

Dating multiply overprinted Sn-mineralized granites—examples from the Erzgebirge, Germany

Rolf L. Romer · Rainer Thomas · Holly J. Stein ·
Dieter Rhede

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Abstract Granites and primary tin mineralization in the Erzgebirge were dated using (1) conventional U–Pb dating of uraninite inclusions in mica, (2) Rb–Sr dating of inclusions in quartz that represent highly evolved melts, (3) Re–Os dating of magmatic–hydrothermal molybdenite, and (4) chemical Th–U–Pb dating of uraninite. Conventional isotope dilution and thermal ion mass spectrometry and chemical Th–U–Pb dating of uraninite in granites from the Ehrenfriedersdorf mining district provide ages of 323.9 ± 3.5 Ma (2σ ; Greifenstein granite) and 320.6 ± 1.9 and 319.7 ± 3.4 Ma (2σ , both Sauberg mine), in agreement with U–Pb apatite ages of 323.9 ± 2.9 and 317.3 ± 1.6 Ma (2σ , both Sauberg mine). Rb–Sr analysis of melt inclusions from Zinnwald gives highly radiogenic Sr isotopic compositions that, with an assumed initial Sr isotopic composition, permit calculation of precise ages from single inclusions. The scatter of the data indicates that some quartz-hosted melt inclusions have been affected by partial loss of fluid exsolved from the melt inclusion. Re–Os dating of two molybdenite samples from Altenberg provides ages of 323.9 ± 2.5 and 317.9 ± 2.4 Ma (2σ). Together with age data from the literature, our new ages demonstrate that primary

tin mineralization and the emplacement of the large Sn-specialized granites in the Erzgebirge fall in a narrow range between 318 and 323 Ma. Primary Sn mineralization occurred within a short interval during post-collisional collapse of the Variscan orogen and was essentially synchronous over the entire Erzgebirge. In contrast to earlier claims, no systematic age difference between granites of the eastern and western Erzgebirge was established. Furthermore, our data do not support a large age range for Late-Variscan granites of the Erzgebirge (330–290 Ma), as has been previously suggested.

Keywords U–Pb · Rb–Sr · Re–Os · Uraninite · Mineral inclusion · Melt inclusion · Molybdenite · Erzgebirge

Introduction

The emplacement age of magmatic rocks may be obscured by later overprinting of the rocks by metamorphism, deformation, and fluid–rock interaction. In particular, magmatic rocks that are mineralized or that have exploited tectonic disturbances during emplacement may have been multiply disturbed during redistribution of metals or later reactivation along zones of weakness. For instance, the Rb–Sr isotope systematics of granites from the Erzgebirge shows anomalously low apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g., Gerstenberger 1989) that are due to an increase in $^{87}\text{Rb}/^{86}\text{Sr}$ some time after emplacement and crystallization of the granites. Similarly, monazite crystals from multiply reworked magmatic and metamorphic rocks may show highly heterogeneous ages among crystals from the same rock or even within single crystals, which could be due to either selective local Pb loss or the presence of several generations of monazite. Highly evolved granites may

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R. L. Romer (✉) · R. Thomas · D. Rhede
GeoForschungsZentrum Potsdam, Telegrafenberg,
14473 Potsdam, Germany
e-mail: romer@gfz-potsdam.de

H. J. Stein
AIRIE Program, Department of Geosciences,
Colorado State University,
Fort Collins, CO 80512-1482, USA

H. J. Stein
Geological Survey of Norway,
7491 Trondheim, Norway

prove problematic for zircon dating using U–Pb, as zircon in such rocks commonly has high U contents [several thousand parts per million (ppm)] and, thus, becomes metamict within a short time, allowing the U–Pb system to be readily disturbed during thermal overprint or interaction with fluids and brines (e.g., Geisler and Schleicher 2000; Kurz 2000). Different chronometers may result in a wide range of conflicting ages. For instance, dating of Late-Variscan granites of the Erzgebirge yields an age range of ~50 million years (e.g., Kempe et al. 2004). This uncertainty in dating magmatic rocks that are associated with magmatic, pneumatolytic, or hydrothermal mineral deposits inhibits the construction of reliable models for ore deposit formation, including the process of mobilization, transport, and metal deposition. A proper geologic model is essential for efficient exploration. Poor age constraints result in poor exploration models.

In this paper, we report comprehensive dating approaches to overcome these sample-specific issues using U–Pb and Rb–Sr dating of inclusions and Re–Os dating of molybdenite. For inclusions, the essential points are:

1. The host mineral represents a container that prevents the inclusion from exchanging the geochronologically relevant elements (parent and daughter) with its external surroundings and, thus, keeps the system closed.
2. The high content of the parent element in the inclusion, with time, eventually results in a highly radiogenic daughter element composition that renders any uncertainties about the initial isotopic composition of the system irrelevant.
3. The inclusion has much higher affinity for parent and daughter element than the host mineral (even if the overall compatibility of the daughter element should be low), i.e., the distribution coefficients K_D for the geochronologically relevant elements between inclusion and host are high, implying no exchange of the geochronologically relevant elements between inclusion and host, even during reheating and recrystallization.
4. In addition for the U–Th–Pb system, the host receives and retains a portion of the α -recoiled U-daughters and prevents their loss, which is important to maintain a closed geochronologic system—the smaller the inclusion (or crystal), the more critical is the role and analysis of the container (cf. Kigoshi 1971; Ludwig 1978; Romer 2001, 2003).

For the Re–Os system in molybdenite, the essential point is that practically all Re (hence, radiogenic Os) remains in the molybdenite, as typical hosting silicate phases do not accept Re and Os. Thus, even if Os is relatively incompatible in molybdenite (especially in comparison to Re), its accumulation and even its redistribution within older

molybdenite does not result in any significant loss of Os from molybdenite (Stein et al. 2001, 2003). Therefore, if the analyzed molybdenite sample is large enough or involves individual grains, grain-internal redistribution of Os is overcome and the Re–Os system in molybdenite remains closed at the scale of the dated sample (Stein et al. 2001, 2003; Selby and Creaser 2004; Stein 2006).

The above outlined dating approaches are used to determine the age of granites and granite-related tin mineralization in the Erzgebirge, Saxony (Germany). By analyzing U–Th-rich inclusions by isotope dilution and thermal ion mass spectrometry (ID-TIMS) and electron microprobe, we additionally demonstrate that samples fulfilling the requirements for conventional wet-chemical U–Pb dating of inclusions can be correctly dated using the electron microprobe. Furthermore, we discuss the requirements and limitations of our analytical approaches, and in the final section, we compile our new and published age data for Late-Variscan granites and discuss the age constraints for tin mineralization in the Erzgebirge metallogenic province.

Late-Variscan magmatism in the Erzgebirge

The granites in the Erzgebirge were emplaced into Early Paleozoic metamorphic basement at a relatively shallow level ($P \leq 200$ MPa) according to isochores on primary fluid inclusions and water concentrations in melt inclusions (e.g., Thomas 1989; Thomas and Klemm 1997). $^{40}\text{Ar}/^{39}\text{Ar}$ dating of white mica from granulite and eclogite facies metamorphic rocks in the Erzgebirge yields ages between 340 and 330 Ma (e.g., Werner and Lippolt 2000). The youngest ages for metamorphism of the wall rocks at 330 Ma (Werner and Lippolt 2000) constrain the maximum age for emplacement of the Late-Variscan granites. Earlier age determinations on these granites include K–Ar WR/mica ages (Haake 1972), Rb–Sr WR ages (Gerstenberger et al. 1983), U–Pb TIMS ages on monazite (Warkus 1997), and Th–U–Pb chemical ages on uraninite, monazite, and xenotime (Förster et al. 1999). Zircon from most Late-Variscan granites of the Erzgebirge shows complex chemical zoning and abundant evidence for alteration (Förster et al. 1999; Förster 1998, 2001; Thomas et al. 2006) and may, to a large part, also be inherited from the protoliths, which makes this mineral unattractive for dating. Therefore, there are essentially no credible U–Pb zircon ages. The K–Ar ages are problematic, as they spread over a range of ca. 50 million years and imply two events of granite magmatism and Sn–W mineralization. One group of K–Ar ages for these post-metamorphic granites falls in the range between 354 and 336 Ma. K–Ar systems yielding these ages are disturbed as they are older than the possible maximum age given by ultrahigh-pressure metamorphism and exhumation of the Erzgebirge. The younger

group of K–Ar ages (311 to 300 Ma), possibly also disturbed, is generally interpreted to date a younger phase of granite emplacement with a close genetic relation to the skarn and greisen mineralization, dated at 293 to 302 Ma, at the margins of the granite (cf. Hösel 1994). A younger age for the Sn mineralization has also been advocated by Nasdala et al. (1998), based on a $^{206}\text{Pb}/^{238}\text{U}$ sensitive high-resolution ion microprobe (mass spectrometer) age of 278 ± 5 Ma for zircon from a rhyolite (some 30 km north of Ehrenfriedersdorf) that because of its relatively high Sn content, has been correlated genetically with the Sn granites in the Erzgebirge (e.g., Kempe et al. 2004).

Rb–Sr WR ages fall in a broad range from ca. 328 to 290 Ma (e.g., Gerstenberger et al. 1982, 1983, 1995), apparently supporting subdivision of the granites into an older and younger group. It should be noted, however, that some of these ages are based on isochrons that are defined by rocks from several intrusions or that show anomalously low initial $^{87}\text{Sr}/^{86}\text{Sr}$ values. TIMS and chemical U–Pb ages obtained on granites from the eastern (Niederbobritsch), central (Pobershau), and western (Kirchberg, Eibenstock, Bergen) Erzgebirge (Warkus 1997; Förster et al. 1999) fall in a relatively narrow range (325–316 Ma) that agrees well with the U–Pb zircon ages for granites of comparable setting and chemistry in the western continuation of the Erzgebirge (i.e., Fichtelgebirge, Oberpfalz, and Bavarian Forest) that range from 326 to 320 Ma (cf. Carl and Wendt 1993; Chen et al. 2003; Siebel et al. 2003).

Sample locations

Ehrenfriedersdorf

In the Ehrenfriedersdorf–Geyer area (80 km southwest of Dresden, Fig. 1), Late-Variscan granites intruded post-Cadomian paragneisses, mica–schists, and phyllites (cf. Oelsner 1952; Tichomirowa et al. 2001). Several smaller cupolas of the Ehrenfriedersdorf granite have received local names, among others the Greifenstein and Sauberg granites investigated here. Closely associated with these granites is extensive, high-temperature Sn-mineralization in skarns, pegmatites, greisens, and pneumatolytic–hydrothermal vein deposits. Recurrent attempts, to date, of the Ehrenfriedersdorf granite and its associated Sn-mineralization yield ages ranging from 327 ± 5 to 291.3 ± 2.3 Ma (Gerstenberger et al. 1983, 1995). We prepared samples for U–Pb dating from two hand specimens that show no macroscopic or microscopic evidence of metasomatic overprint. The first hand specimen is a fresh, light-red to light-brown granite (Greifenstein); the second sample is from a melt pocket hosted by the stockscheider pegmatite in the Sauberg tin mine (Ehrenfriedersdorf). The granite is dominated by

quartz, alkali–feldspar, plagioclase ($< \text{An}_{12}$), and up to 5 vol.% Li–mica. Accessory minerals include topaz, cassiterite, zircon, monazite, xenotime, uraninite, apatite, tourmaline, and Sn-rich pyrrhotite. Melt inclusions in accessory topaz indicate this mineral is magmatic and did not form during pneumatolytic or hydrothermal overprinting. High Sn contents (up to 800 ppm) in melt inclusions in quartz demonstrate that the granite is closely related to the formation of associated Sn deposits (Thomas et al. 2003). The second sample, from a $2\times 10\times 10$ -m pegmatite body, is located in the endocontact of the Sauberg granite (Sauberg mine), which hosts a Sn–W deposit. The pegmatite consists of quartz, orthoclase, albite, muscovite, and Li-bearing mica, with minor topaz, cassiterite, beryl, fluorapatite, and other rare phosphates. Boron-bearing minerals include tourmaline, boron-rich mica, and alkali feldspar, as well as borax in the interstitial space between cassiterite crystals. Within the stockscheider pegmatite, centimeter- to decimeter-scale pockets of a fine-grained peraluminous rock displaying unidirectional solidification textures consisting mainly of feldspar, quartz, and mica are observed. These isolated pockets, separated from it by large K–feldspar crystals, are interpreted as quenched and crystallized melt (see Thomas et al. 2000, 2003). Accessory minerals, such as uraninite (up to 30 μm in diameter), monazite, xenotime, zircon, and cassiterite, are related to the peraluminous melt evolution of these pockets and remained largely unaltered by pervasive, post-pegmatite hydrothermal fluids (Thomas et al. 2006). The radioactive elements U and Th are predominantly hosted in tiny crystals of zircon, uraninite, monazite, and, less commonly, xenotime (Thomas 1989; Förster 1998; Förster et al. 1999). These crystals are readily recognized by their distinctive pleochroic halos in the mica host (Fig. 2a). Although the pleochroic halos make identification of datable minerals straightforward, the small size of these crystals makes mechanical separation difficult and, in many cases, undesirable as they are likely to have experienced loss of daughter isotopes by α -recoil.

