2019).

As a significant repository for REE (> 5 wt%) and the dominant REE host in the RDG (unpublished MLA data), the destabilisation of titanite and subsequent element recycling likely contributed to the overall anomalous REE concentrations reported at Olympic Dam. The work presented here further substantiates the utility of titanite and its alteration products to reflect physicochemical changes in intrusion-hosted magmatic-hydrothermal deposits.

5 Conclusions

Breakdown of titanite is selective and typically affects primary cores more than rims. The resultant alteration assemblage (clinochlore + calcite + Ti-oxide + REE-fluorocarbonates + quartz) is indicative of interaction with dominantly F- and CO_2 -bearing fluids, with additional elements likely scavenged from concomitant alteration of adjacent phlogopite and plagioclase.

With increased proximity to the ODBC, fluorapatite in sericite-hematite-altered RDG samples is favored as the source of PO_4^{2-} for crystallization of REE-phosphates in polymineralic pseudomorphs (after titanite). This is consistent with later/retrograde stages of deposit genesis.

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