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Textural and chemical changes undergone by zircon during the Pb-evaporation technique

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ABSTRACT

This study provides details of the textural and compositional changes in zircon as a result of heating from approximately 1400 to 1650 °C under vacuum in a mass spectrometer during analysis by Pb-evaporation from a single zircon grain. Electron microprobe analyses of partially analyzed zircon grains show that the zircon reacts preferentially around the margins, along cracks, and around inclusions at low temperatures, whereas the more crystalline internal portions of the zircon react at higher temperatures. The reaction involves the breakdown of zircon to form a porous zirconium oxide with concomitant release of silica and other trace elements, including Pb, which are collected on a filament and subsequently ionized to measure the isotopic composition of the Pb. The reaction front migrates inwards from the margin of the zircon sample with increasing temperature, such that Pb from the most retentive sites in the crystal is released at the highest temperatures. These domains are the least likely to have undergone Pb loss, and thus the $^{207}Pb/^{206}Pb$ ratios obtained at these temperatures are considered to represent best the age of the zircon. The Hf isotopic composition of zircon cannot be obtained using the evaporation technique because of uncorrectable mass interferences with ^{176}Hf. The use of this technique to determine the $^{207}Pb/^{206}Pb$ age of other U-bearing minerals such as titanite, baddeleyite, and apatite is complicated by different breakdown reactions within these minerals, especially the lack of silica, which is needed for successful analysis of the isotopic composition of the Pb.

INTRODUCTION

Zircon is the most commonly used mineral for U-Pb geochronology because it has a high U/Pb ratio, is generally resistant to isotopic resetting, and occurs in a variety of rock types. The single-zircon Pb-evaporation technique (Kober, 1986, 1987) is now being used for routine analysis of single zircon grains in a number of laboratories worldwide. The technique consists of loading an untreated single zircon grain in an outgassed Re filament. The sample is then heated in steps from about 1400 to about 1650 °C. The Pb driven off from the zircon is deposited on a second filament and subsequently analyzed for its isotopic composition. However, only $^{207}Pb/^{206}Pb$ ages are obtained because the zircon grains are not spiked. Conventional U-Pb geochronologists consider $^{207}Pb/^{206}Pb$ ages obtained by Pb-evaporation to represent minimum crystallization ages for zircon because there is no independent evidence that zircon ages are concordant (e.g., Heaman and Parrish, 1991). However, a variety of studies comparing ages from the single-zircon Pb-evaporation technique with ages obtained using conventional and high-precision U-Pb geochronology indicate that the $^{207}Pb/^{206}Pb$ ages are usually identical to concordant U-Pb ages (Kober, 1986, 1987; Kroner and Todt, 1988; Ansdell and Kyser, 1991; Ansdell et al., 1991).

The $^{207}Pb/^{206}Pb$ age profiles obtained during step heating (e.g., Kober, 1986; Kober et al., 1989) are analogous to the age profiles obtained during $^{40}Ar/^{39}Ar$ step heating, which are considered to represent a profile of the distribution of radiogenic ^{40}Ar within a given sample (Turner et al., 1966). Recently, the interpretation that Ar-Ar profiles are related to volume diffusion of Ar during step heating has been questioned by Gaber et al. (1988) and Lee et al. (1991). These workers show that during step heating in a vacuum, hydrous minerals such as biotite and amphibole undergo phase changes at various temperatures that are concurrent with extensive Ar release. The internal character of hydrous phases and how they are affected by heating to temperatures of about 1200 °C in vacuum are thus important in correctly interpreting Ar-Ar age profiles. The objective of this study is to document the morphological and compositional changes that zircon undergoes as a result of heating to temperatures of 1650 °C under vacuum during Pb-isotope analysis. This information is vital to determine the process by which Pb is released from zircon and to provide constraints on the geological significance of the $^{207}Pb/^{206}Pb$ ages obtained (see Ansdell et al., 1991). Results of preliminary attempts to obtain both $^{207}Pb/^{206}Pb$ ages from baddeleyite, titanite,

