Chemical Geology 300–301 (2012) 81–87

Contents lists available at SciVerse ScienceDirect

Chemical Geology

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

Research paper

The effect of grain orientation on secondary ion mass spectrometry (SIMS) analysis of rutile

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ARTICLE INFO

Article history:
Received 23 February 2011
Received in revised form 11 January 2012
Accepted 16 January 2012
Available online 25 January 2012

Editor: K. Mezger

Keywords:
Rutile
U–Pb
SIMS
Geochronology
EBSD
Orientation effects

ABSTRACT

In situ high precision U–Pb analysis of rutile by secondary ion mass spectrometry (SIMS) reveals that instrumental bias for isotope ratios and count rates vary due to crystal orientation. Electron backscatter diffraction (EBSD) techniques have been combined with SIMS data to show consistent and systematic crystal orientation effects, whilst confirming that all analyses are on single crystals and that there is random variation from grain to grain. The result of the orientation effect is to produce an extremely large calibration slope, more than an order of magnitude larger than for other minerals, which can result in highly inaccurate and spurious U–Pb ages from rutile if not taken into account. We present a large standard dataset to highlight this effect and show that by collecting good standard data, from grains in multiple orientations, these effects can be negated and accurate U–Pb SIMS data for rutile can be obtained using a standard calibration slope of $\ln(Pb^+/U^+)$ vs $\ln(UO_2^+/UO^+)=1.12$. Examples from the Anantangiri region, Eastern Ghats, India are used to show the magnitude of these effects on the calibration of unknowns. Evidence is presented to show that the cause of these orientation effects is most likely a combination of channelling of primary ions into the crystal and preferential emission of secondary ions along preferred lattice directions.

1. Introduction

Rutile (TiO_2) is a common accessory phase in mafic igneous and high-grade metamorphic rocks. It is typically present as a detrital component in sedimentary rocks due to its high physical and chemical stability during weathering (Zack et al., 2004b). Rutile is not commonly used for SHRIMP (Sensitive High Resolution Ion MicroProbe) U–Pb analysis due to its low U content and high initial Pb (Ireland and Williams, 2003). However, it has a relatively low U–Pb closure temperature of 600–650 °C (Davis et al., 1994; Cherniak, 2000; Clark et al., 2000; Vry and Baker, 2006), which makes rutile U–Pb information useful in assessing the cooling rates of metamorphic rocks, particularly when combined with Zr-in-rutile thermometry (Zack et al., 2004a).

For geological materials, SIMS analysis has generally been thought to be insensitive to crystal orientation effects because the high-energy primary beam is thought to destroy the crystal structure at depths of up to 10 nm in the sputtered area (Benninghoven, 1994). However, a few studies have reported crystal orientation effects in non-silicate mineral samples during SIMS analysis, for example U/Pb in baddeleyite (Wingate and Compston, 2000; Schmitt et al., 2010), $\delta^{18}O$ in magnetite (Lyon et al., 1998; Huberty et al., 2010), $\delta^{56}Fe$ in magnetite (Kita et al., 2011) and $\delta^{34}S$ in sphalerite and galena (Kozdon et al., 2010). In addition, recent SIMS U–Pb analyses from high-pressure rutile showed significant apparent concentration variations that appear to represent fractionation associated with crystal lattice effects (Li et al., 2011).

One of the problems with resolving the effects of crystal orientation on the concentrations and isotope ratios determined by SIMS analysis is the complexity of the interaction between the primary ion beam and the sample. The material sputtered from the sample comprises a variety of species, including simple atoms and ions and more complex molecules and ionic species. To form a secondary beam of sample material that can be analysed, SIMS requires ionic species that in general comprise less than 10% of the sputtered material (Berrisch and Eckstein, 2007). Understanding the effects of crystal orientation on SIMS analysis therefore requires knowledge of both the microstructural (orientation) characteristics of the sample and the amount and energy spread of sputtered ions (Riciputi et al., 1998; Valley and Kita, 2009).

In this study we investigate the crystal orientation effects encountered during SIMS rutile analysis. Data from a rutile standard are used to characterise the effects of orientation on a known reference material and the results are applied to the interpretation of two samples of unknown age. The results are used to outline some implications for rutile U–Pb geochronology and provide an analytical protocol for obtaining the best SIMS data from rutile.

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doi:10.1016/j.chemgeo.2012.01.013

2. SIMS analysis and U/Pb calibration

The use of well-characterised standards in ion microprobe analysis is essential due to the process by which sample material is extracted. The isotope ratios measured by the instrument are a reflection of the target composition, but are not necessarily the true isotope ratios. A number of effects, generally referred to as 'instrumental mass bias', can alter this measured ratio. These include instrumental mass fractionation and matrix effects (Huberty et al., 2010). For this reason, the analysis of unknowns in a session must be accompanied by a number of standard analyses which are used to calibrate the instrumental effects of that specific session. For the best calibration, standards should be as close in chemical and structural composition as possible to the unknowns, or have a well established 'working curve' for solid solution series minerals (Hervig et al., 1992; Eiler et al., 1997; Riciputi et al., 1998; Valley and Kita, 2009).

There are two common forms of SHRIMP calibration for U–Pb analysis. The 1-D calibration is the most simple, and can be performed once you have just a single standard analysis. The Pb^+/U^+ ratio of that analysis is compared to the known ratio of the standard providing a 'mean sensitivity factor'(Compston et al., 1984). This factor is then applied to all further unknown analyses, converting their measured isotope ratios to the true value.

