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Microstructural, trace element and geochronological characterization of TiO_2 polymorphs and implications for mineral exploration

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ABSTRACT

The geochemistry of rutile (TiO_2) has recently found its use in mineral exploration with some studies reporting anomalous concentrations of Fe, W, V, Sn and Sb in rutile associated with mineralized ore systems. However, the use of rutile as a prospecting tool is likely to be complicated by the systematic changes in trace element composition with TiO_2 polymorph type (anatase, brookite and rutile).

Here we present TiO_2 trace element and U–Pb geochronological data from the mineralized and barren portions of the Palaeoproterozoic Moorarie Supersuite and (Capricorn Orogen, Western Australia), with a focus on the Minnie Creek Molybdenum Prospect in the northern part of the Gascoyne Province. The barren samples contain all three TiO_2 polymorphs (anatase, brookite and rutile). Textures suggest anatase and brookite may have formed during low-T metamorphism, either through replacement of previous rutile grains or titaniferous minerals. Rutile grains from barren samples yield variable U–Pb ages (ca. 3.0–2.2 Ga) as well as variable textures and chemical compositions suggesting detrital origins, thus most likely representing metasedimentary units intruded by the Moorarie Supersuite. Rutile grains from the Minnie Creek prospect yield Palaeoproterozoic (ca. 1.77–1.75 Ga) U–Pb cooling ages and Nb + Ta concentrations of up to 17 wt% that along with inclusions of manganocolumbite, oscillatory and patchy zonation of Nb and Fe, suggest a magmatic origin.

The commonly used pathfinder elements for gold and base-metal mineralisation (Fe, Cr, V, W, Sn and Sb) are shown to be systematically lower in anatase and brookite, thus yielding false negatives if polymorph type is not identified during reconnaissance studies. For this reason, a ternary diagram was constructed based on the systematic changes in chemistry of TiO_2 polymorphs to provide a relatively fast and easy chemical discrimination of polymorphs in large volumes of reconnaissance data. Furthermore, it is shown that high Al concentrations are characteristic of brookite and, to a lesser degree, anatase but not rutile. In addition, Sn, Nb, Ta and W concentrations in rutile may be more sensitive to igneous processes and may be used to track processes occurring in strongly fractionated granitic magmas such as pegmatites and associated deposits.

1. Introduction

Titanium dioxide (TiO_2) is a common accessory phase that occurs in many different rock types. In nature, it occurs as four main polymorph types, including the low temperature and low pressure polymorphs anatase (*$I4_1/amd$*) and brookite (*Pbca*), medium to high and ultra-high pressure and temperature polymorph rutile (*$P4_2/mnm$*), and the high-pressure polymorph TiO_2(II) (Fig. 1) (Dachille et al., 1968; Jamieson and Olinger, 1969). Of these, rutile is the most common polymorph in Earth's crust and is stable over range of metamorphic conditions (of up to and > 20 kbar and > 500 °C, Fig. 1, Dachille et al., 1968). Rutile is also commonly found as a detrital mineral in sedimentary rocks (Zack et al., 2002, 2004a) and as an accessory mineral in felsic igneous rocks, where it occurs either as a magmatic phase in highly fractionated felsic rocks, alkaline rare-metal granites and pegmatites or as inherited grains (Carruzzo et al., 2006; Force, 1980; Černý and Ercit, 1989; Černý et al., 1999, 2007). In contrast, anatase and brookite typically form as authigenic minerals or during low-T metamorphism (Fig. 1) (< 500 °C, Dachille et al., 1968; Morad, 1986; Triebold et al., 2011), with aqueous low-T conditions promoting anatase stability (Smith et al., 2009). The TiO_2(II) has a αPbO_2 type structure and is typically stable at very high pressures (> 20 kbar) and lower temperatures (Fig.1) (e.g. subduction