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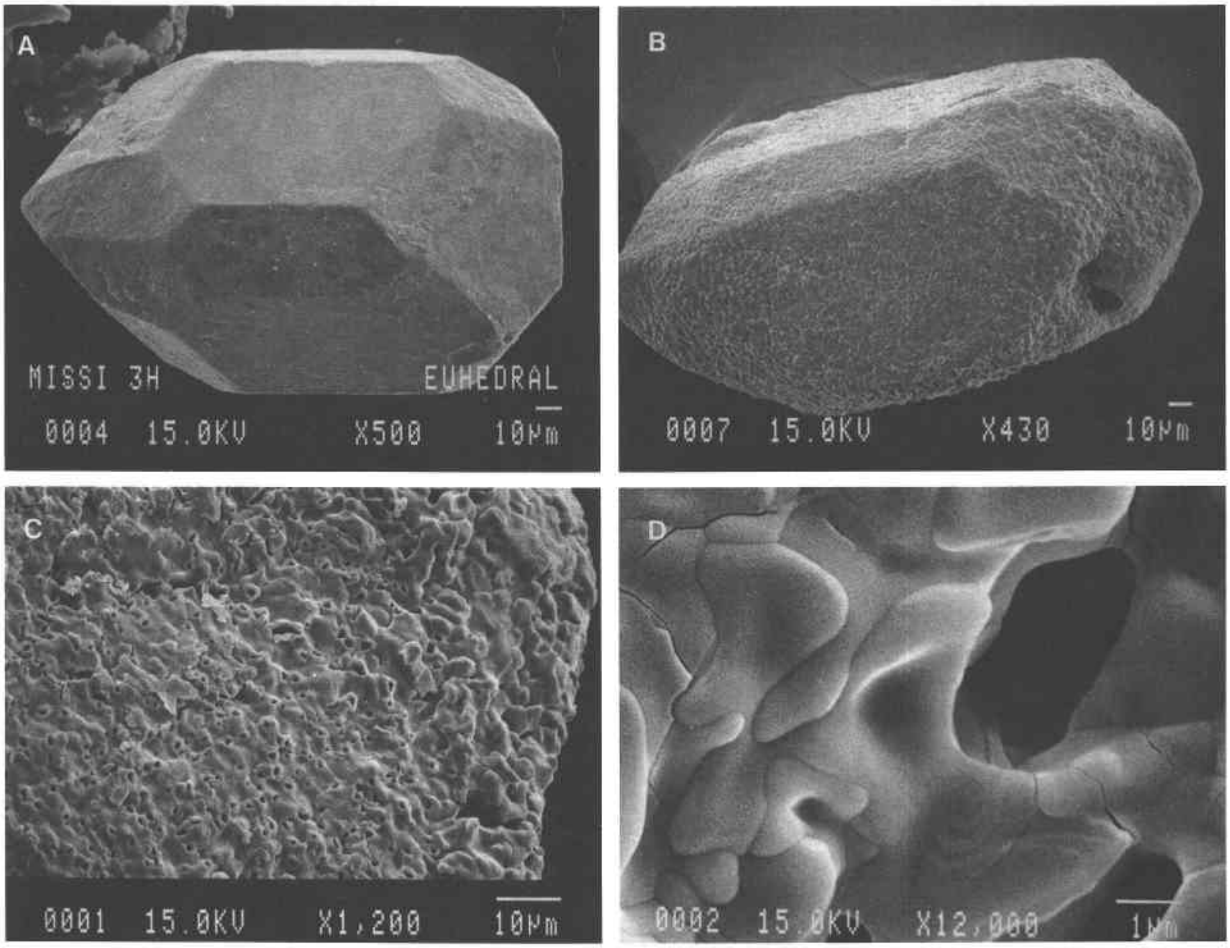

Fig. 1. Secondary electron images of zircons. (**A**) Typical euhedral zircon from a suite of detrital zircon grains analyzed by Ansdell et al. (1992). (**B**) Typical appearance of zircon after heating in mass spectrometer to 1620 °C. Euhedral zircon from Missi 5 suite, which yielded a ^{207}Pb/^{206}Pb age of 1865 ± 25 Ma (Grain 2, Missi 5; Ansdell et al., 1992). (**C**) Close-up of surface showing porous texture. (**D**) Close-up of surface showing channels and annealed texture with triple junctions.

and apatite and Hf isotopic compositions of single zircon grains are also reported.

