Chemical Geology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Rutile alteration and authigenic growth in metasandstones of the Moeda Formation, Minas Gerais, Brazil – A result of Transamazonian fluid–rock interaction

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ARTICLE INFO

Editor: K. Mezger

Keywords:
Moeda Formation
Rutile
Alteration
U–Pb dating
Microstructures
Trace elements
Fluid overprint
Transamazonian orogeny

ABSTRACT

Microstructures, trace elements and U–Pb ages of rutile grains are reported from two metasandstone samples of the Moeda Formation, which is the basal unit of the Minas Supergroup in the Quadrilátero Ferrífero, Minas Gerais, Brazil. The Moeda metasandstones, deposited between 2.68 and 2.65 Ga, are intercalated with Witwatersrand-like, pyritiferous and auriferous metaconglomerate layers. Rutile from both samples shows unusually high contents of Th (1–142 ppm) and rare-earth elements (ΣREE = 1–132 ppm), with chondrite-normalized middle REE humps, and reveals post-depositional U–Pb ages of ≤2.25 Ga; only three grains yielded significantly older ages of up to 2.72 Ga, pointing to a detrital origin. The combined data set suggests that rutile formation and alteration at 2.25 Ga was caused by distinct fluid-mediated processes, which erased nearly all provenance information. Detrital, rounded rutile grains in sample A were altered by a coupled dissolution–reprecipitation process (type 1), resulting in highly porous grains. These show variable contents of rutile-compatible and -incompatible trace elements: Th (1–48 ppm), Zr (25–796 ppm), U (12–167 ppm), Pb (9–52 ppm), Cr (900–12,878 ppm), W (143–3939 ppm), Nb (1148–6168 ppm), Sb (6–63 ppm), as well as variable ratios of Zr/Hf, Y/Ho and Th/U. Rutile grains in sample B are mostly authigenic (type 2), and formed after dissolution of pre-existing detrital rutile grains and subsequent transport and homogenization of trace elements. This interpretation is supported by the anhedral shape of some grains and the finding of numerous, randomly oriented muscovite laths. The authigenic population has significantly lower, and less variable contents of trace elements compared to type-1 rutile: Th (0.5–16 ppm), Zr (21–67 ppm), U (5.8–24 ppm), Pb (6-18 ppm), Cr (1379–3153 ppm), W (9.4–70 ppm), Nb (921–3058 ppm), Sb (3.3–10 ppm), and distinctively lower ratios of Zr/Hf (7.9) and Th/U (0.2), but variable Y/Ho ratios. Significant contents of Th and REE are explained by co-precipitation with TiO_2 aggregates prior to structural ripening. The close association of rutile with muscovite, the rutile $MREE_N$ humps and the results of Zr-in-rutile thermometry suggest that rutile formation and alteration in the investigated sandstones was mediated by K(Na)–Si–P-bearing aqueous fluids at temperatures of about 490 °C. The rutile $MREE_N$ humps are interpreted to result from the tetrad effect during leaching of spatially associated detrital zircon grains. Uranium–Pb ages of ≤2.25 Ga indicate that the fluid overprint started at the onset of the Transamazonian orogeny, perhaps related to the opening of the Sabará foreland basin.

1. Introduction

Over the past ten years, rutile has successfully been used as tracer mineral in a number of provenance studies (e.g., Zack et al., 2002, 2004a; Meinhold et al., 2008, 2011; Meinhold, 2010; Triebold, 2011; Triebold et al., 2007, 2012). This success relies on the capacity of rutile for incorporating trace elements, mostly high-field strength elements (HFSE), such as U, Zr, Hf, Nb, W, Ta, which can be used not only for U–Pb dating, but also for characterising source areas, from which rutile grains are derived (Zack et al., 2004a, 2004b). Furthermore, rutile is