Light blue, purple, and green apatite crystals occur in small pockets in the Sauberg mine and the Greifenstein granite. Apatite marks the end of the pneumatolytic–hydrothermal cassiterite stage of the lode/greisen Sn deposit at Ehrenfriedersdorf. Apatite formed between main- and late-stage cassiterite, which is also verified by homogenization temperatures. The homogenization temperature (T_{H}) for main-stage cassiterite from the Ehrenfriedersdorf deposit is $383\pm 11^\circ\text{C}$, whereas for late-stage cassiterite, the temperature is $292\pm 4^\circ\text{C}$ (Thomas 1982; Thomas et al. 2003). Apatite samples used for dating show homogenization temperatures between the values of the two cassiterite generations (greenish apatite-2: $T_{\text{H}}=365\pm 5^\circ\text{C}$, $n=10$; blue apatite-1: $T_{\text{H}}=309\pm 5^\circ\text{C}$, $n=10$; blue apatite-0: $T_{\text{H}}=300\pm 6^\circ\text{C}$, $n=30$; purple apatite: $T_{\text{H}}=289\pm 3^\circ\text{C}$). The purple apatite is

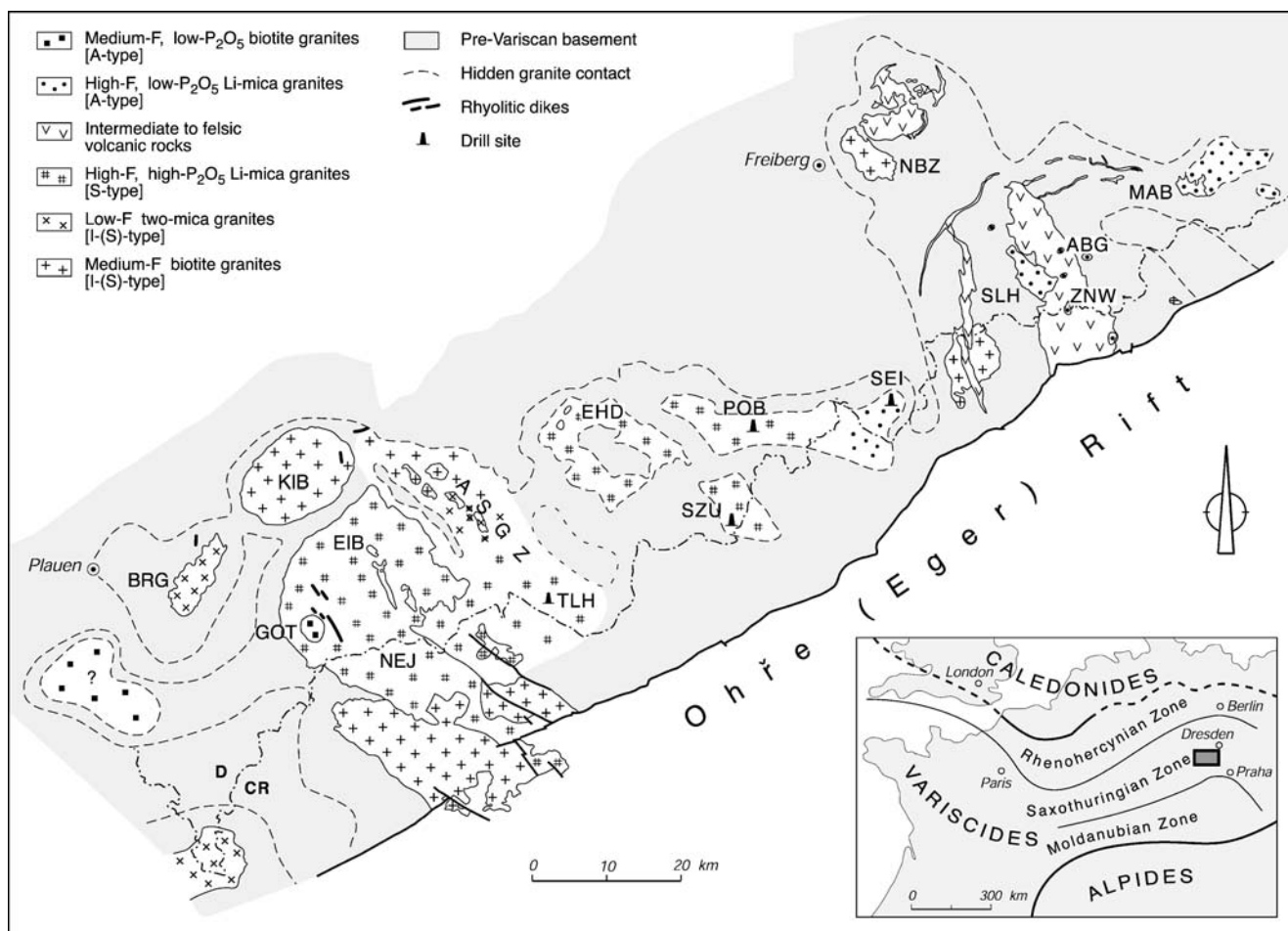


Fig. 1 Simplified map of the Erzgebirge showing the occurrence of Late-Variscan granites (after Förster 1999). Samples were dated from the Greifenstein granite and the Sauberg Mine (both in the Ehrenfriedersdorf district, EHD), and the granites at Zinnwald (ZNW), and Altenberg (ABG). Granites marked with a drilling symbol do not have surface outcrops and are only known from exploration drilling. Dashed lines correspond to subsurface granite extent known

from mining and exploration drilling (*inner line*) or gravity (*outer line*). ABG Altenberg, ASGZ Aue-Schwarzenberg Granite Zone (including, among others, Bernsbach, Beierfeld, and Schlema), BRG Bergen, EHD Ehrenfriedersdorf, EIB Eibenstock, GOT Gottesberg, KIB Kirchberg, MAB Markersbach, NEJ Nejdek, NBZ Niederbohritzsch, POB Pöbershau, SEI Seiffen, SLH Schellerhau, SZU Satzung, TLH Tellerhäuser, ZNW Zinnwald

unique in its high content of Li_2CO_3 (1.5 wt%) and a NaCl equiv. of 5.6 wt% in fluid inclusions. Because the hydrothermal apatite crystals are younger than the magmatic Li-micas, the apatite U–Pb age represents a minimum estimate for the age of the uraninite inclusions in mica and is used to demonstrate that the U–Pb ages obtained for the inclusions are sound. The ages of apatite and uraninite bracket the main-stage cassiterite mineralization. Furthermore, the age of apatite provides a maximum age for late-stage cassiterite.

Zinnwald

The investigated pale pinkish gray fine-grained porphyritic topaz–albite granite sample (TH212) is associated with the Variscan Sn–W mineralization at Zinnwald. It contains about 30 vol% phenocrysts of up to 5-mm large smokey quartz and albite, orthoclase, and various Li-micas and muscovite crystals. The fine-grained groundmass is com-

posed mainly of quartz, orthoclase, albite, micas, and topaz. Accessory magmatic phases include fluorite, rutile, cassiterite, zircon, xenotime, monazite, and pyrochlore. Quartz crystals from topaz–zinnwaldite–albite granites at Zinnwald contain abundant recrystallized silicate-melt inclusions (Fig. 2b), with diameters up to 200 μm (Thomas et al. 2005). The melt inclusions selected for Rb/Sr dating are characterized by very high concentrations of trace and ore-forming elements. Some melt inclusions contain (in parts per million) >800 Sn, >1,100 Nb, >450 Mo, >8,800 Rb, and >4,800 Cs, as well as a few tens of parts per million of Ta and W (see Thomas et al. 2005).

Altenberg

The Sn–(W–Mo) deposit at Altenberg, in the eastern Erzgebirge, is located about 40 km south of Dresden. Most of the tin was produced from small veins in an extensive

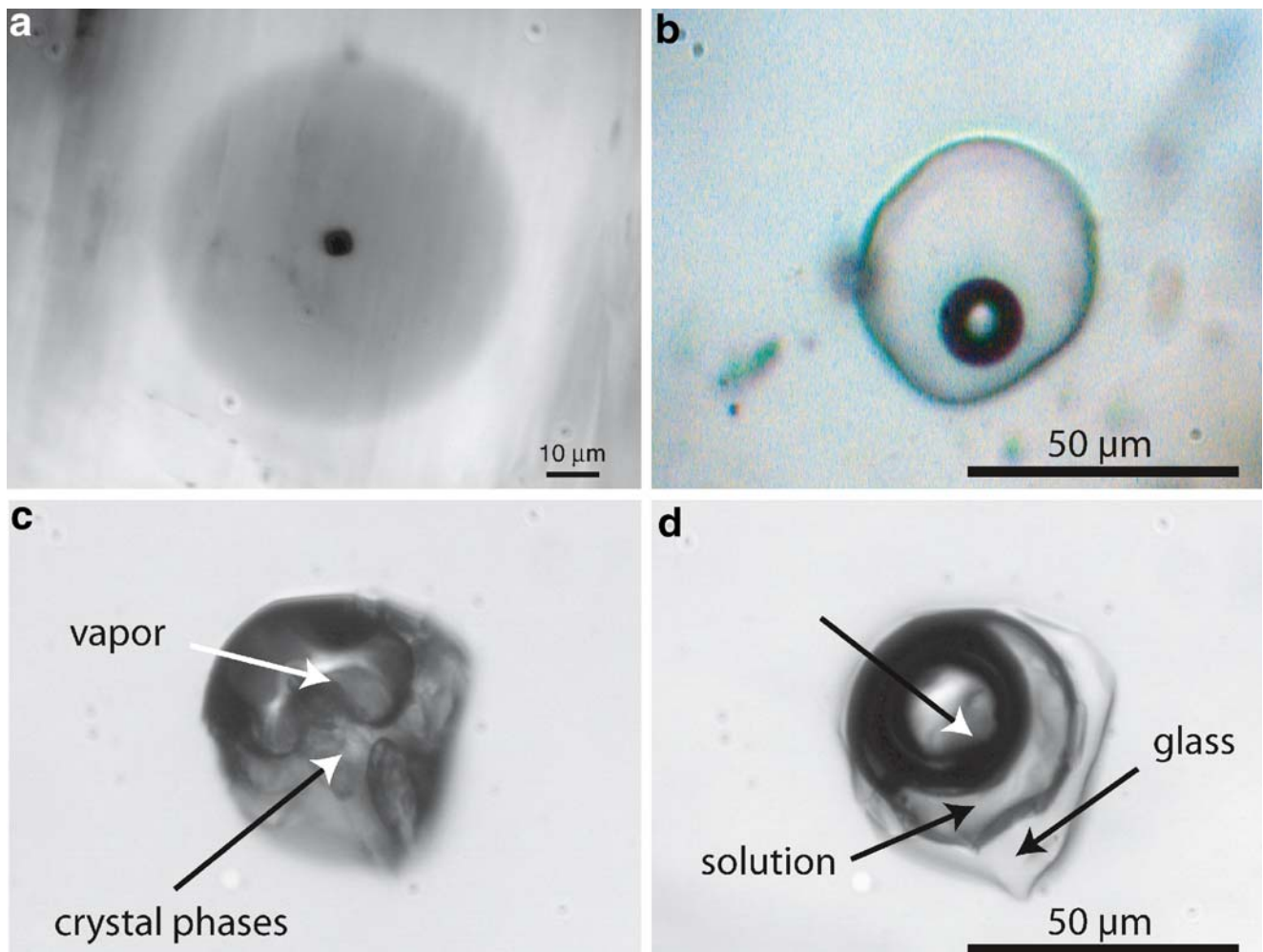


Fig. 2 **a** Typical uraninite inclusion in Li-bearing dark mica (Lisiderophyllite to protolithionite) with pleochroic halo. The pleochroic halo is caused by emission of α -particles and their interaction with ions in the crystal lattice. Since α -particles are much lighter than the recoiled nuclei, they travel for a larger distance into the crystal and interact to a lesser extent than recoiled ions with the ions in the crystal lattice. For instance, α -particles associated with the ^{238}U , ^{235}U , and ^{232}Th decay series travel 9.9 to 29.5 μm in zircon, depending on the energy of the decay (cf. compilation of Nasdala et al. 2001). Thus, the volume of recoil implantation is several orders of magnitude smaller

than the halo of radiation damage. **b**. Melt inclusion in quartz from Zinnwald after rehomogenization at 920°C, ambient pressure, and 20 h. **c, d** Typical volatile-rich type-B melt inclusion in pegmatite quartz. Note that these melt inclusions are from Ehrenfriedersdorf, whereas the analyzed melt inclusions are from Zinnwald (Thomas et al. 2000) **c** Melt inclusion in quartz at room temperature before rehomogenization. **d** Melt inclusion in quartz after rehomogenization at 700°C, 1 kbar, and 20 h using standard cold-seal pressure vessel experiments

zone of greisen alteration (quartz±muscovite±topaz), spatially associated with a monzogranite stock and an underlying albite granite body (Breiter and Seltmann 1995; Baumann et al. 2000). The paragneiss–orthogneiss basement complex hosts various leucogranite intrusions described as associated with the Altenberg–Teplce caldera (Seltmann et al. 2001; Müller et al. 2005). From the Sn–(W–Mo) deposit at Altenberg, two molybdenite samples were obtained for Re–Os dating.

Previous age determinations for the Altenberg area include $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Seltmann and Schilka 1995) and single zircon $^{207}\text{Pb}/^{206}\text{Pb}$ evaporation ages (Kempe et al. 1999). $^{40}\text{Ar}/^{39}\text{Ar}$ dating of hornblende, biotite, and potas-

sium feldspar from three Altenberg granite porphyry samples yields ages of 309–307 Ma, when argon loss portions of the release pattern are omitted (Seltmann and Schilka 1995). The biotite ages were interpreted to represent closure ages for biotite associated with the granite porphyry. The K–feldspar ages trail behind at 300–290 Ma and were interpreted as the age of greisen-related tin mineralization in the eastern Erzgebirge (Seltmann and Schilka 1995). Müller et al. (2005) mentions an amphibole K–Ar age of 297 ± 13 Ma for Altenberg. Zircon $^{207}\text{Pb}/^{206}\text{Pb}$ evaporation ages of 290 ± 5 and 333 ± 8 Ma for the Altenberg granite porphyry are reported (Kempe et al. 1999). The older zircon age was interpreted by Kempe et al.

(1999) as the emplacement age for the of the Altenberg granite porphyry, whereas the younger zircon age of 290 Ma was taken as the age of greisenization and tin mineralization in the region. Thus, Kempe et al. (1999) interpreted these zircon $^{207}\text{Pb}/^{206}\text{Pb}$ evaporation ages as evidence for the presence of two separate magmatic events.

