Rutile occurrence and trace element behavior in medium-grade metasedimentary rocks: example from the Erzgebirge, Germany

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Abstract Metamorphic textures in medium-grade (~500–550°C) metasedimentary rocks from the Erzgebirge give evidence of prograde rutile crystallization from ilmenite. Newly-crystallized grains occur as rutile-rich polycrystalline aggregates that pseudomorph the shape of the ilmenites. In-situ trace element data (EMP and SIMS) show that rutiles from the higher-grade samples record large scatter in Nb content and have Nb/Ti ratios higher than coexisting ilmenite. This behavior can be predicted using prograde rutile crystallization from ilmenite and indicates that rutiles are reequilibrating their chemistry with remaining ilmenites. On the contrary, rutiles from the lowest grade samples (~480°C) have Nb/Ti ratios that are similar to the ones in ilmenite. Hence, rutiles from these samples did not equilibrate their chemistry with remaining ilmenites. Our data suggest that temperature may be one of the main factors determining whether or not the elements are able to diffuse between the phases and, therefore, reequilibrate. Newly-crystallized rutiles yield temperatures (from ~500 to 630°C, Zr-in-rutile thermometry) that are in agreement with the metamorphic conditions previously determined for the studied rocks. In quartzites from the medium-grade domain (~530°C), inherited detrital rutile grains are detected. They are identified by their distinct chemical composition (high Zr and Nb contents) and textures (single grains surrounded by fine grained ilmenites). Preliminary calculation, based on grain size distribution of rutile in medium-grade metapelites and quartzites that occur in the studied area, show that rutiles derived from quartzites can be anticipated to dominate the detrital rutile population, even if quartzites are a minor component of the exposure.

Introduction

Several studies have recently promoted the application of in-situ trace element analyses of accessory minerals as a tool to monitor geochemical processes in metamorphic and igneous rocks. This is a reflection of the continuous development of several in-situ analytical techniques (i.e., higher spatial resolution and lower detection limits) and the fact that accessory minerals are frequently the main carrier of trace elements used as tracer of geochemical processes.
Rutile is one of the major Ti-phases, frequently occurring as an accessory mineral in diverse metamorphic and igneous rocks, siliciclastic sediments, placer deposits and hydrothermal ore deposits. As it incorporates several highly-charged trace elements (e.g., Ti, Zr, Nb, Ta, Sn, Sb, W, V, Cr and Mo, see summary in Zack et al. 2002) rutile has successfully been applied as a tool to monitor geochemical processes such as subduction-zone metasomatism, magma evolution and element cycling (e.g. Saunders et al. 1980; McDonough 1991; Brenan et al. 1994; Stalder et al. 1998; Münker 1998; Foley et al. 2000; Rudnick et al. 2000; Klemme et al. 2005). With the calibration of the Zr-in-rutile thermometer (Zack et al. 2004b; Watson et al. 2006; Tomkins et al. 2007) rutile has become an important tool for assessing metamorphic temperatures, especially in eclogite- and granulite-facies rocks (Zack and Luvizotto 2006; Spear et al. 2006; Harley 2008; Luvizotto and Zack 2009). In provenance studies, Nb and Cr systematics in rutile can be used to distinguish pelitic from mafic rocks from the Erzgebirge display textures that support prograde rutile crystallization associated with ilmenite breakdown. Their results support that elements that are usually interpreted to be immobile at whole rock scale (e.g., Zr, Nb and Ti) were able to diffuse and reequilibrate between rutile and biotite under granulite-facies conditions.

In the present study we investigate whether or not equilibrium partitioning of trace elements is operating between rutile and other minerals during metamorphism in lower-grade conditions. Medium-grade metasedimentary rocks from the Erzgebirge display textures that support prograde rutile crystallization associated with ilmenite breakdown. These textures are similar to the ones described by Luvizotto and Zack (2009), since in either case rutile is forming from pre-existing Ti-bearing phases (high-Ti biotite and ilmenite).

In this study we also address an issue highlighted in a companion study by Triebold et al. (2007). Several rutiles from present-day drainage sediments sampled within the lowest-grade domain (greenschist-facies) of the studied area record high temperatures (up to 1000°C). These rutiles are interpreted as inherited detrital grains, preserved in the metasedimentary rocks of the studied area (source for the present-day sediments). High temperatures are attributed to a former metamorphic cycle. In order to shed more light on the occurrence of such inherited grains we discuss the temperature records in rutiles from greenschist-facies rocks. Additionally, we briefly investigate which rock type is capable of delivering the highest amount of rutile to sediments derived from low- to medium-grade metasedimentary rocks, taking into account the occurrence of inherited rutiles as discussed above.

**Geological setting and studied samples**

The Erzgebirge is situated at the northwestern border of the Bohemian Massif and is part of the metamorphic basement of the Mid-European Variscides (Fig. 1). It is characterized by a large-scale antiformal structure consisting of five tectonometamorphic units (Willner et al. 1997; Rötzerl et al. 1998). From the base to the top these units are: Red and Grey Gneisses (RGG); Gneiss/Eclogite Unit (GEU); Mica schist/Eclogite Unit (MEU); Garnet-Phyllite Unit (GPU), and Phyllite Unit (PU). The tectonometamorphic stacking is interpreted as a result of continent-continent collision processes during the Variscan Orogeny (e.g., Willner et al. 1997; Rötzerl et al. 1998; Mingram 1998). Geochemical discriminations suggest that the protoliths of all metamorphic units are similar (mature sediments, exposed to prolonged tropical weathering and extensive reworking), leading to the conclusion that they represent a repetition of metasedimentary sequences (Mingram 1998). Peak pressure ($P$) and temperature ($T$) conditions published for the western part of the Erzgebirge are presented in Fig. 1 (references are given in the figure caption) and can be summarized as follows: PU, 400°C and 2 kbar; GPU, 480°C and 6 to 9 kbar; MEU, 500 to 550°C and 7 to 12 kbar; GEU, 100 to 800°C and 12 to 24 kbar; RGG, 600 to 650°C, and 6 to 8 kbar.

The present study focuses on the GPU, MEU and GEU in the western part of the Erzgebirge, more specifically, on metasedimentary rocks from the GPU and MEU. Clockwise $P$-$T$ paths are documented for the Western Erzgebirge. For the GEU, decompression at very high temperatures is accompanied by cooling. $P$-$T$ paths for the MEU and GPU indicate heating during early pressure release. $P$-$T$ paths of these three units converge at pressures corresponding to 0.6–0.8 GPa, suggesting that these units were juxtaposed at the corresponding depths (Willner et al. 1997; Rötzerl et al. 1998). Metasediments from the GPU are characterized by the occurrence of graphite phyllites, garnet- and albite-bearing phyllites, feldspar-free, chloritoid-bearing phyllites, quartzites, marbles and metaturfites. Garnet-free phyllites are the most common rocks in the GPU. Metasediments from the MEU are characterized by the occurrence of garnet-bearing mica schists (that may
contain variable amount of graphite, albite and chloritoid), paragneisses and marbles. Garnet- and chloritoid-bearing mica schists are the most common rock types. Metasediments from the GEU are characterized by the occurrence of migmatitic paragneisses, feldspar-bearing mica schists and feldspar-free, kyanite-bearing mica schists (Willner et al. 1997; Rötzler et al. 1998; Mingram 1998). Although mafic rocks are beyond the scope of the present work, it is worth mentioning that eclogites occur as local intercalations in both MEU and GEU.