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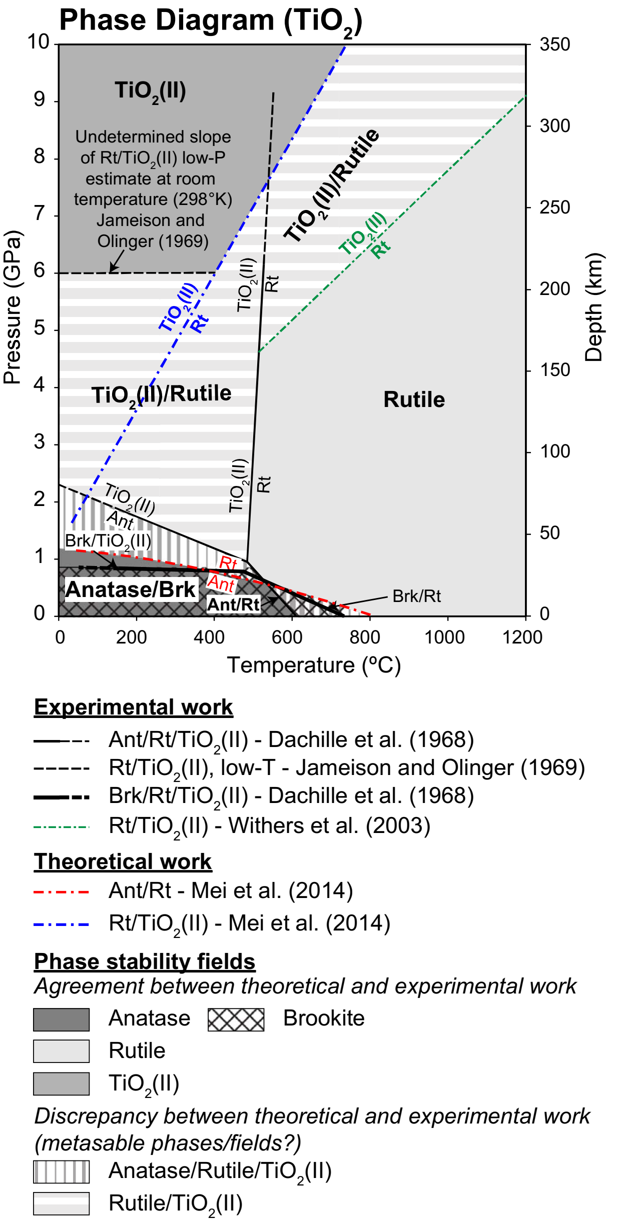

Fig. 1. TiO_2 phase diagram: compilation from literature; Dachille et al. (1968), Jamieson and Olinger (1969), Withers et al. (2003) and Mei et al. (2014).

zones and meteorite impact layers, Bromiley and Redfern, 2008; Bromiley et al., 2004; Smith et al., 2016; Wu et al., 2005) It is not a common mineral in typical crustal rocks that are the subject of this paper and will not be discussed further.

The ability of TiO_2 polymorphs to incorporate variable concentrations of U and Pb, HFSE (Zr, Hf, Nb, Ta) as well as transition and base metals (Al, V, Cr, Mn, Zn, Fe, Mo, W, Sb, Sn) makes them particularly useful for a variety of geological applications (Meinhold, 2010 and references therein). The variable concentrations of these elements in TiO_2 polymorphs are affected by the composition of the host rocks, type and composition of magmatic/metamorphic fluids (Cl- vs. F-bearing), pressure and temperature conditions and oxygen fugacity (Candela and Bouton, 1990; Liu et al., 2014; Luvizotto and Zack, 2009; Sobolev and Yefimova, 2000; Tanis et al., 2015; Vlassopoulos et al., 1993; Zack et al., 2002, 2004a).