Philosophical approach in dating inclusions

Dating magmatic rocks with multiple overprinting events such as deformation, fluid ingress, and repeated mineralization is highly problematic as most samples carry the imprint of more than one geologic event, i.e., the magmatic emplacement and some memory of one or more subsequent disturbances. On the small scale, these rocks may still retain domains where textural evidence demonstrates a primary magmatic mineral assemblage. Minerals extracted from these domains would yield the emplacement age of the magmatic rock, independent of its later history. Many minerals in these texturally primary domains, however, represent geochronologically open systems either because of their small size or because of their high reactivity. For instance, uraninite may be an open system with respect to U–Th–Pb dating because of Pb loss due to α -recoil (cf. Ludwig 1978; Mattinson 1994; Romer 2003; Romer and Rocholl 2004), Pb migration on the microscale, and reaction of the mineral with fluids, all of which may result in heterogeneous apparent ages on the scale of individual grains. These dating problems may be overcome if small and chemically reactive minerals are entirely enclosed by one single, fracture-free host mineral that acts as barrier or container for material exchange between the dated mineral and its further surroundings (e.g., Romer and Thomas 2005). This approach of analyzing inclusion and host together is not restricted to minerals, but may also be applied to fluid or melt inclusions (e.g., Pettke and Diamond 1995; Christensen and Halliday 1996) and their containers. Similarly, if the chemical element of the daughter isotope is highly incompatible in its immediate host and migrates within that host, analyzing entire grains rather than small subvolumes (e.g., electron microprobe or laser ablation spot) may overcome the problem of migration-induced daughter dispersion and, concomitantly, variation in apparent age. In the following, we test this approach using U-rich mineral and melt inclusions, as well as molybdenite. There are basically three requirements that must be fulfilled for inclusions to be attractive for dating: (1) demonstrably closed system, (2) strong parent-to-daughter fractionation, and (3) high parent contents. To ensure that the closed system is maintained during sample handling, the inclusions should be analyzed together with

their host. Whereas this point seems trivial for fluid and melt inclusion (the latter may exsolve fluids during recrystallization), it also should be applied to U–Pb dating of minerals where daughter isotopes have been implanted into the host mineral (cf. discussion in Romer and Thomas 2005). The parent and daughter budget of the host should be very low so that there are no significant inherent contributions of these elements to the bulk analysis of parent–daughter.

1. Closed-system behavior requires that neither the parent nor the daughter isotope is lost from or added to the inclusion. For instance, a single, fracture-free host prevents the inclusion from interaction with migrating fluids. However, such a host does not guarantee closed-system behavior of the inclusion relative to its host. The host also must prevent loss through diffusion, which is dependent not only on the temperature, diffusivity of the considered element, cooling history of the sample, and distance to the inclusion–host surface, but also on potential transport away from the surface of the inclusion. Significant transport, beyond the co-analyzed inclusion plus host, would affect the age. If a host cannot accommodate ions lost from the inclusion, these ions will concentrate on the surface of the inclusion and help to shield additional loss from the inclusion. An example of an inclusion that remained a closed system at high temperature has been presented by Kühn et al. (2000). These authors showed that biotite in Sveconorwegian granulite-facies garnet recorded and retained the age information for the older Sveconorwegian event rather than the Caledonian eclogite-facies overprint. In a similar way, melt inclusions that crystallize and eventually consist of crystals, glass, and fluid (Fig. 2) represent a heterogeneous system with parent-to-daughter fractionation occurring among the various phases. Still, a closed system may be maintained at the scale of the inclusion if the host does not exchange with the inclusion.
2. Inclusions must have high parent-to-daughter ratios to allow the daughter to develop a highly radiogenic composition with time. This is important for the following reason: It may not be possible to accurately determine the initial isotopic composition of the daughter element for multiply overprinted and altered rocks. At best, the initial value may be estimated (assumed) within a reasonable range. For instance, to calculate an age based on the Sr isotopic composition (and the Rb and Sr contents) for a single melt inclusion, a correction is needed for initially present radiogenic Sr. The more radiogenic the measured Sr isotopic composition, the less important is the uncertainty in the assumed or estimated isotopic composition of the

initially present Sr. Thus, for measured Sr isotopic compositions that are extremely radiogenic, even a poorly known initial Sr isotopic composition permits an accurate age determination at high precision. Materials that typically contain high Rb/Sr (parent/daughter) ratios include micas (biotite, phlogopite, muscovite, lepidolite) and highly evolved granite melts. Favorable host minerals are those with very small contents of both parent and daughter elements.

3. The concentration of the parent isotope (and the age) is a controlling factor for good analytical results. Analytical uncertainties originating from counting statistics depend on signal intensity. To obtain small analytical uncertainties, the signal has to be strong, i.e., many ions have to be available for counting. For small inclusions to yield high signal intensities, the amount of the produced daughter isotope(s) has to be high, which depends directly on the concentration of the parent isotope and the passing of geologic time. Thus, for an optimal analytical result, the content of the parent element and the concentration ratio between parent and daughter element have to be high.

For the U–Pb system, the situation is additionally complicated by α -recoil. The preservation of impulse requires that the emission of an α -particle recoils the nucleus some 200 to 350 Å, depending on the surrounding mineral, the mass of the nucleus, and the energy of the emitted particle (e.g., Matzke 1982; Ziegler et al. 1985). Displacement of the daughter isotope by α -recoil results in an open system at the nanoscale. Whether or not this inherent open-system behavior affects U–Pb dating depends on the distribution of Th and U and on sample size (Romer 2003). For samples with homogeneous U and Th distribution and a grain size that is large (e.g., >10–20 μm , Kigoshi 1971; Holliger et al. 1989) in comparison to the recoil distance, the U–Pb age will generally not be affected, unless with time metamictization approaches a level, where mobility of parent and daughter isotopes becomes possible. For samples with heterogeneous small-scale U and Th distribution, however, U–Pb dating may result in anomalous $^{207}\text{Pb}_{\text{rad}}/^{206}\text{Pb}_{\text{rad}}$ and scattered $^{206}\text{Pb}_{\text{rad}}/^{238}\text{U}$ and $^{207}\text{Pb}_{\text{rad}}/^{235}\text{U}$, yielding normal and reverse discordance when selective dissolution or step-leaching procedures access domains <1 μm wide (e.g., Mattinson 1994; Corfu 2000; Romer 2003). For material with short distances to pathways for fast transport, a deficit or excess of ^{206}Pb due to preferential loss or gain of the relatively long-lived intermediate daughters ^{222}Rn and ^{226}Ra may cause additional problems (e.g., Ludwig 1978; Romer 2001).

For spatially highly resolved analysis, grain internal redistribution of the daughter element may present a problem that results in spurious ages. Some sections of

the mineral may yield ages that are too old, whereas other sections may yield ages that are too young. Furthermore, these ages may differ from bulk analyses of individual grains by TIMS. Grain internal redistribution of the daughter element is likely to be problematic if large amounts of the daughter are present or the daughter element is highly incompatible in the dated mineral. The first case may occur for minerals where the radioactive parent is a major constituent of the mineral. For instance, uraninite accumulates Pb through time at the percent level (a 300 million years old uraninite contains about 3.5 wt% Pb) that eventually may collect in subsequently forming galena with uraninite (e.g., Janeczek and Ewing 1995; Finch and Murakami 1999). The uraninite eventually would contain less Pb than expected from its age, i.e., yield a too young apparent Pb/U age. It is easy to demonstrate the effect of Pb mobilization in uraninite with the development of a new phase that can be detected by elemental mapping using an electron microprobe (Pb contents should otherwise be heterogeneous within uraninite). Daughter element mobility may be difficult to assess, however, if the daughter element does not form a phase on its own. For instance, redistribution of Pb in monazite or xenotime may result in domains of contrasting Pb contents and contrasting Pb/U ages. Since such age heterogeneities may also arise from geological disturbances, daughter element redistribution may in some cases go unrecognized and meaningless ages may be unduly interpreted as representing geological events.

Similar age heterogeneities produced by parent–daughter decoupling were recognized early on in the development of the Re–Os chronometer for molybdenite (Stein et al. 2001). Os is highly incompatible in molybdenite, but remains associated with molybdenite as it is completely incompatible in silicate minerals. Grain-internal redistribution of Os, resulting in a kind of nugget effect, decouples parent and daughter isotopes in molybdenite, particularly molybdenite with a deformational or metamorphic overprint (Stein et al. 2003). As a result, micron-scale laser ablation inductively coupled plasma mass spectrometry dating of molybdenite has been shown to yield a wide range of meaningless ages (Stein et al. 2001, 2003; Kosler et al. 2003; Selby and Creaser 2004), whereas isotope dilution and negative thermal ion mass spectrometry (ID-NTIMS) dating of single silicate-hosted molybdenite grains at milligram to submilligram sizes yields robust Re–Os ages.

Analytical methods and results

The ID-TIMS work for U–Pb, Rb–Sr, and Sm–Nd, and the electron microprobe work were done at GeoForschungs-Zentrum (GFZ) Potsdam. The analytical setup is described in Romer (2001), Romer et al. (2005), and Rhede et al.

(1996). Additional details, specifically concerning the operating conditions of the mass spectrometers and the electron microprobe, are given in Tables 1, 2, 3, 4, and 6. The ID-NTIMS work for Re–Os dating was performed under the AIRIE Program (Colorado State University) and is described in detail in Stein et al. (2003) and Stein (2006), with the analytical details pertinent to this study presented in Table 5.

For U–Pb dating of U-rich mineral inclusions in mica, two different approaches were used. In a first series, Li–mica flakes were separated from polished 500- μm thick thin sections. Mineral inclusions in the mica included uraninite, xenotime, and monazite. The complete dissolution of host and inclusions was expected to represent a closed U–Pb system despite redistribution of daughter isotopes between inclusions and host. The dissolution of the mica in HF also dissolves the uraninite inclusions, whereas the xenotime and monazite inclusions may remain undissolved. The presence of undissolved monazite and

xenotime inclusions produces an excess of radiogenic Pb in the host phase, i.e., yields reversely discordant data. To obtain a closed U–Pb system for xenotime and monazite inclusions, the residue may preferentially be separated from the solution and dissolved in a second step, using concentrated H_2SO_4 , and then recombined with material from the first dissolution. A major problem of this approach might be that the tiny phosphates could be lost during the separation of the residues from the acid. In this study, no samples have been passed through this selective dissolution procedure.

In a second series, the samples were drilled from a polished thick section using a Kunzmann WF 4 CNC tool milling machine at GFZ Potsdam. The purpose of this modification was to reduce the amount of host mineral present in the sample. Our smallest sample diameter was 450 μm for mica hosting uraninite. Further reduction of sample size may not be advisable as too small of a drill core diameter may result in fragmentation of the drill core along

Table 1 U–Pb analytical results for uraninite and xenotime/monazite inclusions in biotite from the Greifenstein granite and a melt pocket in the stockscheider pegmatite in the Sauberg Mine (both in the Ehrenfriedersdorf tin district), Erzgebirge, Germany

Sample ^a	Content (ng)		Pb composition ^b					Atomic ratios ^b			Apparent ages (Ma) ^c		
	U	Pb	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{238}\text{U}}{^{204}\text{Pb}}$	$\frac{^{232}\text{Th}}{^{238}\text{U}}$	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$
Greifenstein granite													
1 Uraninite	5,890	811	58.392	17.631	65.189	775	2.1	0.05201	0.36292	0.05059	327	314	222
2 Uraninite	13,100	4,620	29.540	16.195	45.374	223	2.0	0.05147	0.37406	0.05270	324	323	316
3 Uraninite	24,700	3,050	69.398	18.260	55.349	998	1.1	0.05144	0.36893	0.05201	323	318	286
4 Mona	11,000	3,240	62.817	17.965	56.976	403	1.3	0.11099	0.81193	0.05305	679	604	331
5 Mona	22,300	7,950	45.616	17.033	50.248	273	1.4	0.10090	0.72876	0.05238	620	556	302
6 Xeno	11,500	3,110	52.350	17.386	41.114	355	0.3	0.09658	0.69764	0.05238	594	537	302
7 Mona	21,800	5,110	53.518	17.425	59.629	481	1.9	0.07366	0.52562	0.05174	458	429	274
8 Xeno	7,450	4,770	44.896	17.019	43.933	144	0.7	0.18604	1.3660	0.05325	1100	875	339
Melt pocket in stockscheider pegmatite, Sauberg Mine													
9 (1655)	0.15	380	19.621	15.669	38.270	13.2							
10 (1658)	9,820	1,070	57.062	17.618	39.429	768	2.2	0.05877	0.36680	0.05229	320	317	298
11 (1660)	39,400	1,730	3146.5	180.78	84.897	61700	0.1	0.05073	0.36936	0.05281	319	319	320
12 (1662)	1,010,000	5,420	891.51	61.832	49.773	16100	0.2	0.05411	0.39505	0.05296	340	338	327
13 (1663)	582,500	4,770	111.54	20.514	40.347	1821	1.2	0.05132	0.37358	0.05279	323	322	320
14 (1665)	3,070	3,680	23.233	15.869	38.461	56.1							
15 (1667)	2,290	2,030	23.375	15.845	38.419	76.2							
16 (1651)	5,500	1,140	30.918	16.332	38.988	360							
17 (1652)	33,400	2,620	103.17	20.092	39.451	1795	1.2	0.04737	0.34638	0.05303	298	302	330
18 (1656)	4,760	2,340	22.707	15.849	38.446	136							
19 (1659)	2,900	1,560	23.720	15.863	38.526	126							
20 (1661)	101,100	6,260	198.31	25.129	42.469	3710	0.7	0.04858	0.35388	0.05298	306	309	328

^a All samples were cleaned using 7 N HNO_3 , H_2O , and acetone. The fragments were transferred in screw-top teflon vials; a ^{205}Pb – ^{235}U mixed tracer and HF were added. The samples were dissolved on the hot plate at 160°C for 2 days, dried, and redissolved in H_2SO_4 at 220°C for 1 day. All samples were taken up in 3 N HCl, and Pb and U were separated using the ion exchange procedure described in Romer et al. (2005).