Key information on the studied samples is presented in Table 1. Mingram (1996, see Table 1) investigated seven of the studied samples. Sample EGB04-S56 corresponds to the quartzite sample presented in Triebold et al. (2007).

Analytical techniques

Electron microprobe (EMP)

Electron microprobe analyses of rutile and ilmenite were carried out at the Institut für Geowissenschaften, Universität Heidelberg with a CAMECA SX51 equipped with 5 WDS detectors. The beam was set to 20 kV and 100 nA and analyses followed the method outlined by Luvizotto et al. (2009). The following elements were analyzed: Si, Ti, V, Cr, Fe, Zr, Nb and W. With this setup, the detection limits are 220 ppm for V, 50 ppm for Cr, 40 ppm for Fe and Zr, 60 ppm for Nb and 350 ppm for W. To control zero-concentration peak intensities and instrument drift, every block of ten analyses of unknown was bracketed by two analyses of synthetic rutile with nominal zero-concentration of trace elements. Concentrations of Si were used to detect and avoid contamination associated with submicroscopic zircon inclusions (according to the method outlined by Zack et al. 2004b). Rutile measurements with apparent Si concentrations higher than 300 ppm that showed unusually high Zr contents were excluded from the data set (same procedure applied to SIMS analyses). EMP beam diameter was set to 5 μm. However, due to secondary fluorescence the minimum grain size for obtaining reliable analyses (i.e., analyses with Si content <300 ppm) was ~ 20 μm. For small (ca. 20 μm) rutile grains and for rutile aggregates, measurements with Si content above 300 ppm and Zr concentrations similar to
rutiles with low Si contents were not excluded (high Si values were interpreted as secondary fluorescence from silicates).

Secondary ion mass spectrometry (SIMS)

SIMS measurements of rutile and ilmenite were performed at the Institut für Geowissenschaften, Universität Heidelberg with a Cameca ims 3 f. Analyses were carried out using a 14.5 keV / 10–20 nA 16O− primary ion beam, which resulted in spot sizes of 20–30 μm. By using a field aperture the effective spot size was reduced to 12 μm. With this setup, the smallest grain size for obtaining contamination free analyses was ca. 20 to 30 μm. Positive secondary ions were nominally accelerated to 4.5 keV (energy window set to ±20 eV) and the energy filtering technique was used with an offset of 90 eV at mass resolution m/Δm (10%) of 370. Count rates were normalized to 47Ti. TiO2 in rutile is assumed to be 100 wt.%, which introduces an error of <1%, as elements other than Ti and O occur only in minor amounts in the studied rutiles. In ilmenite, the Ti concentration was based on the values obtained by EMP. The following isotopes were analyzed: 27Al, 30Si, 47Ti, 90Zr, 93Nb, 118Sn, 120Sn, 121Sb, 123Sb, 178Hf, 181Ta, 184W, 186W, 232Th, 238U. Concentrations were calculated based on relative sensitivity factors (RSF) determined using a set of rutile reference materials presented by Luvizotto et al. (2009). Since Th concentrations are not available for the reference materials used here, no reliable RSF can be calculated for Th. However, intensity ratios obtained for the studied rutiles suggest that Th concentrations are extremely low (below the 0.1 ppm level when using RSF of U).

Micro-Raman spectroscopy

Laser micro-Raman spectroscopy was applied to selected grains in order to identify the TiO2 structure type. Raman spectra were obtained using a Horiba Jobin Yvon Labram HR-UV 800 (equipped with a Peltier-cooled CCD detector) at the Geowissenschaftliches Zentrum, Universität Göttingen. Analyses were carried out using 633 nm laser excitation, 20 mW laser power, 1200 l/mm grating and a Peltier-cooled CCD detector.

Results

Textural evidence for rutile growth in medium-grade metapelitic rocks

In GPU rocks rutiles occur as polycrystalline aggregates, which are characterized by a fine-grained intergrowth of rutile and chlorite that mimic the shape of ilmenites that

| Coordinates Other Phases | Ti Concentration in Rutile (wt.%) | Other Phases |
|--------------------------|----------------------------------|--------------|
| EGB04-S56               | 10 to 20%                        |               |
| EGB04-R10d              | 10 to 20%                        |               |
| EGB04-R11e              | 10 to 20%                        |               |
| A15ca                   | 10 to 20%                        |               |
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Table 1: Summarized description of the studied samples. Modal proportions are estimates based on visual inspection with a petrographic microscope and BSE images. Coordinates correspond to the location of the borehole (depths: 2.12–100 m, 2.12–338 m, 3.1–19 m).
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Coexist in the rock. Similar textures, although with a higher rutile/ilmenite ratio, can still be found in some metasedimentary rocks from the MEU (Fig. 2). These textures indicate rutile grow from ilmenite breakdown (Fig. 2). As the content of Ti is higher in rutile than in ilmenite (100 wt.% TiO₂ in rutile vs. ~53 wt.% TiO₂ in ilmenite), the physical volume once occupied by ilmenite is not entirely filled by rutile (Fig. 2). The Fe released from the breakdown of ilmenite is used, together with the elements available in matrix minerals (quartz and phyllosilicates), to crystallize chlorite according to the simplified metamorphic reaction: 

\[ \text{Ilm} + \text{silicates} + \text{H}_2\text{O} \rightarrow \text{Rt} + \text{Chl} \]

(mineral abbreviations after Kretz 1983). The BSE images presented in Fig. 2 are arranged according to an increasing rutile/ilmenite ratio, which we interpret to represent the prograde evolution of the textures. In Figs. 2a and 2b only minor amounts of rutile are present and ilmenite grains still preserve their euhedral/subhedral elongated (lath) habit. Figs. 2c to 2e show more evolved stages of the texture. The occurrence of a large polycrystalline rutile aggregate only a few micrometers apart

**Fig. 2** BSE images exemplifying the textures observed in metasedimentary rocks from the GPU and MEU. The images are arranged in order of increasing rutile/ilmenite ratio. Numbers given in the figures correspond to Nb concentrations (in ppm) and Nb/Ti ratios. All scale bars represent 100 μm. See text for further information. Samples: A, B and D—P38c; C and E—P2; G—2/12; H—2/2
from an apparently unreacted ilmenite (representing different
evolutional stages of the reaction) indicate the small size of
the reaction domain (Fig. 2e). In Figs. 2f and 2g ilmenite is
virtually absent. However, rutiles still occur as aggregates
that have the elongated shape inherited from ilmenites.
Rutiles are often present as inclusions in garnet bearing rocks
from the MEU (Fig. 2f).