Anomalous rutile compositions (enrichment in V, W, Sn and Sb) have been reported from various orogenic, porphyry gold and base-metal deposits (Agangi et al., under review; Clark and Williams-Jones, 2004; Rice et al., 1998; Scott and Radford, 2007; Scott et al., 2011; Urban et al., 1992; Williams and Cesbron, 1977). However, systematic changes in concentrations of certain elements (Nb, V, Cr, Zr, Sn and Fe) between anatase, brookite and rutile are apparent (Triebold et al., 2007, 2011) and there is a lack of understanding about the effect of systematic changes of certain pathfinder elements (elements enriched in rutile associated with Au and base-metal mineralisation, e.g. W, V, Sn, Sb and Fe) with polymorph type. Consequently, differences in trace element compatibility amongst different TiO_2 polymorphs have the potential to complicate the use of rutile as a pathfinder mineral if anatase and brookite are mistaken for rutile. Although optical properties such as colour, presence of twinning and birefringence can be used to discriminate between the polymorphs by optical microscopy techniques (Triebold et al., 2011), the presence of fine-grained aggregates and intergrowths (here used as a descriptive term only) of different polymorph types (Triebold et al., 2011) can obscure any distinctive optical properties. Therefore, rapid analytical techniques for polymorph discrimination in grain mounts/thin sections are much more useful.

In this contribution, we investigate the trace element geochemistry of the three TiO_2 polymorphs (anatase, brookite and rutile) that coexist in a suite of igneous rocks (Moorarie Supersuite) exposed in the Capricorn Orogen of Western Australia. We show that electron backscatter diffraction (EBSD) can be successfully used for TiO_2 polymorph discrimination and provide lattice orientation information to constrain TiO_2 microstructure. Trace element compositional data and U–Pb dating of TiO_2 polymorphs is carried out by Laser Ablation Split Stream (LASS) ICP-MS. Integration of these two techniques provides constraints on polymorph geochemistry that permits revision of the common discrimination diagrams used for large-scale reconnaissance studies of TiO_2 geochemistry.

2. Geological setting

The Palaeoproterozoic Capricorn Orogen formed during a two-stage collision between the Archaean Pilbara and Yilgarn Cratons in Western Australia (inset Fig. 2). In the first stage, an allochtonous Archaean Glenburgh terrane collided with the Pilbara Craton during the Ophthalmian Orogeny (ca. 2215–2145 Ma, Johnson et al., 2011, 2013; Müller et al., 2005; Rasmussen et al., 2005). Subsequently, a north-dipping subduction established beneath the combined Pilbara Craton/Glenburgh Terrane, produced a continental magmatic arc (the Dalgaringa Supersuite), which was subsequently deformed and metamorphosed during the collisional Glenburgh Orogeny (ca. 2005–1970 Ma, Johnson et al., 2011; Occhipinti et al., 2004). This collisional event resulted in the final amalgamation of the greater West Australian Craton.

Following amalgamation, punctuated intracontinental reworking affected the Capricorn Orogen at various times with accompanying sedimentation, deformation and metamorphism, and (in some cases) magmatism. The two earliest intracontinental tectonothermal events, the Capricorn (ca. 1820–1780 Ma, Sheppard et al., 2010b) and Mangaroon orogenies (ca. 1580–1620 Ma, Sheppard et al., 2005) were accompanied by significant granitic magmatism, while the younger tectonic events, the Mutherbukin Tectonic Event (ca. 1320–1170 Ma, Korhonen et al., 2015 and references therein), the Edmundian Orogeny (ca. 1030–950 Ma, Johnson et al., 2009), the recently proposed Kuparr Event ca. 960–830 Ma (Cutten and Zwingmann, under review; Oilerook et al., under review) and the Mulka Tectonic Event (ca. 570 Ma, Bodorkos and Wingate, 2007), recorded little to no magmatism. The Palaeoproterozoic to Mesoproterozoic periodic tectonothermal reworking is best preserved in the high-grade metamorphic Gascoyne Province (Fig. 2) in the western part of the Capricorn Orogen. The basement rocks further north and east are concealed under thick Mesoproterozoic basins. The Gascoyne Province is further subdivided into six tectonothermal domains (Fig. 2 and Table 1) based on the different temporal and deformational histories (Johnson, 2013; Sheppard et al., 2010b).