ANALYTICAL METHODS

The analysis of single zircon grains by the Pb-evaporation technique at the University of Saskatchewan follows the procedure of Kober (1987), with slight modifications as outlined by Ansdell and Kyser (1991) and Ansdell et al. (1992). Analysis of Pb from the zircon is usually continued until all the Pb has been removed, and the ^{207}Pb/^{206}Pb age for each heating step is calculated using the technique outlined by Kroner and Todt (1988). An age plateau is considered to represent the age of the zircon, similar to the step-heating Ar-Ar method. If a well-formed plateau is not attained, then the highest temperature step represents the minimum age of the zircon. A selection of zircon samples, some of which still retained some Pb, were removed from their filament and analyzed using a Jeol JXA-8600 electron microprobe at the University of Saskatchewan. Backscattered electron images and wavelength-dispersive analyses were obtained from C-coated samples, and secondary electron images were obtained from Au-coated samples.

RESULTS

Inspection of zircon after its removal from the mass spectrometer indicates that every zircon sample turned a milky white color irrespective of original color and irrespective of the number of heating steps. The majority of samples retained their original morphology, but became very friable after heating, primarily as a result of the changes in the chemical composition of zircon during heating. Secondary electron microscopy of the surface of partially reacted zircon reveals that the surface is more irregular and porous than unreacted zircon (Fig. 1A, 1B). Under high magnification, the surface is seen to consist of channels into the crystal, up to a few micrometers wide, indicating a highly porous material (Fig. 1C, 1D). The foam texture of the surface is suggestive of annealing with formation of triple junctions (Fig. 1D). The high porosity