An important exception to the samples descrided
above is the only analyzed quartzite (EGB04-S56,
MEU) in this study. This sample contains some large
single crystals of rutile that are surrounded by fine-
grained ilmenite (Fig. 3). These rutiles do not have the
typical lath shape of the newly-grown rutiles. We interpret
these grains as inherited detrital rutiles that are still
preserved in the quartzite.

Metapelitic rocks from the GEU are ilmenite-free. In
these rocks rutiles show no traces of the texture described
above and have a rounded shape (Fig. 4).

Identification of TiO₂ polymorphs

Rutile was identified by Raman bands at 242, 449 and
614 cm⁻¹ (for a compilation of Raman bands for Ti
polymorphs see Meinhold et al. 2008) and anatase was
identified by Raman bands at 146, 199, 400, 517 and
642 cm⁻¹ (Fig. 5). Brookite was not found in the studied
samples. In the investigated rocks rutile is brownish/reddish
under the optical microscope (transmitted light) while
anatase is light-brown to colorless. Some Ti-oxides dis-
played cathodoluminescence (CL) emission during EMP
measurements (visible as a bright spot when the mineral
was under the focused electron beam). All of these grains
were identified as anatase by Raman. BSE images of
coexisting Ti-polymorphs show that rutile is brighter than
anatase in the studied samples (Fig. 5). All these character-
istics were used as identification criteria.

The current work focuses only on the textural and
chemical relationships between rutile and ilmenite. A more
detailed work on the identification and chemical composi-
tion of TiO₂ polymorphs in Erzgebirge rocks and present-
day drainage sediments will be published by Triebold et al.
in prep.).

Comparison between Nb concentrations in rutile
and ilmenite

Figure 6 summarizes Nb concentrations obtained for rutiles
and ilmenites (for a complete data set, please refer to
Appendix A, Table 3). Nb contents in ilmenite are rather
constant when compared to those in rutile, with average
concentration of ca. 500 ppm in almost all samples. In
contrast, Nb concentrations in rutile are characterized by
three distinct patterns, closely connected to the metamor-
phic unit from which they derive. Rutiles from the GPU
have lower Nb contents (max. concentration of 1330 ppm)
than those from MEU and GEU (total of 11 grains with
concentrations higher than 2500 ppm; max. concentration
up to 9500 ppm). Moreover, their Nb/Ti ratios are
comparable with values obtained for ilmenites from the
same samples. Rutiles from the MEU have higher Nb
contents and display larger spread in Nb concentrations
with Nb/Ti ratios spanning from values as low as the ones
obtained for the ilmenites to values significantly higher.
Rutiles from the GEU show a narrow spread in Nb
concentration. These samples are ilmenite-free and, there-
fore, no direct comparison can be made.

Zirconium concentrations in rutile

For each analysis, a Zr-in-rutile temperature (Fig. 7 and
Appendix A, Table 3) was calculated (calibration of
Tomkins et al. 2007 at pressure conditions defined in
Fig. 1 for each metamorphic zone). Zr contents in all rutiles
from the GPU are below the EMP detection limit
(<40 ppm, corresponding to ca. <500°C) and are in
agreement with peak temperatures reported for this unit
(<500°C, Rötzler et al. 1998). A SIMS measurement of
46 ppm of Zr obtained for sample P2 match the EMP data.
About half of the rutiles analyzed from the MEU (15 out of
28) have Zr contents below the EMP detection limit. The
other grains have higher Zr contents (60–80 ppm), which
are confirmed through EMP as well as SIMS analyses.
These results are in agreement with concentrations back-
calculated from peak metamorphic conditions known for
this area (500–550°C, 0.7–12. GPa). The only exception is

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**Fig. 3** BSE images of rutiles interpreted as inherited detrital
grains in the quartzite. Concentrations (in ppm) stand for Nb
and Zr (in italic). Pure numbers represent Nb/Ti ratios. Scale
bars represent 100 μm. bd -
below detection limit (EMP)
one rutile grain with Zr concentration of 390 ppm from the quartzite sample (Fig. 3a).

Only few rutiles from the higher-grade samples (EGB04-R11e, A15c) have Zr contents below the EMP detection limit. Zr contents obtained through SIMS and EMP are in agreement with mineral assemblage and metamorphic textures observed in these rocks with Zr concentrations up to 200 ppm for sample A15, corresponding to temperatures of ca. 630°C.

We would like to note that highest Zr contents in rutiles from garnet bearing rocks are usually obtained for rutiles included in garnet (see also discussion in Triebold et al. 2007).

Discussion

Behavior of Nb during rutile formation from ilmenite

Samples from the GPU and MEU record intermediate stages of a reaction where rutile is forming from ilmenite breakdown. The prograde evolution of this reaction can be summarized by the simplified model presented in Fig. 8 and can be described as follows: Initially, only ilmenite occurs and hosts the main portion of Nb and Ti of the whole rock (WR). Under metamorphic conditions of the GPU (~480°C, 0.6–0.9 GPa) rutile starts to grow associated with the breakdown of ilmenite. With increasing metamorphic grade, the reaction progresses and the rutile/ilmenite ratio increases. In these intermediate stages rutiles occur as polycrystalline aggregates inside the volume previously occupied by ilmenite. Nb is distributed between both phases. The excess Fe is used to crystallize chlorite, with other elements available in the surrounding silicates. At higher metamorphic grade, rutile is the only Ti-phase and consequently the main carrier of Nb and Ti. It is coarser grained as a result of re-crystallization and/or ripening and forms rounded grains (see, e.g., Fig. 4). Notice that biotite and phengite can incorporate significant amounts of Ti and its incorporation is temperature-dependent (Patiño Douce 1993; Henry and Guidotti, 2002; Henry et al. 2005). Hence, in rocks where rutile coexists with Ti-bearing micas, rutile may not have the WR Nb/Ta ratio.

A distinct geochemical signature is observed in rutiles formed from biotite breakdown in felsic granulites from the Ivrea-Verbano Zone (Luvizotto and Zack 2009). In these rocks, Nb concentrations in rutiles from lowest-grade samples (ca. 850°C) show a larger spread when compared

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**Fig. 4** BSE images exemplifying rutiles occurring in metasedimentary rocks from the GEU. Fe-Sulf—Fe sulfide

**Fig. 5** a and b: High-contrast BSE images showing rutile coexisting with anatase. Notice that rutile is brighter. c Raman spectra of anatase and rutile (spot location presented in B)
to those from higher grades (up to 930°C). According to the authors, this behavior can be predicted assuming inter-grain diffusion of Nb during continuous crystallization of rutile from biotite and considering that rutile strongly favors Nb over Ti when compared with biotite ($\frac{(Nb/Ti)_{Rt}}{(Nb/Ti)_{Bt}}$ ratio is ca. 50, see discussion in Luvizotto and Zack 2009).