^b Lead corrected for fractionation, blank, isotopic tracer, and initial lead with $^{206}\text{Pb}/^{204}\text{Pb}=18.075$; $^{207}\text{Pb}/^{204}\text{Pb}=15.59$, and $^{208}\text{Pb}/^{204}\text{Pb}=38.20$ (galena associated with post-Variscan granites of the Erzgebirge; Bielicki and Tischendorf 1991). Pb and U were corrected for 15 pg Pb and 1 pg U blank contributions, respectively.

^c Apparent ages were calculated using the constants recommended by IUGS (Steiger and Jäger 1977).

Table 2 U–Pb analytical results for apatite from the Ehrenfriedersdorf tin district

Sample ^a	Weight (mg)	Pb ^b (ppm)	U ^b (ppm)	$\frac{^{206}\text{Pb}^c}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}^c}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}^c}{^{204}\text{Pb}}$	$\frac{^{238}\text{U}^d}{^{204}\text{Pb}}$
E1, blue, $T_H=309\pm5^\circ\text{C}$, Sauberg Mine							
1	1.887	56.0	69.2	22.216	15.817	38.386	82.7
2	9.934	16.2	15.1	21.155	15.757	38.236	61.7
E2, greenish, $T_H=365\pm5^\circ\text{C}$, Sauberg Mine							
3	5.912	56.7	74.9	22.530	15.831	38.427	88.8
4	4.875	48.5	14.4	19.005	15.641	38.343	19.0
5	2.819	44.3	12.6	18.967	15.638	38.596	18.3
6	8.838	44.7	9.96	18.768	15.630	38.599	14.3
Qu8-N, purple, $T_H=324\pm5^\circ\text{C}$, $T_e=-2.1^\circ\text{C}$, Sauberg Mine							
7	11.62	7.04	14.5	24.728	15.943	38.675	142.7
8	17.18	6.49	13.3	23.587	15.871	38.538	139.8
9	22.45	6.42	12.8	23.524	15.878	38.582	136.2
10	18.18	6.41	8.50	21.782	15.801	38.429	88.2
11	18.78	5.94	0.255	18.266	15.601	38.162	2.71
12	13.20	78.2	16.8	19.110	15.648	38.303	13.75
Sn-120, white, $T_H=338\pm3^\circ\text{C}$, $T_e=-21.2$, -5.2°C , Sauberg Mine							
13	3.33	16.7	62.5	31.644	16.307	44.282	302.
14	14.60	1.72	7.69	42.304	16.842	61.556	470
V1, purple, $T_H=289\pm3^\circ\text{C}$, $T_e=-11.6$, -5.6°C , Greifenstein granite							
15	11.02	4.80	0.594	18.741	15.609	38.141	7.85
16	19.07	6.26	0.118	18.171	15.597	38.166	1.19
17	21.47	5.02	0.321	18.329	15.589	38.117	4.04

T_H temperature of total homogenization, T_e temperature of eutectic

^a All apatite samples are small fragments of individual, perfectly clear crystals that have grown into voids. The apatite crystals belong to late stages of mineralization, and show lower homogenization temperatures than cassiterite. All fragments were cleaned with multiply distilled H_2O and acetone before addition of ^{205}Pb – ^{235}U mixed tracer and dissolution in 7 N HNO_3 on the hot plate. Ion exchange procedures for the separation and purification of Pb and U, as well as measurement conditions using static multicollection on Faraday cups, are described in Romer et al. (2005).

^b Pb and U concentration were determined by isotope dilution.

^c Isotope ratios were corrected for 15 pg Pb blank, tracer Pb, and 0.1%/amu mass discrimination. Note that each sample contained more than 50 ng Pb; thus, corrections for blank and tracer Pb are insignificant.

^d Isotope ratios were corrected for 15 pg Pb blank, tracer Pb, 1 pg U blank, and 0.1%/amu mass discrimination.

mica cleavage planes, an exposure of the inclusion, and even opening the U–Pb systematics before analysis. For CNC drilling, the polished samples were glued on a glass plate using Araldit. Other glues commonly used in thin section preparation had a high tendency for sample loss, as the drilled core readily separated from the glass plate. Cores were removed from the section using a droplet of acetone.

The CNC drilling was used for the U–Pb work on inclusions in biotite and the Rb–Sr and Sm–Nd work on melt inclusions in quartz. Molybdenite samples used for Re–Os dating consisted of extracted crystals or large single grains and were prepared as described in Stein et al. (2003) and Stein (2006).

Results from U–Pb dating of inclusions

The total amount of Pb and U in all samples is several orders of magnitude higher than the laboratory blank. Therefore, the blank correction does not introduce addi-

tional uncertainties and the blank-corrected Pb isotopic composition can be viewed as a mixture of inclusion Pb and host Pb only, both being co-genetic. For a 7- to 10- μm diameter inclusion and a host sample with 0.5 to 1 m diameter, the volume of the host is $\sim 10^5$ times larger. Thus, radiogenic bulk Pb compositions similar to those shown in Table 1 are only obtained for inclusions that have a high $^{206}\text{Pb}/^{204}\text{Pb}$ value and a high Pb content. These conditions are met for inclusions with U contents of several weight percent.

Greifenstein granite The Pb-isotopic composition of the combined mica + inclusion samples is not very radiogenic; $^{206}\text{Pb}/^{204}\text{Pb}$ values range from 29.54 to 69.4 (Table 1). Such low values, however, are not surprising considering that the inclusion makes up only a very small part of the analyzed sample. All nine samples fall on straight lines in $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ – $^{207}\text{Pb}/^{235}\text{U}$ diagrams (Fig. 3). In the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagram,

Table 3 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of melt inclusions in quartz from Zinnwald

Sample ^a	Rb ^b (ng)	Sr ^b (ng)	$\frac{^{87}\text{Rb}^b}{^{86}\text{Sr}}$	$\frac{^{87}\text{Sr}^c}{^{86}\text{Sr}}$
1	160	1.58	392	4.151±2
2	403	2.22	696	4.0596±3
3	164	0.76	1,550	7.429±3
4	53.2	1.34	120	1.138±2
5	3.69	0.34	32	0.833±3
6	2.15	0.19	35	0.883±5

^a Melt inclusions were identified under the optical microscope in double-polished thick sections and drilled from the sections using a CNC tool milling machine in a similar manner as described for the uraninite samples in biotite. All melt inclusions were extracted from sample ZW TH 2R-G (Thomas et al. 2005). Before dissolution, the quartz host was washed in 2 N HCl. After addition of a mixed ^{84}Sr – ^{87}Rb tracer, the samples were dissolved in teflon vials using 40% HF on the hot plate over night.

^b The melt inclusion forms only part of the analyzed sample. Therefore, no concentration data are given. Instead, the contents of Rb and Sr as determined by isotope dilution are indicated. The Sr isotopic composition was determined on a VG54 sector mass spectrometer using static multicollection. Rb was analyzed in static mode on a VG54 sector mass spectrometer. Note that the concentrations, concentration ratios, and isotopic compositions reported here were not corrected for blank contribution. The effect of Rb and Sr blank contribution is illustrated in Fig. 7, where the data are shown with corrections for a wide range of different blank contributions. See text for a discussion of the blank contribution on the Rb–Sr systematics.

^c The Sr isotopic composition was determined on a VG54 sector mass spectrometer using static multicollection. Sr is normalized with $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$ and adjusted to $^{87}\text{Sr}/^{86}\text{Sr}=0.710256$ for strontium reference material NBS987 ($n=18$; $^{87}\text{Sr}/^{86}\text{Sr}=0.710270\pm14$).

the data are perfectly fitted to the regression line [Fig. 3a; mean square weighted deviate (MSWD)=1.06] and yield a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 300 ± 26 Ma (2σ). The large uncertainty of the age is due mainly to the small spread in $^{207}\text{Pb}/^{204}\text{Pb}$.

Table 4 $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition of melt inclusions in quartz from Zinnwald

Sample ^a	Nd ^b (ng)	Sm ^b (ng)	$\frac{^{147}\text{Sm}}{^{144}\text{Nd}}$	$\frac{^{143}\text{Nd}^c}{^{144}\text{Nd}}$	$\epsilon_{\text{Nd}} (T)^d$
1	0.927	0.287	0.187	0.512529±65	−1.7
2	3.52	0.982	0.174	0.512446±20	−2.8
3	2.42	0.697	0.174	0.512499±20	−1.8

^a Nd isotopic compositions were determined on the melt inclusions described in Table 3. The same sample numbers were used.

^b The melt inclusion represents only part of the analyzed sample. Therefore, no concentration data are given. Instead, the contents of Sm and Nd as determined by isotope dilution are indicated. All analytical work was performed on a Finnigan MAT262 in dynamic multicollection experiments.

^c Nd is normalized with $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ Neodymium reference material LaJolla gave $^{143}\text{Nd}/^{144}\text{Nd}=0.511850\pm7$ ($n=11$ measurements).

^d $\epsilon_{\text{Nd}}(T)$ values were calculated for $T=323$ Ma

Three analyses fall on the concordia curve in the $^{207}\text{Pb}/^{235}\text{U}$ – $^{206}\text{Pb}/^{238}\text{U}$ diagram. These data were obtained on Li–mica containing U-rich mineral inclusions. The weighted average of the $^{206}\text{Pb}/^{238}\text{U}$ ages of these samples, which is 323.9 ± 3.5 Ma (2σ), represents the best age for the formation of the U-rich minerals. The remaining six samples fall above the concordia, i.e., reflect an excess of radiogenic Pb. All data show a perfect fit to a straight line (Fig. 3b, MSWD=0.96), which, within error, passes through the origin of the diagram (Fig. 3b, -15 ± 59 Ma) and indicates that fractionation between U and Pb—shifting most of the data above the concordia—was a very young or recent event. It also implies that the regression line in the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ diagram represents an isochron and its slope corresponds to an age. The excess Pb for the six samples with monazite and/or xenotime inclusions originates from recoil implantation, in combination with incomplete dissolution of monazite and xenotime.

Melt pocket from stockscheider pegmatite in the Sauberg mine The Pb isotopic composition is variably radiogenic; $^{206}\text{Pb}/^{204}\text{Pb}$ values range from 19.621 to 3,146.5 (Table 1).

In particular, the highly radiogenic Pb isotopic compositions permit, in addition to the determination of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages, the determination of precise and accurate $^{207}\text{Pb}/^{206}\text{Pb}$ ages. The slope of the Pb line on the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ diagram is entirely controlled by the most radiogenic Pb isotopic composition ($^{206}\text{Pb}/^{204}\text{Pb}=3,146.5$), whereas the scatter, reflected in a MSWD of 65, is largely due to the unradiogenic samples (Fig. 4). The large MSWD possibly indicates significant contribution of host Pb to the Pb budget of samples with lower $^{206}\text{Pb}/^{204}\text{Pb}$ introducing scatter in the data. Furthermore, it is possible that some of these samples have a poly-stage evolution. The age is not affected by this scatter at the low $^{206}\text{Pb}/^{204}\text{Pb}$ end of the regression line (cf. Kullerød 1991). The same scatter is also observed in the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram, where all samples are shown. Sample 12 falls slightly above the isochron, which suggests that this sample has experienced up to 2% recent U loss or has a poly-stage history, with a higher $^{238}\text{U}/^{204}\text{Pb}$ value during the early stages, rather than later stages. Two low $^{206}\text{Pb}/^{204}\text{Pb}$ samples fall markedly below the isochron, possibly indicating some Pb loss. It should be noted that the $^{206}\text{Pb}/^{238}\text{U}$ isochron age is controlled by the sample with the highest $^{238}\text{U}/^{204}\text{Pb}$ and is little affected by samples 17 and 20. Omitting potentially disturbed samples only affects MSWD and uncertainty of the age. Therefore, the given age estimate is conservative and robust. One possible reason for the apparent open-system behavior of some samples (U-rich mineral inclusions in mica) may be linked to drilling of the samples for analytical preparation. For a very small diameter and an unfavorable orientation of the cleavage

Table 5 Re–Os data for molybdenite samples from Altenberg

AIRIE Run #	Sample	Brief description	Re (ppm) ^a	¹⁸⁷ Os (ppb) ^a	Age (Ma) ^b	Age _{corr} (Ma) ^c
CT-350A	5000	Massive molybdenite in the greisen ore body	0.0852 (2)	0.292 (1)	326.2±1.5	323.9±2.5
CT-357A	TS 1	Quartz veinlets with molybdenite	0.1207 (2)	0.405 (1)	319.3±1.4	317.9±2.4

^a Molybdenite samples (25 mg) were dissolved using the Carius tube method. Individual ¹⁸⁵Re and ¹⁹⁰Os spikes were added to each sample before dissolution. Os was recovered by distilling directly from the Carius tube aqua regia into HBr and was subsequently purified by micro-distillation. Re was recovered by anion exchange. Re and Os were loaded onto Pt filaments and isotopic compositions were determined using NTIMS on NBS 12-in radius, 68° and 90° sector mass spectrometers at AIRIE, Colorado State University. Absolute 2-sigma uncertainties are indicated for the last digit. These Re–Os data were obtained in 1999. The procedure employed here differs from Markey et al. (2003) in two respects: (1) instead of a mixed Re–double Os (¹⁸⁸Os–¹⁹⁰Os) spike, a single ¹⁹⁰Os spike was used. (2) Present levels for Re and Os blanks at AIRIE are an order of magnitude smaller with much smaller uncertainties than for these early samples. Age comparisons using the single and the double Os spike method are discussed in Stein (2006).