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https://doi.org/10.1016/j.chemgeo.2018.03.007
Received 23 December 2017; Received in revised form 1 March 2018; Accepted 3 March 2018
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considered to be resistant during weathering, transport, and diagenesis. Consequently, the mineral is an ideal candidate for portraying the hinterland of unconsolidated sedimentary rocks, which remained widely unaffected by metamorphism (Zack et al., 2004a; Triebold et al., 2007, 2012; Meinhold et al., 2008). This situation, however, can be much different for metasedimentary rocks, where detrital rutile grains could potentially have been affected by several post-depositional processes during diagenesis and metamorphism, modifying or even erasing provenance information. Under medium- to high-grade metamorphic conditions, detrital rutile can severely be affected by volume diffusion (Sasaki et al., 1985; Cherniak, 2000; Cherniak et al., 2007; Marschall et al., 2013), causing a differential loss of certain elements. For example, at temperatures > 500 °C, rutile can quantitatively lose its radiogenic Pb (e.g., Cherniak, 2000), with partial or total reset of the U–Pb clock. The effect of Pb loss can also occur at lower temperatures by interaction of rutile with aqueous fluids (e.g., Ayers and Watson, 1993; Audétat and Keppler, 2005; Manning et al., 2008; Hayden and Manning, 2011).

Under relatively low-temperature conditions, minerals can be affected by two distinct processes. One is a coupled dissolution–reprecipitation process that leads to a pseudomorphic transformation of pre-exiting solid-solution minerals either partially or entirely. The pseudomorphic transformation involves significant compositional changes and age reset, which are well known from major mineral constituents (e.g., Putnis, 2002; Putnis and Putnis, 2007; Putnis and Austrheim, 2010), as well as from accessory minerals such as zircon (Geisler et al., 2007; Zeh et al., 2010a, 2010b), but it has not been investigated in detail for rutile.

The other process is the dissolution of detrital grains in aqueous fluids, followed by significant transport of major and trace elements, prior to the precipitation of new (authigenic) minerals elsewhere. The latter process is in good agreement with the finding of rutile in Alpine quartz veins (e.g., Shulaker et al., 2015), and in deep crustal eclogite-facies veins (Gao et al., 2007) and with other field-based observations and experiments carried out under medium- to high-grade metamorphic conditions. These experiments suggest high solubility and mobility of rutile in Cl- and F-rich fluids (Ayers and Watson, 1993; Barsukova et al., 1979; Gieré, 1990; van Baalen, 1993), and in aqueous solutions that interacted with albitic plagioclase (Stalder et al., 2000; Audétat and Keppler, 2005; Antignano and Manning, 2008). Such interactions can increase the rutile solubility by several orders of magnitude, in particular by complexing Ti (and perhaps the HFSE) to promote transport. “Hydrothermal” **dis**solution–trans**po**rt–**rep**recipitation (DISPOREP) processes are well known for the mineral zircon in metasedimentary rocks that were affected by low to amphibolite-facies temperatures between 250 and 650 °C (e.g., Dempster et al., 2004; Rasmussen, 2005; Hay and Dempster, 2009; Zeh et al., 2010a; Zeh and Gerdes, 2014). In addition, DISPOREP processes have also been suggested for rutile occurring in eclogite-facies metamorphic rocks (e.g., Philippot and Selverstone, 1991; John et al., 2008). On the other hand, little is known about alteration processes and the dissolution of rutile in siliciclastic metasedimentary rocks, in particular sandstones, which experienced low- to medium-grade metamorphic overprints.

To close this gap of knowledge, we present results of a detailed study of rutile grains from two metasandstone samples of the Neoarchaean Moeda Formation, Quadrilátero Ferrífero, Minas Gerais, Brazil (Fig. 1). The Moeda sediments were deposited between 2.68 and 2.65 Ga, and potentially affected by two major orogenic events, the ~2.1-Ga Transamazonian orogeny and the ~0.5–0.6-Ga Pan-African–Brasiliano orogeny (e.g., Cordani et al., 1980; Romano et al., 1991; Chauvet et al., 1994; Alkmim and Marshak, 1998; Cabral and Zeh, 2015a, 2015b). Based on rutile microstructures, U–Pb ages and trace-element data, including REE data, we provide new information about the processes that caused formation and transformation of the Moeda rutile grains.