Klemme et al. (2005, 2006) presented experimentally derived rutile/melt and ilmenite/melt partition coefficients for several elements, including Nb. The experiments were carried out at atmospheric pressure and temperatures ranging from 1200 to 1300°C. Results confirm previously obtained data (e.g., Green and Pearson 1987; Foley et al. 2000; Green 2000; Horng and Hess 2000; Schmidt et al. 2004) and show that Nb is strongly compatible in rutile ($D_{Nb}^{Rt/melt} = 22$ for andesitic melt composition) and moderately compatible to incompatible in ilmenite ($D_{Nb}^{Ilm/melt} = 0.88 - 1.9$ for basaltic and $D_{Nb}^{Ilm/melt} = 0.55$ for basaltic andesite melt compositions). These data show that rutile strongly favors the incorporation of Nb when compared with ilmenite (assuming similar partitioning behavior for the andesitic and basaltic andesite melt composition). In fact, using these partition coefficients a $\frac{(Nb/Ti)_{Rt}}{(Nb/Ti)_{Ilm}}$ ratio of ca. 50 can be calculated. This value is identical to the one calculated by Luvizotto and Zack (2009) for the rutile/biotite pair. Hence, the same Nb behavior described by the authors is expected to be observed in the studied rocks (i.e., rutiles coexisting in chemical equilibrium with ilmenite are expected to have significantly higher Nb/Ti ratios). As Nb is strongly more compatible in rutile than in ilmenite, rutiles formed during early stages of the reaction are expected to have Nb contents significantly higher than the ilmenite. As the reaction continues, Nb concentrations in both rutile and ilmenite decrease strongly. Calculations carried out by Luvizotto and Zack (2009) show that during the initial stages of the reaction the decrease of only 3% in the modal proportion of biotite leads to a reduction of one order of magnitude in the Nb concentration of both rutile and biotite. Such large variations are also expected to be recorded in rutiles formed from ilmenite breakdown.

Niobium concentration data presented in Fig. 6 show that rutiles from the MEU display the highest variations in Nb content among all the studied samples. Furthermore, they have Nb/Ti ratios significantly higher than ilmenite (up to ~15 times in sample 3/1). According to the partition coefficients presented above, the Nb behavior in rutiles from these samples is consistent with rutile crystallization in equilibrium with ilmenite. The highest Nb concentration obtained for a rutile from sample 3/1 (9526 ppm) is consistent with a rutile occurring in equilibrium with an ilmenite containing ~100 ppm of Nb. Hence, our results support that Nb locally mobilized and is able to equilibrate between rutile and ilmenite under the metamorphic conditions of the MEU.

Rutiles from the GEU rocks are ilmenite-free. We interpret the absence of ilmenite as an indication that the rutile forming reaction was completed. Rutiles from these rocks show a small spread in Nb concentrations. Assuming the analyzed samples to be representative, the data suggest homogenization of the variable Nb contents generated during the early stages of rutile crystallization. Such homogenization can take place through mechanisms like dynamic recrystallization and/or inter-grain diffusion, in accordance with the observation of Luvizotto and Zack (2009). These processes are facilitated by higher temperatures and therefore more probable to take place in rocks from the GEU than in those from the GPU and MEU.
Exceptions to the Nb behavior discussed above are samples from the lower grade GPU. Rutiles from this unit are characterized by small scatter in Nb content and by Nb/Ti ratios close to the ones obtained for ilmenites. Results indicate that these rutiles are not in chemical equilibrium with ilmenite (higher Nb/Ti ratios in rutile are expected). One possible interpretation is that at metamorphic conditions of the GPU (ca. 480°C and <0.9 GPa) chemical diffusion was too slow and Nb was not able to exchange between rutile and ilmenite. This observation suggests that temperature is one of the main factors controlling the Nb behavior, i.e., chemical mobility. However, other variables such as presence of fluids and slow cooling rates may favor the mobility of Nb as well.

Temperature records in rutile from medium-grade metasedimentary rocks

The textures observed in metasedimentary rocks from the GPU indicate that rutile crystallization took place under PT conditions of ca. 480°C and 0.6–0.9 GPa. Zr concentrations obtained for rutiles from this unit (Fig. 7) confirm previous geothermometric data as all EMP measurements were below detection limit (<40 ppm of Zr, <500°C). All but one rutile from the MEU rocks give temperatures that match the thermobarometric literature data (500–560°C, Rötzler et al. 1998). Temperatures in the 560–680°C range are obtained for rutiles from the two investigated samples from the GEU and are consistent with peak mineral assemblages (garnet plus biotite, Table 1) and metamorphic textures observed in these rocks. None of the metamorphically-grown rutiles record unrealistically high temperatures (i.e., high Zr contents) and are therefore consistent with metamorphic condition under which they were formed. Low temperatures obtained for some rutiles may either be a record of an early stage during the prograde path or re-equilibration during the retrograde path.

Detrital rutiles from medium-grade metasedimentary rocks

Triebold et al. (2007) showed that several rutiles from present day drainage sediments from the catchment area of PU, GPU and MEU record temperatures up to ca. 1000°C (Zr-in-rutile, after calibration of Zack et al. 2004b). Since the sediments are derived from medium-grade metamorphic rocks (max. T of ca. 600°C for the MEU—see Fig. 1), these high-T rutiles are interpreted to be inherited detrital grains.
that are preserved in these rocks. High temperatures registered by these grains are further interpreted to be records of former metamorphic cycles seen by the source rocks for the sediments that compose the present-day metasedimentary rocks of the PU, GPU and MEU. Such high-\(T\) rutiles are not found in the catchment area of the GEU. Based on these observations, the authors concluded that the complete reequilibration of Zr contents in inherited detrital rutile grains takes place only above ca. 600°C. The existence of a minimum reequilibration temperature has also been discussed by other authors (Stendal et al. 2006; Meinhold et al. 2008).

Triebold et al. (2007) observed a high frequency of high-\(T\) rutiles (and hence inherited detrital rutiles) in a mineral separate from a quartzite sample from the MEU (EGB04-S56, the same investigated in this paper). Such observation contradicts results showing that highest frequencies of high-\(T\) rutiles are observed in sediments derived from the PU and GPU, thus raising the hypothesis that quartzites may be the main source of high-\(T\) rutiles in present-day sediments derived from greenschist-facies metasediments that contain quartzite. This hypothesis is based on the fact that quartzites are less reactive when comparing to other metamorphic rocks, as the lack of Ca- and Fe-bearing phases reduces their ability to crystallize titanite and ilmenite under conditions where rutile is not stable (e.g., greenschist facies). The downside of using mineral separates is that petrographic textures are not preserved. Here, we present BSE images from the quartzite sample (Fig. 3) showing how these inherited rutiles occur in the rock. They are clearly distinguishable from the polycrystalline aggregate that represent the newly formed rutiles, since they occur as large single crystals surrounded by fine grain ilmenite (interpreted to be formed during prograde metamorphism under green-schist facies or below). In addition, inherited rutiles have much higher Nb and Zr contents (up to 3900 and 390 ppm respectively, see data in Fig. 3).