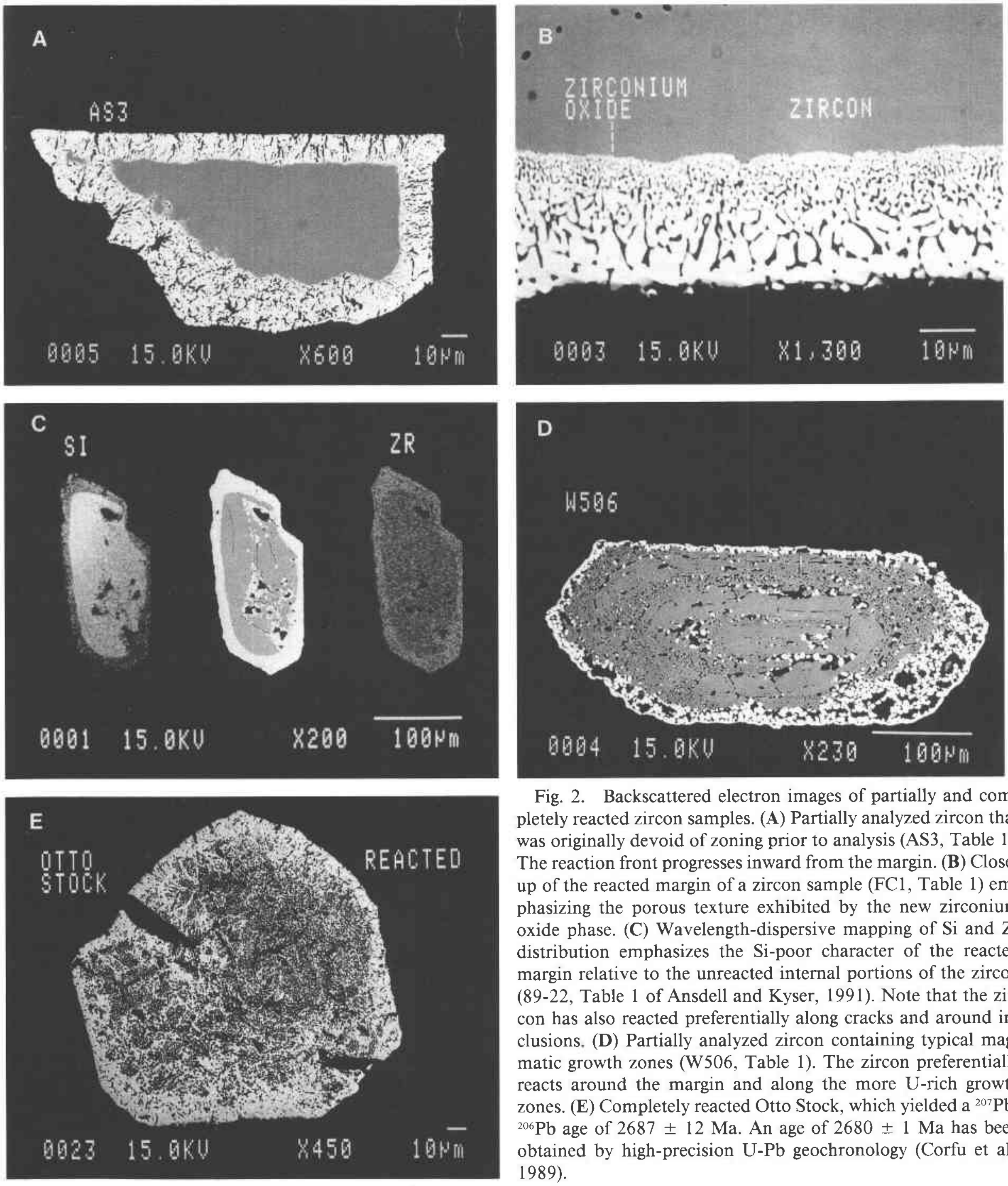

Fig. 2. Backscattered electron images of partially and completely reacted zircon samples. (**A**) Partially analyzed zircon that was originally devoid of zoning prior to analysis (AS3, Table 1). The reaction front progresses inward from the margin. (**B**) Close-up of the reacted margin of a zircon sample (FC1, Table 1) emphasizing the porous texture exhibited by the new zirconium oxide phase. (**C**) Wavelength-dispersive mapping of Si and Zr distribution emphasizes the Si-poor character of the reacted margin relative to the unreacted internal portions of the zircon (89-22, Table 1 of Ansdell and Kyser, 1991). Note that the zircon has also reacted preferentially along cracks and around inclusions. (**D**) Partially analyzed zircon containing typical magmatic growth zones (W506, Table 1). The zircon preferentially reacts around the margin and along the more U-rich growth zones. (**E**) Completely reacted Otto Stock, which yielded a $^{207}Pb/^{206}Pb$ age of 2687 ± 12 Ma. An age of 2680 ± 1 Ma has been obtained by high-precision U-Pb geochronology (Corfu et al., 1989).

indicates that a volume decrease occurs during the alteration process.

Backscattered electron images and microprobe analyses show the physical and chemical effects of the heating process on zircon. In partially analyzed zircon with no compositional zoning or structural defects (e.g., Fig. 2A), the zircon has reacted preferentially from the margins inwards, as shown by the porous texture of the margin (Fig. 2B). Heating of the zircon converts the reacted portion to a porous zirconium oxide with an associated loss of silica (Table 1, Fig. 2C).