^b Ages were calculated assuming an initial ¹⁸⁷Os/¹⁸⁸Os=0.1203 and $\lambda^{187}\text{Re}=1.666\times 10^{-11}\text{ year}^{-1}$ (Smoliar et al. 1996). Uncertainties for the reported ages, calculated using ¹⁸⁷Os=¹⁸⁷Re ($e^{\lambda t}-1$), include all analytical and the ¹⁸⁷Re decay constant uncertainties.

^c Blank-corrected ages were calculated using the parameters listed in b. The Re and Os data were additionally corrected for 15±5 pg and 0.5±0.25 pg blank for Re and Os, respectively. The ¹⁸⁷Os/¹⁸⁸Os blank composition was less than 0.3. The difference between the non-corrected and the blank-corrected ages illustrates the significance of the blank on the age for low Re (ppb level) samples. The blank-corrected ages are the correct ages and only these should be used for age discussion.

planes to the drill core, the previously closed container “mica” may become open and expose the U-rich mineral inclusion. During the sample cleaning procedure, which involves 7 N HNO₃, some U and Pb may have been mobilized.

Hydrothermal apatite from the Sauberg mine Five apatite crystals were selected for U–Pb dating. The analytical

results are shown in Table 2 and Fig. 5. There is a large variation in U and Pb content among apatite from different locations, whereas the variation within an individual sample is much smaller. Individual crystals show similar patterns of in situ Pb growth, with essentially no Pb growth for apatite V1 and significant Pb growth for apatite Sn-120 (Table 2). The Pb isotopic composition falls on a linear trend with only minor excess scatter in the ²⁰⁶Pb/²⁰⁴Pb–²⁰⁷Pb/²⁰⁴Pb

Table 6 Chemical composition of uraninite crystals in aplite sample Q8 representing a melt pocket in the Stockscheider in the Sauberg Mine

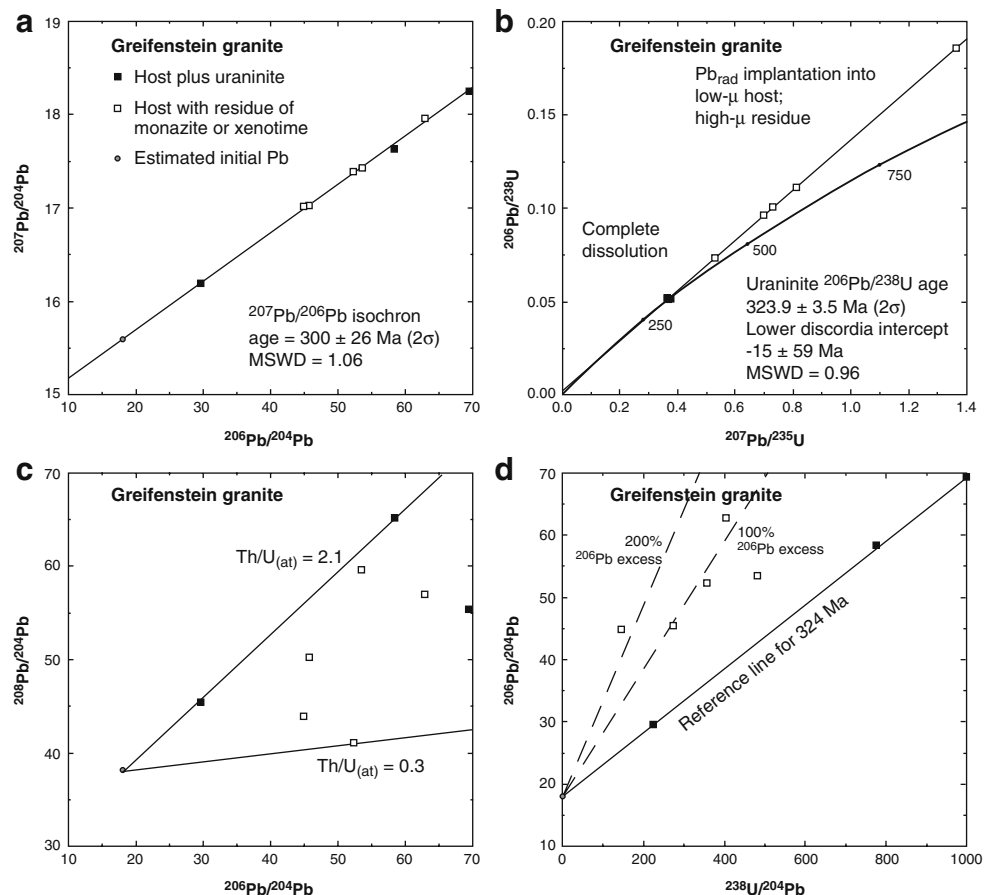
Sample ^a	UO ₂	ThO ₂	PbO	REE ₂ O ₃	Y ₂ O ₃	SiO ₂	Al ₂ O ₃	Sum ^b	Age ^c
1 (U1)	88.93	4.39	3.94	0.42	0.15	0.06	0.00	97.89	316
2 (U2)	88.41	4.70	4.02	0.29	0.20	0.10	0.00	97.72	324
3 (U2)	90.58	3.24	4.02	0.35	0.11	0.03	0.00	98.33	318
4 (U3)	88.97	3.83	3.98	0.29	0.09	0.23	0.00	97.39	320
5 (U3)	89.95	2.92	3.97	0.44	0.09	0.23	0.00	97.60	317
6 (U4)	87.91	4.47	3.97	0.27	0.16	0.23	0.07	97.08	322
7 (U5)	88.99	4.98	3.96	0.38	0.06	0.23	0.02	98.62	317
8 (U6)	91.60	2.08	3.98	0.39	0.18	0.03	0.01	98.27	313
9 (U6)	89.10	3.36	3.94	0.21	0.13	0.25	0.02	97.01	317
10 (U6)	89.76	3.62	4.01	0.40	0.14	0.04	0.00	97.97	320
11 (U7)	87.29	5.92	3.93	0.20	0.15	0.02	0.00	97.51	320
12 (U7)	89.52	3.95	4.01	0.51	0.11	0.03	0.02	98.15	320
13 (U8)	87.74	4.90	3.89	0.31	0.23	0.28	0.02	97.37	316
14 (U8)	87.98	5.32	4.02	0.26	0.23	0.01	0.00	97.82	325
15 (U9)	84.85	3.74	3.82	0.33	0.12	1.03	0.45	94.34	322
16 (U10)	89.58	3.84	3.95	0.47	0.17	0.08	0.06	98.15	316
17 (U10)	91.38	2.63	4.07	0.25	0.09	0.00	0.01	98.43	320
18 (U11)	89.14	3.70	4.01	0.32	0.18	0.01	0.00	97.36	322
19 (U11)	91.20	4.18	4.22	0.38	0.20	2.04	0.42	102.64	330

^a Microprobe spots on uraninite crystals included in mica, feldspar, or quartz. Individual grains are numbered in parantheses. All analyses were made on the same thin section using a CAMECA SX-50 electron microprobe operated at 20 kV accelerating potential, 40 nA current, and 2-μm beam diameter (for details see Rhede et al. 1996). All contents are in weight percent.

^b Combined contents of P₂O₅, CaO, MnO, and TiO₂ are below 0.2 wt%.

^c Single point ages were calculated by solving the equation for the radioactive decay of U and Th with an iteration procedure (Rhede et al. 1996), assuming that all measured Pb is radiogenic and using the decay constants of U and Th recommended by IUGS (Steiger and Jäger 1977).

Fig. 3 **a** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ Pb diagram showing the excellent fit of sample data to a Pb-isochron for the Greifenstein granite (Ehrenfriedersdorf). **b** Concordia diagram for inclusions from the Greifenstein granite. Reversely discordant samples are due to selective dissolution of host minerals with residual U-rich inclusions, such as xenotime and monazite, and illustrating the effect of recoil-implantation of U-daughters. **c** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ diagram showing the heterogeneity in the $\text{Th}/\text{U}_{(\text{at})}$ ratio of individual samples. Note that these values represent mixtures of the $\text{Th}/\text{U}_{(\text{at})}$ values of the inclusion and its host. Typical uraninites from the Erzgebirge (cf. Förster 1999) have $\text{Th}/\text{U}_{(\text{at})}$ values <0.1 . **d** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram. Note that incomplete dissolution of inclusions results in an apparent excess in ^{206}Pb . Data from Table 1



diagram, originating mostly from the unradiogenic Pb of apatite V1 and, to a lesser extent, from sample Sn-120, which seems to be heterogeneous with respect to its Th–U–Pb systematics (e.g., U and Pb concentrations, $\text{Th}/\text{U}_{(\text{at})}$, Table 2). Excluding these anomalous samples, the data constrain a regression line that corresponds to a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 335 ± 45 Ma (2σ , MSWD=1.2, $N=17$). The large age uncertainty is mainly due to the small variation on $^{207}\text{Pb}/^{204}\text{Pb}$ (cf. Fig. 5). The $^{207}\text{Pb}/^{206}\text{Pb}$ slope does not change significantly if data from different apatite crystals are omitted. On the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ diagram, most apatite data fall on a flat trend, corresponding to a $\text{Th}/\text{U}_{(\text{at})}$ of 0.23, with the exception of the two samples from apatite Sn-120, whose Pb isotopic composition indicates $\text{Th}/\text{U}_{(\text{at})}$ values of 1.4 and 3.1 (Fig. 5). No $\text{Th}/\text{U}_{(\text{at})}$ values have been calculated for apatite E2, which seems to be heterogeneous and relatively unradiogenic (Table 2). The good colinear alignment for various apatite samples breaks down on the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram, where the data fall between two trends (Fig. 5a). The steeper trend is defined by the samples E1, E2, V1, and Sn-120; the flatter trend is defined by samples from apatite Qu8-N and Sn-120. The steeper trend, if interpreted as an isochron, corresponds to an age of 323.2 ± 4.5 Ma (2σ ; MSWD=

166; $N=11$). Omitting sample Sn-120 yields an age of 323.9 ± 2.9 Ma (2σ ; MSWD=26; $N=9$). It should be noted that a similar age is obtained if data from a single apatite crystal are used. For instance, apatite samples E1 and E2 define a slope that corresponds to an age of 317.3 ± 1.6 Ma (2σ , MSWD=0.08; $N=6$).

The younger trend, e.g., the reference line at 280 Ma, shows much more scatter than the older trend on the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram (Fig. 5a). This suggests that the disturbance resulted in an incomplete resetting or that some samples scattered along the 280 Ma trend contained variable, but minor amounts of older apatite or Pb derived from the older apatite. Most of the excess scatter in the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ diagram originates from sample Sn-120 (Table 2), which is not only isotopically anomalous, but differs from the other apatite samples by high and variable $\text{Th}/\text{U}_{(\text{at})}$ values, contrasting temperatures for the eutectic composition ($T_e = -21.2$ and -5.2), and a higher salinity in fluid inclusions. The heterogeneous $\text{Th}/\text{U}_{(\text{at})}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages for the two fragments of sample Sn-120 indicate that the mineral is heterogeneous and the ages possibly represent mixed ages. The older age may be close to the formation age, as it agrees with U/Pb ages for the other geochemically homogenous apatite

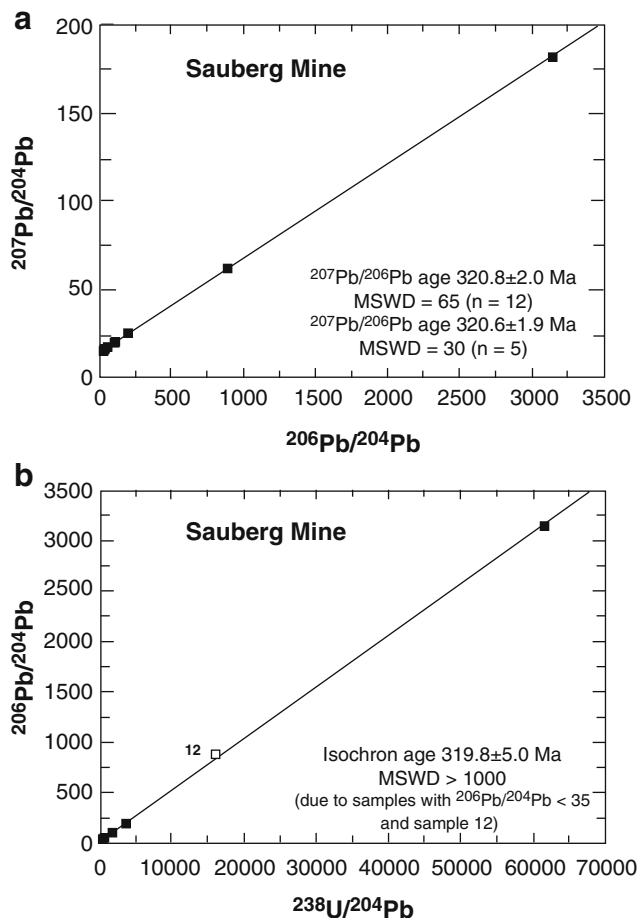


Fig. 4 Uraninite inclusions from a melt pocket in the stockscheider pegmatite, Sauberg Mine (Ehrenfriedersdorf). **a** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ isochron diagram showing an overall good alignment of the data with significant excess scatter originating mainly from samples with low $^{206}\text{Pb}/^{204}\text{Pb}$ values. The isochron fit to all samples yields an age of 320.8 ± 2.0 Ma (2σ , MSWD=65). Omitting those samples with suggestive Pb loss does not affect the age 320.6 ± 1.9 Ma (2σ , MSWD=30). Note that the isochron slope is controlled by the highly radiogenic Pb isotopic composition of a few samples (data from Table 1) **b** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram showing some scatter of the data about a straight line. The calculated isochron age is based on samples shown as filled squares. The large MSWD value is due to the scatter endemic to samples with relatively low $^{206}\text{Pb}/^{204}\text{Pb}$ values

samples. The younger age around 280 Ma represents a maximum age for the second generation of apatite. The younger apatite contains an order of magnitude more U and Pb than the older one. This suggests that the Pb isotope systematics of this sample is dominated by the younger apatite, which would imply that the younger age could be close to the geological event that gave rise to the formation of the younger apatite.