The results show, therefore, that quartzites may preserve size and chemical composition of inherited detrital rutiles up to higher metamorphic conditions when compared to pelitic rocks. Preliminary calculations were carried out to evaluate the impact of our observations for the sediment record of rutile. More specifically, we evaluate which rock type liberates/delivers the highest amount of detrital rutile during erosion of a greenschist-facies metasedimentary catchment. We focus here on sand-sized grains, because rutile in provenance studies is mostly related to heavy mineral analyses, which usually concentrates on the finer-grained sand fraction. Based on BSE images (see, e.g., Figs. 2 and 7) and petrographic observation, average rutile grain sizes (size of the smallest dimension) of 50 \(\mu\)m and 100 \(\mu\)m can be roughly estimated for the metapelites (phyllites/schists) and quartzites, respectively.

Calculations were performed assuming a Gaussian grain size distribution and a standard deviation of 20% (in accordance with results obtained for garnet porphyroblasts by Hirsch 2008). Probabilities of occurrence of rutiles in metapelites and quartzites were calculated for three grain size fractions (Table 2): 63 \(\mu\)m, which corresponds to the silt-sand threshold, a fraction used in traditional heavy mineral analyses; 80 \(\mu\)m, grain size fraction employed in our quantitative provenance studies of rutile (see von Eynatten et al. 2005; Triebold et al. 2007); and 100 \(\mu\)m, the average rutile

### Table 2
Probabilities of occurrence of rutiles with grains sizes of 63, 80 and 100 \(\mu\)m in metapelites and quartzites; and percentage contribution of quartzites in the sedimentary record of rutiles from low- to medium-grade metasedimentary sequences

| Rutile Fraction | Prob. Mpel(%) | Prob. Qzt(%) | Prob. Ratio Qzt/Mpel (vol.) | Percentage contrib. in sediment |
|-----------------|--------------|-------------|---------------------------|-------------------------------|
|                 |              |             |                           | 1% Qzt | %5 Qzt | 10% Qzt |
| 63\(\mu\)m      | 10           | 96          | 0.6                       | 0.6   | 3.0    | 6.0     |
| 80\(\mu\)m      | 0.14         | 84          | 38                        | 38    | 100    | 100     |
| 100\(\mu\)m     | <0.003       | 50          | >1000                     | 100   | 100    | 100     |

Parameters: Metapelite (Mpel)—average grain size=50\(\mu\)m, standard deviation=20\%, TiO\(_2\) (whole rock) 1.0\%. Quartzite (Qzt)—average grain size=100\(\mu\)m, standard deviation=20\%, TiO\(_2\) (whole rock) 0.5\%. Prob (%)—probability of occurrence of rutile (calculated assuming a Gaussian distribution). Please notice that the probability ratio of quartzite/pelite is expressed in volume (calculated taking into account the probabilities, the differences in grain sizes (converted to volume) and TiO\(_2\) contents in the whole rock).
diameter in the quartzite, which relates via hydrodynamic equivalence to a typical fine- to medium-grained sand sample of average grain size ~200 \( \mu m \). According to our results, in a catchment area with a quartzite volume of 1.0%, 38% of the rutile grains larger than 80\( \mu m \) would derive from the quartzite. With a volume of 2.5 to 3.0% quartzite, almost all rutile grains larger than 80\( \mu m \) would come from this rock. For the 100\( \mu m \) fraction the effect is even more pronounced, as quartzites would virtually be the only source of rutile, even for quartzite abundances below 1.0%. On the other hand, results show that pelites would still be the main contributor of rutile for the 63\( \mu m \) fraction.

Textures and trace element data presented above show that quartzites may preserve detrital rutile grains (i.e., elastic grains associated with the sedimentary deposition of the protolith) up to temperatures higher than those needed to crystallize new rutiles in metapelitic rocks. Furthermore, these detrital grains may record information (e.g., Nb and Cr systematics and \( T \)) inherited from an earlier geological cycle. This observation, combined with the calculations presented above, suggests that sand-sized rutiles derived from greenschist-facies metasedimentary sequences that also contain quartzites may not provide information on the metapelites, since small volumes of quartzite may dominate the sedimentary record of rutile (see Table 2).

Conclusions

Textures and trace element data indicate rutile growth from ilmenite in medium-grade metasedimentary rocks from the Erzgebirge. In samples from the GPU rutiles occur as polycrystalline aggregates and pseudomorph the shape and Nb/Ti of ilmenite. In MEU rocks, rutile aggregates have the shape inherited from ilmenite. However, rutiles from this unit display a larger scatter in Nb concentrations and have higher Nb/Ti than ilmenite. This behavior indicates that Nb concentrations in rutile are evolving towards equilibration with relict ilmenites (considering that rutile strongly favors the incorporation of Nb when compared with ilmenite). MEU rocks are ilmenite-free. Taking into account that pelitic rocks from the studied units have similar protoliths (Mingram 1998) and assuming that they followed a rather similar prograde path, the absence of ilmenite in MEU rocks indicate that the rutile forming reaction was completed. Rutiles from these rocks show a narrow scatter in Nb contents, are single crystals and do not have the elongated shape inherited from ilmenite. In these rocks, the homogenization of Nb contents in rutile was facilitated by higher temperature and is probably related with mechanisms like dynamic recrystallization and/or inter-grain diffusion.

Temperature records on all but one rutile grain are in accordance with peak metamorphic conditions previously presented for the studied rocks. Rutiles from the GPU give temperatures <500\(^\circ C\). Temperatures within 500–560\(^\circ C\) and 520–630\(^\circ C\) were obtained for rutiles from MEU and GEU rocks, respectively.

The only rutile with an exceptionally high Zr content (390 ppm, \( T=680^\circ C \)) is from a quartzite from the MEU. This grain is interpreted to be an inherited detrital relict. Due to the lack of Fe–Ca-bearing phases, quartzites are less reactive than other rock types (e.g., phyllites and schists). This strongly decreases the ability to form ilmenite and/or titannite.