The 2-D calibration combines all standard data from the session to produce a calibration slope that relates Pb^+/U^+ ratios with UO^+/U^+ ratios, which typically represents instrumental variation during the session (Compston et al., 1984). The covariance of these two ratios should be constant for a target of constant Pb^+/U^+ (Hinthorne et al., 1979). The 'mean sensitivity factor' for Pb^+/U^+ is then calculated from the mean UO^+/U^+ value for the standards, corresponding to the average analytical conditions for the session. All unknown analyses are converted 'along slope' to the mean UO^+/U^+ value of the standards, before the 'mean sensitivity factor' is then applied, thereby giving two dimensions to the calibration. 2-D calibration slopes are typically observed to follow power law relationships (Hinthorne et al., 1979; Compston and Williams, 1992; Claoué-Long et al., 1995) and therefore the slope is commonly defined on a $\ln(Pb^+/U^+)$ vs. $\ln(UO^+/U^+)$ plot.

3. Analytical techniques

3.1. SHRIMP analysis

Following standard heavy mineral separation techniques, two unknown samples from ultra-high temperature metamorphic rocks from Anantangiri, Eastern Ghats, India (Sengupta et al., 1990) each comprising 48 grains, and 15 grains of reference standard 'WHQ' rutile (described later), were mounted in random orientations in a standard 1-inch diameter epoxy mount. The mount was polished using standard diamond paste down to 1 μm. The mount was given a final polish for 3 hours using 0.06 μm colloidal silica in pHx10 NaOH solution to remove surface damage caused by earlier polishing stages.

SIMS data were collected over two sessions on a SHRIMP II ion microprobe at the John de Laeter Centre, Curtin University, Perth, Western Australia. For each session the mount was loaded into the instrument in the same orientation, with session 2 orientation based on images taken during session 1. In this orientation the sample coordinate framework is defined as Z = pole of shrimp mount surface, with the ion beam incidence at 45° to Z, and X is the direction that represents the intersection of the sample surface with the plane containing the ion beam and Z.

For all analyses, the spot produced by the ion beam was an ellipse approximately 25 μm across at the widest dimension. During Session 1 a primary beam current of ~2.4 nA was used, whilst during the second session the instrument had a beam current of ~3 nA, both sessions used an impact energy of 10 keV. A secondary accelerating voltage of 10 kV was used in both sessions. The run table used for the SHRIMP analyses is shown in Table 1, along with the count times on each peak. This run table, along with count times and collector positions, were identical for both sessions.

The rutile standard 'WHQ' from the Windmill Hill Quartzite, Jimperding metamorphic belt, Western Australia has a $^{206}Pb^*/^{238}U$ ratio of 0.5025 (Clark et al., 2000), equivalent to 2625 Ma. Session 1 involved 52 analyses of this standard. In session 2, the two Anantangiri samples (EB-38 and EB-39) together with 15 additional WHQ reference standard analyses, were analysed.

In rutile, $^{208}Pb^+$ has much higher count rates than $^{204}Pb^+$, therefore the correction for common Pb was made using the 208-method (Hinthorne et al., 1979; Compston et al., 1984) rather than using the measured $^{204}Pb^+$. This approach provides a much more precise common Pb correction and is generally more reliable for low Th/U minerals (Wingate and Compston, 2000; Zack et al., 2011). An assessment of potential radiogenic ^{208}Pb from Th was made by measuring ThO^+ at mass 264 u. For all unknowns in this study the Th content is <0.1 ppm and the calculated Th/U ration is <0.01. These data show that the rutile contains very little radiogenic ^{208}Pb and therefore provides a very accurate common 208-correction.

The U content of the WHQ rutile standard is 164 ppm and those for the Anantangiri unknowns were <50 ppm. The U content is variable in the standard, ranging from 90–250 ppm, however it is unclear as to whether this is real or analytical variation, as the nature of the orientation effects in this study cause total counts as well as ratio variations. These low U contents preclude the analysis of the U^+ peak at mass 238 u. Consequently, U^+ peaks were measured using the UO^+ (mass 254 u) and UO_2^+ (mass 270 u). The use of UO^+ and UO_2^+ peaks means that the U/Pb calibration procedure for rutile is modified to $Pb+/UO+$ vs. UO_2^+/UO^+ rather than the Pb^+/U^+ vs. UO^+/U^+ (e.g. Fig. 1b) that is typically used for zircon analyses.

3.2. Electron Backscatter Diffraction Analysis

Prior to SHRIMP analyses, EBSD was used to collect diffraction patterns to confirm that the grains were rutile and not either of the TiO_2 polymorphs anatase or brookite. Following SHRIMP analysis, measurements of rutile orientations from each point of SHRIMP analysis were based on EBSD patterns from the bottom of each SHRIMP pit. Data was collected from both the rutile standard and the two samples of unknown age (EB-38, EB-39). Multiple EBSD analyses (between 2 and 6) were taken from each standard grain (a pattern for each SHRIMP analysis) to test the reproducibility of the intragrain orientation data.

EBSD analysis was undertaken on a tungsten-sourced Zeiss EVO scanning electron microscope (SEM) at Curtin University, Australia. Acquisition, processing and post-processing analysis of EBSD data was conducted using Oxford Instruments Channel 5.10 software. Initial calibration of the EBSD system was conducted using an oriented silicon standard for a known working distance (15.5 mm), camera

Table 1
Peaks analysed and count times used for both the 52 point standards session and the unknowns session of rutile. $Ti_3O_3^+$ reference peak has a nominal mass of 192.

Peak	Count times (s)
Ti_3O_3 (Reference peak)	2
Pb 204	10
Background	10
Pb 206	20
Pb 207	30
Pb 208	20
UO 254	5
ThO_2 264	2
UO_2 270	5