Age of tin-mineralization at Ehrenfriedersdorf The three analyzed uraninite inclusions in Li–mica from the Greifenstein granite yield concordant ages, i.e., the uraninite

inclusions and their host together represent closed systems within analytical resolution. The overlap of the $^{206}\text{Pb}/^{238}\text{U}$ ages of 323.4 ± 1.8 , 323.5 ± 2.5 , and 326.8 ± 3.7 Ma demonstrates that the approach to trade a reduction in $^{206}\text{Pb}/^{204}\text{Pb}$ for a closed system yields reproducible results, although the low $^{206}\text{Pb}/^{204}\text{Pb}$ values may make data reduction sensitive to common Pb correction, which may result in a slightly larger uncertainty in the $^{206}\text{Pb}/^{238}\text{U}$ ages. These three samples with uraninite inclusions define a weighted mean age of 323.9 ± 3.5 Ma (2σ). This age is well within the expected age range for granitic magmatism in the Erzgebirge (e.g., Förster et al. 1999). This age agrees with the older ages obtained for hydrothermal apatite (323.9 ± 2.9 and 317.3 ± 1.6 Ma; 2σ). The age of U-rich mineral inclusions in Li–mica from the melt pocket in the stockscheider pegmatite from Sauberg generally agrees with the age data obtained for the Greifenstein granite and the hydrothermal apatite. Our preferred age for the melt pockets is 320.8 ± 2.0 Ma (2σ).

The U–Pb age of 323.9 ± 2.9 Ma (2σ) for the oldest hydrothermal apatite from Ehrenfriedersdorf demonstrates that (1) the Sn and W mineralizations associated with the Greifenstein granite are older than 320 Ma, and (2) earlier Rb–Sr WR and K–Ar age determinations on pegmatitic, pneumatolitic, and skarn deposits yielding 311–302 Ma (cf. compilation in Hösel 1994) do not date the time of Sn–W mineralization. Since the region has undergone repeated tectonically reactivated, e.g., along the Gera–Jachymov–Zone, as demonstrated by the repeated redistribution and redeposition of U ores in the Aue–Niederschlema U district (Förster 1996), ages younger than ca. 320 Ma could reflect partial or complete resetting associated with one of these younger tectonic reactivations.

Age of tin mineralization at Zinnwald

In the following section, we test the feasibility to date 30- to 120- μm melt inclusions in granitic quartz. Melt inclusions are small blebs of silicate liquid that are trapped in phenocrysts growing at magmatic temperatures and pressures. The relatively stable and incompressible host, such as quartz in granite, acts as a pressure vessel, keeping most trapped melt inclusions from degassing and preventing migration of fluids into or out of the melt inclusion system. Such melt inclusions represent closed systems that may be suitable for geochronology. Melt inclusions representing the last magmatic stage of a highly evolved melt system (high Rb/Sr) are especially ideal as they will develop highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$.

Melt inclusions from Zinnwald yield measured $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.833 to 7.42 and $^{87}\text{Rb}/^{86}\text{Sr}$ values as high as 1,550 (Table 3; Fig. 6). In particular, the extremely

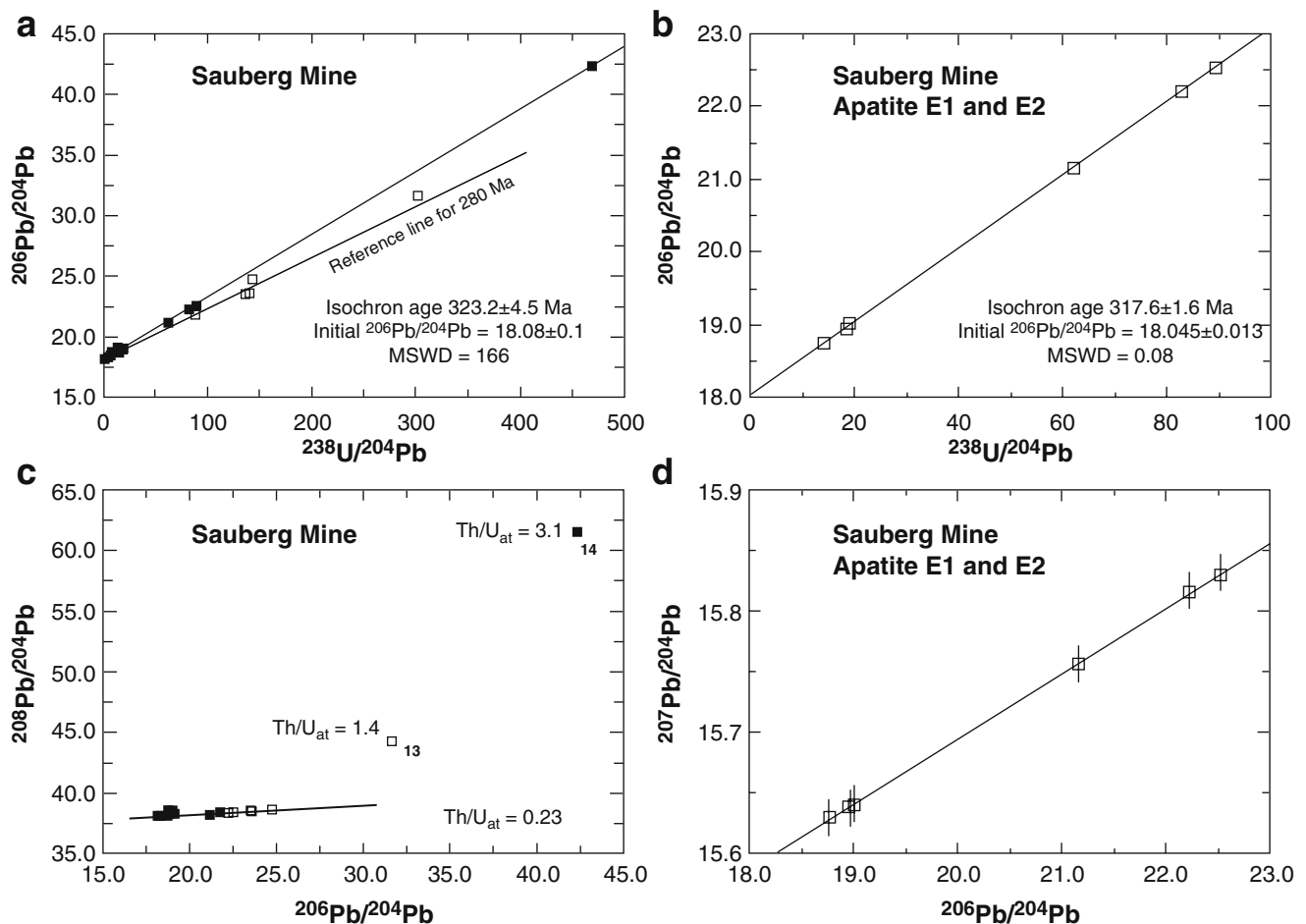


Fig. 5 Pb–Pb and U–Pb data for five apatite crystals from Ehrenfriedersdorf (data from Table 2). **a** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram for all analyzed apatite samples. The scatter shown on the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram (and similarly on the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ diagram; not shown) is largely due to data from apatite samples Sn-120 and Qu8-N that suggest younger ages. **b** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram for apatite samples E1 and E2. Data define a well-constrained isochron. **c** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ diagram. If all samples had similar initial $^{208}\text{Pb}/^{204}\text{Pb}$ values comparable to Late-Variscan granites of Bielicki and Tischendorf (1991), the variation in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ can be used to calculate the

atomic Th/U ratios ($\text{Th}/\text{U}_{\text{at}}$) for the apatite samples. As Th has limited mobility in aqueous fluids, low $\text{Th}/\text{U}_{\text{at}}$ values reflect precipitation of this apatite from an aqueous fluid. In contrast, the high $\text{Th}/\text{U}_{\text{at}}$ for analyses from apatite Sn-120 may indicate the presence of complex-forming elements or ligands (such as F^-) that permitted enhanced mobility of Th and that may have been derived from late-magmatic fluids. The variability in $\text{Th}/\text{U}_{\text{at}}$ and the scatter about the Pb line in the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ diagram, furthermore, suggest that sample Sn-120 had a polystage history. **d** $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ diagram showing the highly linear array of data for apatite E1 and E2

radiogenic values make uncertainties associated with the correction for initially present Sr small and permit calculation of two-point ages by assuming a composition for the initial Sr isotopic composition. Because of the small amounts of Sr, corrections for blank contributions are important. Samples with low Sr content and highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values, which are especially sensitive to the blank contribution, have a major effect on the Sr isotopic composition. A contribution of 50 pg Sr would shift the measured $^{87}\text{Sr}/^{86}\text{Sr}$ from 7.42 (sample 3, Table 3) to 8.27. Owing to the contrasting Rb and Sr contents, the blank correction has little effect on the slope of the isochron, and the age derived from it, if blank Sr and initial Sr of the sample are isotopically similar. Rubidium is

much more abundant than Sr and the Rb blank correction has little influence on the total amount of Rb in the sample (this does not apply to samples 5 and 6). In contrast, the Sr blank affects the $^{87}\text{Sr}/^{86}\text{Sr}$ value and contributes significantly to the total amount of Sr. Accounting for the Sr blank affects not only $^{87}\text{Sr}/^{86}\text{Sr}$, but also $^{87}\text{Rb}/^{86}\text{Sr}$, shifting the data along the isochron. This relationship is illustrated in Fig. 6. Although blank contributions to Sr may result in large uncertainties on the true isotopic composition of Sr and the true $^{87}\text{Rb}/^{86}\text{Sr}$ value, the uncertainties are highly correlated and, thus, still allow for a precise and accurate age determination. This correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ errors for radiogenic Sr is discussed in Brooks et al. (1972).

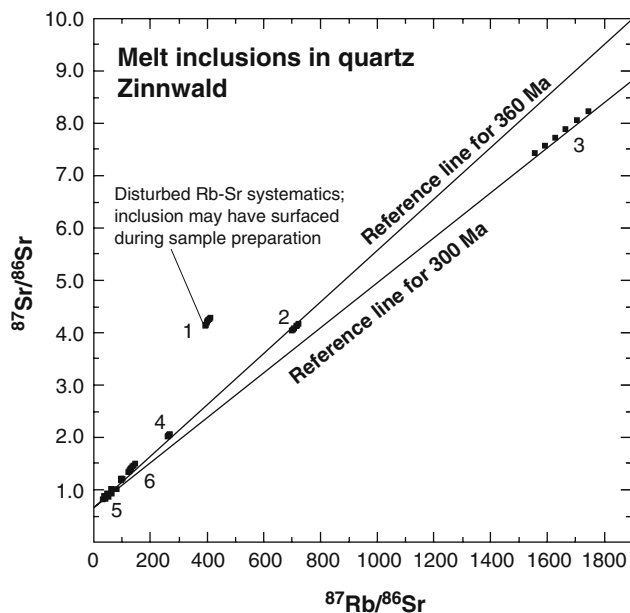


Fig. 6 $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ diagram for melt inclusions in quartz from the Zinnwald tin deposit. Each analysis is represented by a series of symbols illustrating the effect of Rb and Sr blank. The effect of blank correction is largest for samples with high measured $^{87}\text{Sr}/^{86}\text{Sr}$ and low Sr contents. For each sample, the uncorrected analysis has the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ value and the one with the highest blank contribution (10, 20, 30, 40, and 50 pg Sr blank, respectively, with $^{87}\text{Sr}/^{86}\text{Sr}=0.708$) has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ value. The effect of Rb blank (20 and 30 pg Rb, respectively) is subordinate and the results overlap except for samples 5 and 6 that have low Rb contents. Note the large effect of Sr blank correction on the position of individual samples that are shifted along the isochron without changing its slope. For low-Rb samples 5 and 6, Rb blank correction additionally shifts the data to lower $^{87}\text{Rb}/^{86}\text{Sr}$ values, which may affect the slope of the isochron

The scatter in the data (Fig. 6) indicates that more than a single melt inclusion has to be analyzed to demonstrate that the age is not derived from a disturbed system. For instance, recrystallization of initially homogeneous melt inclusions may result in the exsolution of a fluid, which is trapped either in the melt inclusion itself or by its host. Mobility of this fluid phase, however, cannot be always ruled out. Fluid loss may also occur during sample preparation, when drilling of the inclusion results in fracturing of the host. Since the partitioning of Rb and Sr between solid and fluid is likely dissimilar, fluid loss may disturb the geochronologic system of the recrystallized melt inclusion and introduce excess scatter in the form of a geologically excessive range of age values. Preferential fractionation of Rb into the fluid in combination with later fluid loss is reflected by data that fall above the isochron as defined by undisturbed samples. The tendency of some samples to cluster along the 360 Ma reference line (or plotting above it) may highlight this effect. The data in Table 3 do not constrain an isochron. The highly radiogenic character of most samples, however, demonstrates the

potential of the approach used here, although it remains a difficult task to unequivocally identify undisturbed samples and to retain a closed system during sample drilling and handling.

Three of the melt inclusions dated by Rb–Sr have also been used for the determination of the initial Nd isotopic composition. This approach is of particular interest in rocks whose rare earth element (REE) budget is dominated by readily altered phases such as phosphates or carbonates. For instance, the granites of Niederbobritzsch and Markersbach (NBZ and MAB, eastern Erzgebirge) straddle the Elbe Lineament and parallel fault zones, which have been repeatedly reactivated. These granites are characterized by secondary REE minerals, including cerite–(Ce), thorium synchysite–(Ce), synchysite–(Ce), synchysite–(Y), and REE–carbonates (e.g., Förster 2000, 2001). Although REE mobility in the Markersbach granite and particularly the Niederbobritzsch granite may have been on the scale of decimeters (MAB) down to millimeters (NBZ), there are numerous examples where fluid–rock interaction resulted in preferential loss of light rare earth element on the meter to decameter scale (e.g., Leroy and Turpin 1988; Poitrasson et al. 1995). In such rocks, it is not possible to determine the initial Nd isotopic composition on bulk samples (cf. also Poitrasson et al. 1995). Resorting to melt inclusions may provide access to the initial Nd isotopic composition, however, at the price of a larger analytical uncertainty. The three analyzed melt inclusions from the Zinnwald granite (ϵNd_{320} : –1.7, –1.8, –2.8; Table 4) display a narrow range, implying that the procedure is reliable. Furthermore, these Nd data agree with bulk rock samples (that show no textural and chemical evidence for REE mobility), suggesting that this approach also yields accurate data.