Phylites and schists are low- to medium-grade metamorphic products of pelitic sediments (fine-grained elastic sediments of less than 1/16 mm grain size; Pettijohn 1975). On the other hand, quartzites are often the metamorphic product of coarser grained sediments, e.g., sandstones. In the investigated phylites and schists, metamorphically-grown rutiles are fine-grained (smaller axis <50 \( \mu m \)) and occur as polycrystalline aggregates (easily disintegrated during weathering and mechanical transport in sediments). However, large detrital rutile grains inherited from a previous cycle may still be preserved in the quartzites. Preliminary calculations taking into account modal abundance and grain size distribution of rutile in metapelites and quartzites show that quartzites may often be the main source for rutiles in sediments derived from low-grade metamorphic rocks. This seems to be the case of the Erzgebirge, where high-temperature rutile relicts are frequently found in sediments derived from low- to medium-grade rocks, even though the volume of quartzite is less than 5%. If such interpretation is correct, these high-temperature relicts pre-date the peak metamorphism achieved by Erzgebirge rocks. It has indeed been discussed by Triebold et al. (2007) that these high-temperature rutiles fit into the common picture of a derivation of Early Paleozoic sediment of central Europe from source rocks from the West African Craton. Our observations thus encourage further studies, e.g., U-Pb dating of these high-temperature relicts.

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Table 3 Rutile (Rt) and ilmenite (Ilm) trace element concentrations (in ppm) obtained for the studied samples from the Erzgebirge. Textural relationship (Text.): M matrix, I included in garnet, bd below detection limit. Temperatures were calculated according to the calibration of Tomkins et al. (2007) at pressure conditions defined in Fig. 1 for each metamorphic zone.