1.1. Geology of the Moeda Formation and the Minas supergroup

The Minas Supergroup is divided into four groups: Caraça, Itabira, Piracicaba and Sabará (Fig. 2). The Moeda Formation (Wallace, 1958; Dorr, 1969), which is the main subject of this study, forms the basal part of the Caraça Group. It consists mainly of quartzite and metaconglomerate, including gravels that contain both detrital pyrite and epigenetic pyrite (Minter et al., 1990; Garayp et al., 1991; Koglin et al., 2010, 2012), which are similar to those in the Witwatersrand basin (e.g., Feather and Koen, 1975; Dimroth et al., 1979; Barton and Hallbauer, 1996; Frimmel, 1997; England et al., 2002). In the study area, layers of pyritiferous metaconglomerate, locally auriferous, occur either as channels on, or in tectonic contact with Archaean greenstones of the Rio das Velhas Supergroup. The Moeda Formation can be divided into three units informally named as Unit I, II and III, from bottom to top. Each unit comprises a basal metaconglomerate, which is overlain by quartzite and, in some cases, phyllite (e.g., Villaça, 1981). The Moeda Formation is interfingered with, and overlain by, pelitic rocks of the Batatal Formation. Both units form the Caraça Group. The fine-grained metasediments of the Batatal Formation are transitional to the overlying chemical sequence of the Itabira Group. This group has itabiritic rocks that grade upwards into dolomitic rocks. The former are the Cauê Itabirite of Dorr (1969), or the Itabira iron formation of Harder and Chamberlin (1915); the dolomitic rocks are assigned to the upper part of the Itabira Group as the Gandarela Formation. The Cauê Itabirite hosts world-class iron-ore deposits (e.g., Derby, 1910; Rosière et al., 2008), as well as palladiferous gold mineralization (Cabral et al., 2009, and references therein).

Based on detrital zircon dating, Koglin et al. (2014) suggested maximum deposition ages of ≤2.68–2.65 Ga for the Moeda Formation. These data are in agreement with earlier geochronological studies of detrital zircon, for which a depositional age of 2.65 Ga was proposed (Machado et al., 1993; Renger et al., 1994). The depositional age of the superjacent Cauê Itabirite is constrained by a concordant U–Pb zircon age of 2.65 Ga from a metavolcanic layer (Cabral et al., 2012). Other earlier studies indicated similar, but slightly younger ages of 2.61 Ga (Schrank and Machado, 1996; Machado et al., 1996) and 2.58 Ga (Hartmann et al., 2006) for the Moeda Formation. A recent study on a quartz-rich layer within the Cauê Itabirite has determined U–Pb zircon ages that are younger (2.45 Ga) and older (2.79 Ga) – see Martínez Dopico et al. (2017). However, the younger ages most likely reflect Pb loss (see Cabral et al., 2012). An erosion surface marks the contact between the chemical metasedimentary rocks of the Itabira Group and the superjacent rocks of the Piracicaba Group, of predominantly clastic nature (Dorr, 1969). Formerly included as the uppermost unit of the Piracicaba Group, the Sabará Formation was ranked to the category of a group by Renger et al. (1994). The Sabará Group, originally described as an eugeosynclinal flysch assemblage (Dorr, 1969; Barbosa, 1979), consists of chlorite and biotite schist, metagreywacke and quartzite. Their precursors, volcaniclastic and terrigenous sediments, accumulated up to about 3500 m in thickness in a foreland basin related to the Transamazonian orogeny (Renger et al., 1994; Reis et al., 2002). A zircon U–Pb age of 2.125 ± 0.004 Ga provides a maximum deposition age for metagreywacke at the top of the Sabará sequence (Machado et al., 1992).

The sediments of the Minas Supergroup were affected by two major orogenic events: the Transamazonian event, at ~2.1 Ga; and the Brasiliano event at ~0.6 Ga. The Transamazonian metamorphic overprint is recorded in an aureole-like zone of the Sabará Group by a Sm–Nd garnet–muscovite–whole-rock age of 2.095 ± 0.065 Ga for sillimanite–garnet–muscovite schist (Marshak et al., 1997). Aureole-like zones occur along the contact with granitic–gneissic domes; outside these aureoles, supracrustal rocks contain greenschist assemblages (Herz, 1978). The superimposition of the two major orogenic events led to an eastward increase of metamorphic conditions (Herz, 1978), from grunerite and cummingtonite zones in the western and central parts to

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