Re–Os age of Altenberg molybdenite

Re–Os results for two dated molybdenite samples from Altenberg are reported in Table 5. Two ages are shown: one age considers only analytical uncertainty (i.e., weighing errors, uncertainty in spike calibration, uncertainty in measurement of isotopic ratios by NTIMS, plus uncertainty in the ^{187}Re decay constant), whereas a second blank-corrected age is based on the correction for blank and the uncertainty in that blank. These Altenberg molybdenite samples demonstrate the importance of blank correction in dating low Re and/or young molybdenite. Sub-parts per million levels of Re in Altenberg molybdenite are a strong indication for a crustal source for the Re and Mo, and by inference, the other metals (e.g., see Stein 2006). Although previous workers using thermally sensitive, argon-based techniques (e.g., Seltnann and Schilka 1995; Müller et al. 2005) suggest much younger ages for the Altenberg mineralization (ca. 290 Ma), the Re–Os data for Altenberg

support mineralization older than ca. 315 Ma. The Re–Os ages for the two Altenberg molybdenite samples agree well with a 316.6 ± 0.4 Ma (2σ) Re–Os age for cobaltiferous arsenopyrite from Au deposits possibly related to Late-Variscan magmatism in the Sudetes, southwest Poland (Mikulski et al. 2005).

Chemical Th–U–Pb dating of uraninite

Uraninite from a melt pocket in the stockscheider pegmatite from Sauberg is characterized by highly negatively correlated UO_2 and ThO_2 contents (Fig. 7). UO_2 ranges from 87 to 91 wt% and ThO_2 ranges from 2 to 6 wt% (Table 6). The contents of Y_2O_3 and REE_2O_3 are below ca. 0.25 wt% and c. 0.3 wt%, respectively. PbO contents of ~4 wt% represent in situ radiogenic growth. There are significant contributions from SiO_2 and Al_2O_3 in two samples, which may be due to the presence of feldspar or mica below the uraninite. The chemical ages for all uraninite analyses are identical, including two anomalous samples (Table 6).

The chemical composition of uraninite from the Sauberg pegmatite well corresponds with the compositional range defined by more than 200 spot analyses of uraninite (Förster 1999, Förster et al. 1999) from samples associated with Sn mineralization in the Erzgebirge. Förster (1999) analyzed uraninite from various types of late Variscan granites and showed that uraninite from the Erzgebirge typically has UO_2 contents between 97 and 75 wt% and that UO_2 contents correlate negatively with ThO_2 contents

for $\text{ThO}_2 < 6$ wt%. At higher ThO_2 contents, the correlation is lost because of the increasingly more important incorporation of Y_2O_3 and REE_2O_3 in uraninite (Förster 1999). Th-rich uraninite, however, seems to be mainly restricted to the biotite granite from the Kirchberg pluton (Förster 1999).

Based on counting statistics, individual chemical ages reported in Table 6 have uncertainties of 10 to 15 Ma. Such large uncertainties do not permit recognition of small Pb loss in the range of 1 to 2% relative to the total amount of Pb. Only severe Pb loss would be recognizable. All analyzed spots agree within their analytical uncertainty. Therefore, a mean age is calculated assuming that (1) all scatter in the data is due to counting statistics and (2) the data scatter about the true value of the age. The same assumptions, for instance, are also routinely made for U–Pb ion-microprobe dating and $^{207}\text{Pb}/^{206}\text{Pb}$ evaporation dating. As such, the obtained chemical age for uraninite from Sauberg is 319.7 ± 2.2 Ma ($2\sigma_m$, MSWD=0.62; $n=19$; 10 Ma uncertainty for each chemical age) and 319.7 ± 3.4 Ma ($2\sigma_m$, MSWD=0.28; $n=19$; 15 Ma uncertainty for each chemical age), respectively. In the following, only the more conservative estimate with the larger uncertainty will be used. This age compares well with chemical uraninite ages from other granites in the Erzgebirge (Table 7) that define an age range from 325 to 315 Ma (Förster 1999).

Discussion

Comparison of chemical and ID-TIMS uraninite ages from Ehrenfriedersdorf

Uraninite dated by the electron microprobe and by ID-TIMS yields overlapping ages at 319.7 ± 3.4 and 320.8 ± 2.0 Ma, respectively. These ages are in agreement with a $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ isochron age of 323.9 ± 2.9 Ma derived from the oldest hydrothermal apatite. Since fluid inclusions in apatite yield homogenization temperatures of ca. 365°C, apatite yields a minimum age for the emplacement of the granites and tin mineralization. Open-system behavior in uraninite would generally result in younger ages, as Pb is more readily lost than gained. Furthermore, the amounts of Pb that would have to be mobilized to significantly reduce the calculated ages are large. For instance, to shift the chemical U–Pb age of uraninite from 320 to 280 Ma, about 4,500 ppm of Pb has to be lost from the uraninite. Preferential loss of U, which also would shift the chemical age to older values, is unlikely as the totals of the chemical analyses are close to 100 wt%, and almost 10 wt% UO_2 would have to be lost for an age increase of 40 Ma. Thus, the age of ca. 320 Ma is considered robust for the age of the uraninite. Some of the ID-TIMS samples seem to have experienced U–Pb fractionation during sample

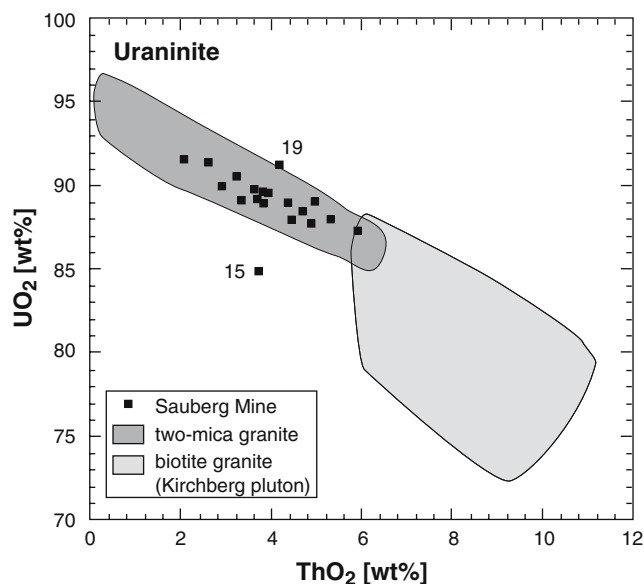


Fig. 7 Chemical composition of uraninite from melt pocket in the stockscheider pegmatite at the Sauberg Mine (data from Table 6). Field shows the compositional range of uraninite relative to other granites in the Erzgebirge (data from Förster 1999). Samples 15 and 19 have elevated SiO_2 contents as the electron beam also activated silicates under the thin uraninite crystal

Table 7 Compilation of age determinations from Late-Variscan granites in the Erzgebirge region

Granite	Age (Ma) ($\pm 2\sigma$)	Method (mineral or whole rock)	Source	Comment
Low-F biotite granites				
Kirchberg				
	321.2 $\pm$ 2.9	K–Ar (biotite)	1	Four biotite fractions analyzed; other fractions yield ages of 317.2 $\pm$ 3.0 Ma, 320.1 $\pm$ 2.9 Ma, and 324.8 $\pm$ 2.7 Ma
	324 $\pm$ 5	U–Pb chemical	2	Monazite + xenotime + uraninite
	309.4 $\pm$ 3.8	Rb–Sr (WR)	1	Isochron based on 11 WR samples
	330 $\pm$ 5	U–Pb chemical	13	Uraninite
	323 $\pm$ 6	Rb–Sr (WR)	3	6 samples; interpreted as Older Granite
	323 $\pm$ 4	Rb–Sr (WR)	3 ^a	7 samples; as above + one sample from Aue/Schlema; interpreted as Older Granite
	316 $\pm$ 8	Rb–Sr (dark mica)	3	4 samples; anomalously high initial $^{87}\text{Sr}/^{86}\text{Sr}$
	318.1 $\pm$ 1.3	$^{40}\text{Ar}/^{39}\text{Ar}$ (biotite)	8	Plateau age for one sample
	328 $\pm$ 1	Rb–Sr (WR, feldspar, mica)	3	3 samples
Niederbobritzsch				
	324 $\pm$ 4	U–Pb chemical	7	Monazite + xenotime + uraninite
	320 $\pm$ 6	$^{207}\text{Pb}/^{206}\text{Pb}$ zircon evaporation	11	Uncertainty based on range of 6 crystals
Bernsbach				
	322 $\pm$ 4	U–Pb chemical	7	Monazite + xenotime + uraninite
Beierfeld				
	331 $\pm$ 6	U–Pb chemical	7	Monazite + xenotime + uraninite
Schlema				
	322 $\pm$ 6	U–Pb ID TIMS (monazite)	2, 4	Single analysis
Low-F two-mica granites				
Bergen				
	323.6 $\pm$ 2.6	K–Ar (biotite)	1	Single fraction; muscovite from the same sample yields an age of 318.2 $\pm$ 3.1 Ma
	323 $\pm$ 2	U–Pb chemical	2	Monazite+xenotime+uraninite
	312.8 $\pm$ 7.0	Rb–Sr (WR)	1	Isochron fitted to 8 out of 9 WR samples
High-F, high P₂O₅ Li–mica granites				
Ehrenfriedersdorf				
	323.9 $\pm$ 3.5	U–Pb ID TIMS (uraninite)	ms	Inclusions in mica
	320.6 $\pm$ 1.9	U–Pb ID TIMS (uraninite)	ms	Inclusions in mica
	319.7 $\pm$ 3.4	U–Pb chemical (uraninite)	ms	Inclusions in mica
	323.9 $\pm$ 2.9	U–Pb ID TIMS (apatite)	ms	Hydrothermal
	317.3 $\pm$ 1.6	U–Pb ID TIMS (apatite)	ms	Hydrothermal
	327 $\pm$ 5	Rb–Sr (WR)	1	Sauberg Mine, 4 samples; isochron defines an anomalously low initial $^{87}\text{Sr}/^{86}\text{Sr}$
	317.2 $\pm$ 4.2	Rb–Sr (WR)	1	Isochron based on 9 WR samples
	291.3 $\pm$ 2.3	Rb–Sr (WR)	1	Isochron based on 10 WR samples; initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.720 is anomalously high. Note that most Erzgebirge granites with ages younger than 315 Ma yield anomalously high initial $^{87}\text{Sr}/^{86}\text{Sr}$ values.
Eibenstock				
	321 $\pm$ 4	U–Pb ID-TIMS (monazite)	2, 4	One single analysis.
	316 $\pm$ 3	U–Pb chemical	2	Monazite+xenotime+uraninite
	311 $\pm$ 5	$^{40}\text{Ar}/^{39}\text{Ar}$ (muscovite, biotite); Rb–Sr (muscovite, biotite)	5	Range defined by six $^{40}\text{Ar}/^{39}\text{Ar}$ mica ages and two Rb–Sr ages; grouping also includes one sample from Greifenstein
	305 $\pm$ 4	Rb–Sr (WR)	6	Abstract; 11 samples, original data not published: no information about statistical fit of data
	303 $\pm$ 8	Rb–Sr (biotite)	6	Abstract; 3-point isochron (WR, biotite, plagioclase); original data not published: no information about statistical fit of data
	325 $\pm$ 7	Rb–Sr (WR)	3 ^a	5 samples; Eibenstock + Nejdek; interpreted as Younger Granite
	323 $\pm$ 1	Rb–Sr (WR)	3 ^a	8 samples; Eibenstock + Nejdek; interpreted as Younger Granite; isochron defines an anomalously low initial $^{87}\text{Sr}/^{86}\text{Sr}$
	311 $\pm$ 24	Rb–Sr (WR + feldspar)	3 ^a	7 samples; Eibenstock + Nejdek; interpreted as Zwischengranite,

Table 7 (continued)

Granite	Age (Ma) ($\pm 2\sigma$)	Method (mineral or whole rock)	Source	Comment
				i.e., falling between the Older and the Younger Granites
	320 $\pm$ 6	Rb–Sr (WR)	3 ^a	4 samples; Eibenstock + Bergen; interpreted as Older Granite
	332 $\pm$ 5	Rb–Sr (WR)	3 ^a	5 samples; Eibenstock + Nejde; interpreted as Older Granite
	320 $\pm$ 8	²⁰⁷ Pb/ ²⁰⁶ Pb zircon evaporation	12	Only 7 of 15 zircon samples yielded usable results and were used to calculate an average age.
Pobershau	293 $\pm$ 9	Rb–Sr (dark mica)	3	5 samples; anomalously high initial ⁸⁷ Sr/ ⁸⁶ Sr
	317 $\pm$ 2	U–Pb chemical	7	Monazite+xenotime+uraninite
	321 $\pm$ 3	U–Pb ID TIMS (monazite)	2, 4	Single analysis
Seiffen	302 $\pm$ 4	U–Pb chemical	14	monazite
	301 $\pm$ 5	K–Ar (siderophyllite)	14	siderophyllite
Microgranites and rhyolites				
Altenberg				
	323.9 $\pm$ 2	Re–Os (molybdenite)	ms	Individual crystal
	317.9 $\pm$ 2	Re–Os (molybdenite)	ms	Individual crystal
	c.309	⁴⁰ Ar/ ³⁹ Ar (biotite)	8	Two biotite samples showing irregular pattern with alteration humps, cleaned spectra interpreted to yield plateau ages around 307–309 Ma
	333 $\pm$ 8	²⁰⁷ Pb/ ²⁰⁶ Pb zircon evaporation	9	Granite-porphyry preceding granite; average based on 5 out of 8 grains; average of all grains is 325 Ma with a large uncertainty.
	290 $\pm$ 5	²⁰⁷ Pb/ ²⁰⁶ Pb zircon evaporation	9	Youngest out of 8 grains
	297 $\pm$ 13	K–Ar (amphibole)	10	Analytical details and data not published
Rhyolite cutting Eibenstock granite				
	290 $\pm$ 5	²⁰⁷ Pb/ ²⁰⁶ Pb zircon evaporation	12	Only 7 of 25 zircon samples yielded usable results; average based on 6 zircon samples that overlap within analytical uncertainties.
	297 $\pm$ 8	U–Pb zircon SHRIMP	12	²⁰⁶ Pb/ ²³⁸ U age based on 15 analyses; according to authors, the U/Pb calibration was problematic

Data sources: 1, Gerstenberger et al. (1995); 2, Förster (1998); 3, Gerstenberger et al. (1982); 4, Warkus (1997); 5, Werner et al. (1997), Werner (1998); 6, Velichkin et al. (1994); 7, Förster (1998); 8, Seltmann and Schilka (1995); 9, Kempe et al. (1999); 10, Müller et al. (2005); 11, Tichomirowa (1997); 12, Kempe et al. (2004); 13, Kempe (2003); 14, Förster and Rhede (2006); *ms* this study

Note: Ages are not included in this list if they (1) have been superseded by subsequent work, (2) are obviously flawed by technical and other problems, or (3) have been discredited by earlier workers for various other reasons. Errors quoted as given in the original work.