| Technique | Sample | Unit | Grain | Text. | Si | V | Cr | Fe | Zr | Nb | Sn | Sb | Hf | Ta | W | U | T°C |
|-----------|--------|------|-------|-------|----|---|----|----|----|----|----|----|----|---|---|---|-----|
| SIMS      | P2     | GPU  | Rt8   | M     | 7947| bd| 46 | 242| 14 | 54 | 3.2| 15 | bd | 76 | 516 |
| SIMS      | P2     | GPU  | Rt9   | M     | 6708| bd| 136| 643| 22 | 54 | 21 | 91 | bd | 13 | 586 |
| EMP       | P2     | GPU  | Rt1   | M     | 1140| bd| 5760| bd | 210| bd | 470 |
| EMP       | P2     | GPU  | Rt2   | M     | 580 | bd| 7240| bd | 340| bd | 508 |
| EMP       | P2     | GPU  | Rt3   | M     | 1310| bd| 90 | 7120| bd | 250| bd | 510 |
| EMP       | P2     | GPU  | Rt4   | M     | 4060| bd| 6989| bd | 1000| bd | 710 |
| EMP       | P2     | GPU  | Rt5   | M     | 2370| bd| 8989| bd | 480| bd | 710 |
| EMP       | P2     | GPU  | Rt6   | M     | 3180| bd| 3530| bd | 760| bd | 710 |
| EMP       | P2     | GPU  | Rt7   | M     | 630 | bd| 6300| bd | 1140| bd | 710 |
| EMP       | P2     | GPU  | Rt9   | M     | 99  | bd| 1257| bd | 880| bd | 710 |
| SIMS      | P2     | GPU  | Ilm1  | M     | bd | 171| 7.5| 0.9| 12 | bd | 0.18| 337 |
| EMP       | P2     | GPU  | Ilm1  | M     | 50  | 440| 303254| bd | 100| bd | 610 |
| EMP       | P2     | GPU  | Ilm2  | M     | 110 | bd| 75 | 306844| bd | 150| bd | 610 |
| EMP       | P2     | GPU  | Ilm3  | M     | 100 | bd| 299524| bd | 70 | bd | 610 |
| EMP       | P2     | GPU  | Ilm4  | M     | 60  | bd| 304604| bd | 370| bd | 610 |
| EMP       | P2     | GPU  | Ilm5  | M     | 120 | bd| 292054| bd | 410| bd | 610 |
| EMP       | P2     | GPU  | Ilm6  | M     | 3890| bd| 280714| bd | 420| bd | 610 |
| EMP       | P2     | GPU  | Ilm7  | M     | 70  | bd| 295684| bd | 540| bd | 610 |
| EMP       | P2     | GPU  | Ilm8  | M     | 160 | bd| 288664| bd | 270| bd | 610 |
| EMP       | P2     | GPU  | Ilm9  | M     | 20  | bd| 310334| bd | 540| bd | 610 |
| EMP       | P2     | GPU  | Ilm10 | M     | 40  | bd| 304944| bd | 450| bd | 610 |
| EMP       | P38c   | GPU  | Rt1   | M     | 190 | bd| 2010| bd | 1330| bd | 470 |
| EMP       | P38c   | GPU  | Rt3   | M     | 170 | bd| 3560| bd | 920| bd | 437 |
| EMP       | P38c   | GPU  | Rt6   | M     | 1160| 311| 101| 9660| bd | 1180| bd | 437 |
| EMP       | P38c   | GPU  | Rt7   | M     | 51  | bd| 2989| bd | 1269| bd | 443 |
| EMP       | P38c   | GPU  | Rt8   | M     | 536 | bd| 2970| bd | 516| bd | 443 |
| EMP       | P38c   | GPU  | Rt9   | M     | 474 | bd| 16283| 46 | 424| bd | 516 |
| EMP       | P38c   | GPU  | Ilm1  | M     | 90  | bd| 321734| bd | 320| bd | 516 |
| EMP       | P38c   | GPU  | Ilm1  | M     | 110 | bd| 320554| bd | 220| bd | 516 |
| EMP       | P38c   | GPU  | Ilm2  | M     | 110 | bd| 318784| bd | 360| bd | 516 |
| EMP       | P38c   | GPU  | Ilm3  | M     | 360 | bd| 314554| 840| 340| bd | 736 |
| Technique | Sample Unit Grain Text. | Si | V | Cr | Fe | Zr | Nb | Sn | Sb | Hf | Ta | W | U | T°C |
|-----------|------------------------|----|---|----|----|----|----|----|----|----|----|----|----|----|-----|
| EMP P38c GPU Ilm4 M | 280 | bd | bd | 294724 | bd | 1110 | bd | 490 |
| EMP P38c GPU Ilm5 M | 120 | bd | bd | 320503 | bd | 700 | bd | 490 |
| EMP P38c GPU Ilm6 M | 3230 | bd | bd | 280545 | bd | 490 | bd | 490 |
| EMP P38c GPU Ilm7 M | 90 | bd | bd | 320963 | bd | 120 | bd | 490 |
| EMP P38c GPU Ilm8 M | 440 | bd | 60 | 319444 | bd | 560 | bd | 490 |
| EMP P38c GPU Ilm9 M | 1300 | bd | bd | 315543 | bd | 120 | bd | 490 |
| EMP P38c GPU Ilm10 M | 150 | bd | bd | 320723 | bd | 330 | bd | 490 |
| EMP P38c GPU Ilm11 M | 400 | bd | bd | 323794 | bd | 220 | bd | 490 |
| EMP P38c GPU Ilm12 M | 30 | bd | bd | 321054 | bd | 360 | bd | 490 |
| EMP P38c GPU Ilm13 M | 100 | bd | bd | 303424 | bd | 570 | bd | 490 |
| EMP P38c GPU Ilm14 M | 240 | 640 | bd | 310324 | bd | 850 | bd | 490 |
| SIMS 3/1 MEU Rt3 I | 34707 | | | | | | | | | | | | | bd | 2840 |
| SIMS 3/1 MEU Rt4 I | 948 | | | | | | | | | | | | | bd | 1012 |
| SIMS 3/1 MEU Rt9 I | 3556 | | | | | | | | | | | | | bd | 1844 |
| SIMS 3/1 MEU Rt10 I | 4576 | | 1444 | | 3.34 | 81 | | | | | | | bd | 5.2 |
| EMP 3/1 MEU Rt1 I | 116 | 293 | 131 | 7997 | 42 | 1275 | | | | | | | bd | 2725 |
| EMP 3/1 MEU Rt2 I | 120 | bd | bd | 8521 | bd | 3156 | | | | | | | bd | 445 |
| EMP 3/1 MEU Rt3 I | 87 | 572 | 163 | 8896 | bd | 5013 | | | | | | | bd | 1603 |
| EMP 3/1 MEU Rt4 I | 37 | bd | 85 | 5972 | bd | 1065 | | | | | | | bd | 516 |
| EMP 3/1 MEU Rt5 I | 97 | 386 | 228 | 9805 | bd | 2091 | | | | | | | bd | 432 |
| EMP 3/1 MEU Rt6 I | 41 | 512 | 205 | 14411 | bd | 9526 | | | | | | | bd | 463 |
| EMP 3/1 MEU Rt8 I | 80 | 353 | 89 | 7356 | 46 | 1257 | | | | | | | bd | 375 |
| SIMS 3/1 MEU Ilm10 M | 34 | | | | | | | | | | | | | bd | 341 |
| SIMS 3/1 MEU Ilm12 M | 1.4 | | | | | | | | | | | | | bd | 525 |
| SIMS 3/1 MEU Ilm14 I | 978 | | | | | | | | | | | | | bd | 388 |
| EMP 3/1 MEU Ilm1 I | 50 | bd | 360823 | bd | 560 | bd | 447 |
| EMP 3/1 MEU Ilm2 M | 150 | bd | bd | 356523 | bd | 610 | bd | 447 |
| EMP 3/1 MEU Ilm3 I | 80 | bd | bd | 360333 | bd | 570 | bd | 447 |
| EMP 3/1 MEU Ilm4 M | 70 | bd | bd | 360783 | bd | 670 | bd | 447 |
| EMP 3/1 MEU Ilm5 M | 190 | bd | bd | 357523 | bd | 460 | bd | 447 |
| EMP 3/1 MEU Ilm6 M | 50 | bd | bd | 357613 | bd | 550 | bd | 447 |
| EMP 3/1 MEU Ilm7 I | 15449 | bd | bd | 359073 | bd | 850 | bd | 447 |
| EMP 3/1 MEU Ilm8 I | 30 | bd | bd | 369102 | bd | 440 | bd | 447 |
| EMP 3/1 MEU Ilm9 M | 40 | bd | bd | 360783 | bd | 650 | bd | 447 |
| EMP 3/1 MEU Ilm10 M | 70 | bd | bd | 355973 | bd | 500 | bd | 447 |
| EMP 3/1 MEU Ilm11 M | 120 | bd | bd | 356523 | bd | 500 | bd | 447 |
| EMP 3/1 MEU Ilm11 M | 70 | bd | bd | 354513 | bd | 580 | bd | 447 |
| EMP 3/1 MEU Ilm12 M | 50 | bd | bd | 361073 | bd | 630 | bd | 447 |
| EMP 3/1 MEU Ilm12 M | 30 | bd | bd | 358273 | bd | 520 | bd | 447 |
| Technique | Sample | Unit  | Grain | Text. | Si  | V   | Cr  | Fe  | Zr  | Nb  | Sn  | Sb  | Hf  | Ta  | W  | U  | °C  |
|-----------|--------|-------|-------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|----|----|
| EMP       | 3/1    | MEU   | Ilm13 | M     | 110 | bd  | bd  | 360423 | bd  | 560 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt3   | I     | 140 | bd  | bd  | 9830  | bd  | 370 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt4   | I     | 50  | 395 | 158 | 5230  | bd  | 810 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt6   | I     | 50  | 657 | 180 | 5090  | 50  | 2490| bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt7   | I     | 60  | 539 | 174 | 5330  | 70  | 1190| bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt10  | I     | 11  | bd  | bd  | 3281  | 203 | 770 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt10  | I     | 297 | bd  | bd  | 2656  | 62  | 499 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt11  | I     | 64  | 486 | 76  | 7934  | 80  | 5640| 2250|     |     |     |    |    |
| EMP       | 61c    | MEU   | Rt12  | I     | 16  | 244 | 53  | 3973  | 77  | 1125| bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Ilm2  | M     | 1400| bd  | bd  | 270625| bd  | 430 | bd  |     |     |     |    |    |
| EMP       | 61c    | MEU   | Ilm2  | M     | 90  | bd  | bd  | 271484| bd  | 670 | bd  |     |     |     |    |    |
| SIMS      | EGB04-R10d | MEU   | Rt1   | M     |     | bd  |     | 2634  | 769 | 84  | 2.1 | 198 | 1046 | 3.4 | 507 |    |
| SIMS      | EGB04-R10d | MEU   | Rt2   | M     | 1.0 |     |     | 2351  | 639 | 72  | 2.2 | 206 | 961  | 4.6 | 504 |    |
| EMP       | EGB04-R10d | MEU   | Rt3   | I     | 40  | 841 | 510 | 4760  | bd  | 4520| 640 |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Rt4   | I     | 90  | 831 | 280 | 5820  | bd  | 4050| 880 |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Rt5   | I     | 70  | 801 | 240 | 6320  | 50  | 1970| 1100|     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Rt6   | I     | 150 | bd  | bd  | 3580  | bd  | 830 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Rt7   | M     | 470 | bd  | bd  | 4892  | bd  | 1720| bd  |     |     |     |    |    |
| SIMS      | EGB04-R10d | MEU   | Ilm1  | M     |     | bd  | 771 | 10    | 0.7 | 0.10| 72  | 0.4 | 348  |    |    |    |
| SIMS      | EGB04-R10d | MEU   | Ilm2  | M     |     | bd  | 751 | 12    | 0.4 | 0.09| 96  | 0.3 | 361  |    |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm3  | M     | 90  | bd  | 58  | 349506| bd  | 430 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm4  | M     | 60  | bd  | bd  | 347311| bd  | 570 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm5  | M     | 30  | bd  | bd  | 348101| bd  | 510 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm6  | M     | 40  | bd  | bd  | 345377| bd  | 300 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm7  | M     | 20  | bd  | bd  | 357262| bd  | 530 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm8  | M     | 110 | bd  | bd  | 348083| bd  | 880 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm9  | I     | 80  | bd  | bd  | 343777| bd  | 570 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm10 | M     | 30  | bd  | 88  | 358461| bd  | 550 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm11 | M     | 50  | bd  | bd  | 338094| bd  | 1140| bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm12 | M     | 60  | bd  | bd  | 341814| bd  | 380 | bd  |     |     |     |    |    |
| EMP       | EGB04-R10d | MEU   | Ilm13 | I     | 40  | bd  | 110 | 342103| bd  | 450 | bd  |     |     |     |    |    |
| EMP       | EGB04-S56 | MEU   | Rt1   | M     | 240 | bd  | 116 | 1153  | 50  | 380 | bd  |     |     |     |    |    |
| EMP       | EGB04-S56 | MEU   | Rt2   | M     | 420 | bd  | 88  | 2493  | bd  | 860 | bd  |     |     |     |    |    |
| EMP       | EGB04-S56 | MEU   | Rt3   | M     | 60  | 659 | 508 | 3590  | 60  | 3920| 1000|     |     |     |    |    |
| EMP       | EGB04-S56 | MEU   | Rt4   | M     | 120 | 407 | 783 | 2948  | 50  | 2550| bd  |     |     |     |    |    |
| Technique | Sample Unit | Grain Text | Si (ppm) | V (ppm) | Cr (ppm) | Fe (ppm) | Zr (ppm) | Nb (ppm) | Sb (ppm) | Hf (ppm) | Ta (ppm) | U (ppm) | T°C |
|-----------|-------------|------------|----------|---------|----------|----------|----------|----------|----------|----------|---------|---------|---|
| EMP       | EGB04-S56   | MEU Rt5    | M        | 90      | 501      | 96       | 3776     | 390      | 1950     | 850      | 680     |         |   |
| EMP       | EGB04-S56   | MEU Rt6    | M        | 120     | 309      | 518      | 2502     | bd       | 1910     | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Rt7    | M        | 110     | bd       | bd       | 15233    | bd       | 290      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Rt8    | M        | 90      | 475      | 454      | 2957     | bd       | 2580     | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Rt9    | M        | 100     | 564      | 679      | 3134     | 60       | 5680     | 400      | 544     |         |   |
| EMP       | EGB04-S56   | MEU Ilm1   | M        | 110     | bd       | bd       | 331241   | bd       | 430      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm2   | M        | 90      | bd       | bd       | 328414   | bd       | 530      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm3   | M        | 50      | bd       | bd       | 353021   | bd       | 90       | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm4   | M        | 140     | bd       | bd       | 340764   | bd       | bd       | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm5   | M        | 40      | bd       | 68       | 334635   | bd       | 440      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm6   | M        | 300     | bd       | bd       | 346037   | bd       | 350      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm7   | M        | 240     | bd       | bd       | 331789   | bd       | 300      | bd       | bd      |         |   |
| EMP       | EGB04-S56   | MEU Ilm7   | M        | 40      | bd       | bd       | 344075   | bd       | 90       | bd       | bd      |         |   |
| SIMS      | EGB04-R11e  | GEU Rt5    | M        | 0.7     |          |          | 88       | 1803     | 112      | 37       | 4.6     | 117     | bd |
| SIMS      | EGB04-R11e  | GEU Rt6    | M        | 511     |          |          | 53       | 1715     | 91       | 47       | 2.6     | 116     | bd |
| SIMS      | EGB04-R11e  | GEU Rt7    | M        | 1675    |          |          | 71       | 1931     | 108      | 57       | 4.5     | 135     | bd |
| SIMS      | EGB04-R11e  | GEU Rt8    | M        | 3.2     |          |          | 79       | 1949     | 92       | 48       | 4.1     | 140     | bd |
| SIMS      | EGB04-R11e  | GEU Rt9    | I        | 225     |          |          | 388      | 2108     | 78       | 36       | 15      | 140     | 2.5 |
| SIMS      | EGB04-R11e  | GEU Rt20   | I        | 19      |          |          | 94       | 2275     | 83       | 22       | 3.2     | 124     | bd |
| EMP       | EGB04-R11e  | GEU Rt1    | M        | 50      | 1045     | 775      | 3246     | 140      | 3050     | 440      | 600     |         |   |
| EMP       | EGB04-R11e  | GEU Rt2    | M        | 20      | 1306     | 579      | 2864     | 50       | 2060     | 510      | 533     |         |   |
| EMP       | EGB04-R11e  | GEU Rt3    | M        | 60      | 905      | 481      | 3199     | bd       | 2480     | 420      | 480     |         |   |
| EMP       | EGB04-R11e  | GEU Rt4    | M        | 40      | 1287     | 461      | 2613     | 70       | 2190     | 370      | 554     |         |   |
| EMP       | EGB04-R11e  | GEU Rt5    | M        | 40      | 1012     | 449      | 2939     | bd       | 1980     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt6    | M        | 130     | 1260     | 600      | 3413     | 80       | 5150     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt7    | M        | 180     | 1161     | 564      | 2781     | bd       | 1930     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt8    | M        | 100     | 527      | 293      | 2846     | 70       | 2020     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt9    | M        | 140     | 1228     | 423      | 3013     | 60       | 1910     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt10   | M        | 280     | 1464     | 317      | 2288     | bd       | 1990     | 450      | 447     |         |   |
| EMP       | EGB04-R11e  | GEU Rt11   | M        | 410     | 960      | 650      | 2860     | 50       | 2090     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt12   | M        | 510     | 1420     | 820      | 2310     | bd       | 2180     | bd       | bd      |         |   |
| EMP       | EGB04-R11e  | GEU Rt13   | M        | 130     | 1560     | 690      | 2270     | 80       | 2320     | 380      | 562     |         |   |
| EMP       | EGB04-R11e  | GEU Rt14   | M        | 180     | 1230     | 750      | 2440     | bd       | 1930     | bd       | bd      |         |   |
| SIMS      | A15c        | GEU Rt1    | M        |         |          |          | 103      | 2578     | 3207     | 219      | 5.8     | 224     | 1110 |
| SIMS      | A15c        | GEU Rt5    | M        |         |          |          | 151      | 2308     | 2835     | 122      | 15      | 210     | 1085 |
| EMP       | A15c        | GEU Rt1    | M        | 21      | 421      | 247      | 4138     | 117      | 2819     | 1228     | 587     |         |   |
| EMP       | A15c        | GEU Rt1    | M        | 36      | 376      | 267      | 4585     | 115      | 2800     | 1058     | 587     |         |   |
| EMP       | A15c        | GEU Rt2    | I        | 550     | 282      | 5212     | 58       | 2461     | 734      | 542     |         |   |
| EMP       | A15c        | GEU Rt3    | I        | 1.1     | 1347     | 459      | 4571     | 148      | 2504     | 676      | 604     |         |   |
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