^aData regionally sampled from the same pluton but from different granites; assignment of samples to younger and older granites are based on prevailing paradigm and local field relations.

treatment, but the ²⁰⁷Pb/²⁰⁶Pb ages, which are insensitive to young fractionation of U from Pb, yield an accurate and precise result for those samples with high ²⁰⁶Pb/²⁰⁴Pb. Our comparison between chemical and ID-TIMS U–Pb dating of magmatic uraninite shows that homogenous uraninite inclusions that are entirely enclosed by a single host mineral provide the same age. For such samples and with the correct analytical procedure, chemical dating may yield the correct answer at considerably less effort than ID-TIMS.

Advantages and limitations of dating inclusions and molybdenite

For rocks and ore deposits with complex metamorphic and deformational histories potentially associated with repeated

elemental redistribution through fluid movement, selection of the proper samples for dating is a crucial first step. For molybdenite, it is essential to work with geologically constrained occurrences from hand specimens taken in an unequivocal geologic context (cf. discussion in Stein 2006). To obtain the age of a specific event in the evolutionary history of the rock, a texturally constrained sample is needed to interpret age information. One advantage of dating inclusions is tight textural control on the sample to be dated, which can be observed and directly drilled from a polished thick section. This removes ambiguities about the relation of the dated mineral to the host and the history of the rock, especially if there are several generations of the dated mineral. Advantages gained from easy sample preparation, however, are more than balanced by problems associated

with the handling and analysis of very small samples. The examples in this study clearly demonstrate that dating of inclusions may yield precise and accurate ages not otherwise possible in geologically complex regions. It should be noted, however, that dating of inclusions is an alternative approach for problematic samples, and not a primary routine approach for dating in general. Furthermore, it should be noted that the textural requirements discussed above must be strictly fulfilled as otherwise the approach of dating inclusions will result in incorrect or ambiguous ages, leading to erroneous geologic interpretations.

The approach presented here works because the host mineral (container) is part of the analysis. The critical property of the container—apart from its primary and shielding character—is its distribution coefficient K_D for the elements making up the chronometer. If the container has a low K_D for these elements, it will contribute little to the combined system *host plus inclusion*, and it will inhibit loss of these elements through diffusion. The critical property of the inclusion is the contrast in K_D between the chemical elements of the parent isotope (high K_D) and the daughter isotope (relatively low K_D). The larger the contrast, the higher the parent-to-daughter ratio, hence, the better the chance of the inclusion to define a single-point age. In summary, the container on one hand guarantees a closed system for the geochronologically relevant elements, while on the other hand, it must contribute only insignificantly to the budget of the parent–daughter elements in the combined system. Thus, the entire geochronological system is captured in the analytical work by extraction of inclusion and its immediate host container. Furthermore, the age calculation will be insensitive to assumptions for the initial ratio when the parent-to-daughter ratio is high. This in turn may allow an accurate age determination at high precision for the dated inclusion.

Although most dated molybdenite samples do not occur as inclusions, as we have defined them at the micron scale in this study, single molybdenite grains sitting in silicate host serve as an effective macroscale analog. Silicate containers, common for molybdenite, are not receptacles for Re and Os. The K_D between molybdenite and surrounding minerals for the chronologically relevant elements Re and Os is comparable to the situation for mineral and melt inclusions. The limited mobility of Re and Os in systems that are not oxidized keeps the Re–Os system in molybdenite closed at the grain boundary when in contact with silicates. If molybdenite is in direct contact with other sulfides (e.g., co-precipitating chalcopyrite), through time radiogenic Os may be absorbed by adjacent sulfides; the effect of this absorption on the age for molybdenite or bordering sulfide is dependent on the inherent concentrations of Re and Os and the K_D and the geologic history of the samples (Stein et al. 2003). Re highly prefers molybdenite, whereas small

quantities of radiogenic Os may migrate to other sulfides along sulfide–molybdenite grain boundaries. The above approach should also apply to the Lu–Hf chronometer for REE minerals, which may show extreme fractionation between Lu and Hf. In contrast, the approach will definitely not work for the Sm–Nd system, as these two elements exhibit similar geochemical behavior (i.e., do not fractionate by orders of magnitude).

The approach of dating inclusions, however, has some limitations. (1) In some situations, the host for ideally datable inclusions is not uniquely related to a certain stage in the history of the rock. In such a situation, the meaning of an age will be unclear and the use of inclusions rather than mineral separates may not be advantageous. (2) The host mineral shows evidence for open-system behavior impacting the credibility of the inclusion, e.g., fractures, deformation bands, or planes of secondary fluid inclusions cutting host and inclusion. These features may give inclusion fluids a way to gain access into the inclusion, permitting loss or gain of the parent or the daughter isotope. In the case of melt inclusions that exsolved a fluid phase during crystallization, subsequent development of such defects may result in the loss of the fluids and the elements dissolved in the fluid. This kind of open-system behavior may result in erroneous ages and is a fundamental violation of the basic requirements for dating based on radiogenic isotopes. For preferential daughter loss, the obtained ages fall in the range defined by the time of formation of the inclusion and the time of disturbance, i.e., they represent mixed ages. For preferential parent loss, the obtained ages are too old. In the case of molybdenite, such a situation could be obtained if molybdenite is exposed to a highly oxidized fluid (e.g., weathering). (3) Inclusions in minerals that are brittle or have a good cleavage may be accidentally opened during drilling of the sample. This problem may become particularly important when the diameter of the drilled core is too small or the cleavage of the hosting mineral is unfavorably oriented with respect to the axis of the drilled sample core. The effect from this differs from limitations under type 2 only in that mixed ages may reach younger values. For samples that show problems of type 1 or 2, other dating approaches are likely to yield more useful results.

Age of Late-Variscan magmatism and related mineralization in the Erzgebirge

Earlier age determinations on Late-Variscan granites—along with the age determinations presented above—are compiled in Table 7. This compilation shows a relatively narrow age distribution for data acquired over the last few years and a broader age range for older geochronologic data and $^{207}\text{Pb}/^{206}\text{Pb}$ zircon evaporation ages. The broader age range does not reflect a more representative sampling of

different lithologies. In contrast, it reflects a series of conceptual and technical problems, with the most prominent among them discussed below:

1. *The concept of an older and younger suite of granites* Before the advent of modern geochronology, the granites of the Erzgebirge were grouped into older and younger granite series. The older series included weakly to moderately evolved biotite and two-mica granites, whereas the younger series included highly evolved and mineralized Li-mica granites. Later, Förster et al. (1998, 1999) showed that such a classification was not compatible with compositional (and available age) data from the granites.
2. *The regional distribution of samples used to obtain an isochron* Early Rb–Sr dating used whole-rock samples typically distributed at the pluton scale in the hope of obtaining a large spread in Rb/Sr ratios. This sampling strategy ignored the possibility of heterogeneous initial Sr isotopic compositions, which may affect the result for samples whose measured Sr isotopic composition is not particularly radiogenic (for discussion, see Romer 1994).
3. *Underestimation of the effect of secondary alteration* Some granites have been locally affected by fluids associated with later tectonic reactivation. Alteration and decomposition of feldspar resulted in a marked loss of Sr, which resulted in high Rb/Sr values and, with time, very high $^{87}\text{Sr}/^{86}\text{Sr}$ values. Gerstenberger (1989) showed that these high Rb/Sr ratios were acquired some 10 to 20 million years after emplacement of the granite; however, he did not relate this age to a secondary event. Whole-rock isochrons based on disturbed samples of this kind may yield ages that are too young, in some cases with WR ages even younger than mica ages (e.g., Gerstenberger et al. 1995).
4. *Overestimation of analytical reliability of the data* Age determinations based on the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio for radiogenic Pb in zircon using the evaporation technique rely on the assumption of a strict single-stage history of the dated zircon. This is unlikely for zircon from most Late-Variscan granites of the Erzgebirge. Erzgebirge zircon typically is complexly zoned and shows signs of alteration (e.g., Förster 1998, 2001; Thomas et al. 2006). Furthermore, as a result of α -recoil, which physically displaces daughter isotopes in the U and Th decay series, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio may be heterogeneous within an individual zircon crystal at the nano-scale. Leaching and selective dissolution of zircon have demonstrated this effect (e.g., Mattinson 1994; Corfu 2000; Davis and Krogh 2000). For instance, Corfu (2000) shows that subsequent leaching steps have different $^{207}\text{Pb}/^{206}\text{Pb}$ values. Although zircon internal redistribution of U daughters has no effect on the bulk

$^{207}\text{Pb}/^{206}\text{Pb}$ value, the sequential release (either due to geological processes or the analytical procedure of stepwise Pb evaporation) may result in a range of $^{207}\text{Pb}/^{206}\text{Pb}$ values. The average of the $^{207}\text{Pb}/^{206}\text{Pb}$ value may be slanted toward too young or too old ages for grains where not all Pb were accounted for in the sequential analysis. Due to the fact that most ^{235}U (parent of ^{207}Pb) has decayed in the first half of Earth's history, the $^{207}\text{Pb}/^{206}\text{Pb}$ value has a high time resolution for old zircon, but a poor one for young zircon. Thus, analytical uncertainties have a severe influence on the apparent $^{207}\text{Pb}/^{206}\text{Pb}$ age for Phanerozoic zircon.

Our new age data in combination with the age data in Table 7 clearly demonstrate that the major episode of Variscan granitic magmatism occurred over a relatively short period of about 10 Ma. The majority of primary tin mineralization was related to the emplacement of the ~320 million years old old granites. Our data do not support prolonged magmatic activity in the Erzgebirge and are incompatible with the interpretation of 290 to 310 Ma ages as emplacement ages for major granite plutons. Our data, however, do not rule out that some smaller Sn-specialized bodies, which are known predominantly from drill holes, may have slightly younger ages. An example of a small and late intrusion is Seiffen, which has a Th–U–Pb chemical age of 301 ± 5 Ma (Förster and Rhede 2006). To the extent that previously published ages are analytically sound, they must reflect later disturbances rather than primary emplacement ages for granitic magmatism. It should be mentioned that during later events not only was it possible to disturb geochronologic systems, but significant chemical redistribution, perhaps including tin, may have taken place.

The formation of the Erzgebirge tin province has been controversial, partly because earlier workers invoked two generations of granite, and partly because some workers favored later addition of tin unrelated to the granite magmatism. The two periods of Sn mineralization—according to the different models—are ca. 320 Ma and at ca. 280 Ma. The high Sn contents in granitic melt inclusions demonstrate that primary tin is related to granitic magmatism. Our data for these Sn-mineralized magmatic rocks yield ages that are older than 315 Ma and generally younger than 324 Ma, although our data do not rule out later Sn redistribution at the scale of individual deposits. The occurrence of a single magmatic event implies that on the scale of the Erzgebirge, a wide range of different magmatic sources were tapped essentially coevally, giving rise to mildly peraluminous, transitional I–S type, peraluminous S-type granites, and mildly peraluminous granites of A-type affinity, which were further subdivided into low-F biotite granites; low-F two-mica granites; high-F, high- P_2O_5 Li–mica granites; high-F, low- P_2O_5 Li–mica granites

(e.g., Zinnwald); and medium-F biotite granites (cf. Förster 1998; Förster et al. 1999), based on their geochemistry and mineralogy. This compositional classification supercedes the earlier classification of older vs younger granites that does not stand the test of geochronology. The various granite varieties mainly represent crustal material. Although the input of mantle material occasionally has been seen as a major source for Erzgebirge magmatism or at least as a heat source to produce the magmatism, ϵNd_{320} values in the range of -2.9 to -7.4 demonstrate the dominance of crustal sources (see compilation in Förster et al. 1999). Over-thickened crust of the Bohemian massif, in combination with U-rich lithologies in the Saxothuringian crust, may have favored intracrustal melting. In such a scenario, the spatial distribution of various types of granitic magmatism and associated mineralization in the Erzgebirge would reflect the heterogeneous nature of the crust in the melt region, giving a wide range of different granites depending on the lithologic character of the melted sources. The spatial distribution of Sn-rich source rocks may also have been a controlling factor on the later distribution of the major Sn-bearing granites.

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