The effects of the breakdown reaction associated with heating zircon are heterogeneous in more internally complex zircon. Figure 2C shows that the reaction process

TABLE 1. Electron microprobe analyses of representative unreacted and reacted zircon, Pb isotopic compositions, and $^{207}Pb/^{206}Pb$ ages obtained using the single-zircon Pb-evaporation technique

Sample no.	AS3		FC1		W506			89-22	
Sample	Duluth anorthosite		Duluth anorthosite		Hoskin Lake granite			Neagle Lake pluton	
Location	Minnesota		Minnesota		Wisconsin			Saskatchewan	
(Wt%)	Unreacted	Reacted	Unreacted	Reacted	Light gray	Dark gray	Reacted	Unreacted	Reacted
SiO_2	30.81	—	32.80	—	32.10	33.10	—	32.30	—
ZrO_2	66.04	97.20	66.49	92.25	66.21	64.16	92.65	65.58	94.41
HfO_2	1.62	2.18	1.05	1.40	1.73	2.24	4.51	1.37	2.76
CaO	—	—	—	—	—	0.05	0.13	—	—
ThO_2	—	0.08	0.05	0.08	0.03	—	0.14	—	—
U_3O_8	—	—	0.05	—	0.03	0.22	—	—	—
TOTAL	98.68	99.85	100.50	94.53	100.18	99.89	97.85	99.26	97.17
$^{207}Pb/^{206}Pb$ age	1098 ± 16		1108 ± 12		1903 ± 12			1831 ± 15	
$^{207}Pb/^{206}Pb$	0.07612 ± 61		0.07648 ± 48		0.11651 ± 78			0.11191 ± 98	
$^{208}Pb/^{206}Pb$	0.1473 ± 27		0.1672 ± 85		0.1835 ± 50			0.0538 ± 15	
$^{204}Pb/^{206}Pb$	<0.00009		<0.00002		<0.00009			<0.00007	
U-Pb zircon U.I. age	1099 ± 1*		1099 ± 1*		—			—	
U-Pb titanite U.I. age	—		—		—			1846 + 14/−6†	
Rb-Sr whole rock age	—		—		1692 ± 69**			—	

Note: Standards used for electron microprobe analyses were quartz (Si), zircon (Zr, Hf), diopside (Ca), monazite (Th), and U_3O_8(U). Dashes indicate that the element was not detectable. Operating conditions: accelerating voltage = 15 kV, probe current for wavelength-dispersive analysis and backscattered electron imagery −10 nA, except for Hf (35 nA), probe current for secondary electron microscopy = 300 pA.

The Pb isotopic compositions and the calculated $^{207}Pb/^{206}Pb$ age were taken from the highest temperature evaporation step. All data are unpublished, except for 89-22 (89-22 Grain1 in Ansdell and Kyser, 1991). Ages are reported in Ma, and errors in Pb isotopic compositions. Ages are quoted at 2σ.

* J. Paces, personal communication, 1991.

** Peterman et al., 1985.

† Ashton et al., 1992.

preferentially affects zircon adjacent to cracks and mineral inclusions, as well as the margins of the crystal. A zircon grain with typical magmatic growth zoning is shown in Figure 2D. Variations in composition are indicated by differences in level of gray, and there is preferential reaction of the growth zones exhibiting the darker gray color. If step-heating analysis is continued until there is no Pb left, the whole of the zircon exhibits a homogeneous porous texture (Fig. 2E). Many of these observations have also been reported recently by Roddick and Chapman (1991).

The ionization filament is usually cleaned by heating to high temperature (about 2200 °C) after each analysis. The material deposited on the ionization filament is thus burnt off, which prevents Pb from the next evaporation step from mixing with Pb derived from the previous temperature step. Ionization filaments prior to thermal cleaning have a residue consisting of silica. No other elements were detectable in the residue at the limit of the EDS analysis. However, during the course of some mass spectrometry analyses, mass scans indicate that Pb, REE, Hf, and a suite of other trace elements are also deposited on the ionization filament during each evaporation step.

Zircon is an important Hf reservoir in the continental crust, and the Hf isotopic composition of zircon may thus provide an important constraint on its source area (e.g., Patchett et al., 1981; Stevenson and Patchett, 1990). The possibility of determining the $^{176}Hf/^{177}Hf$ ratio of the same zircon dated using the Pb-evaporation technique is obviously attractive. The most abundant Hf isotope, ^{180}Hf, was monitored during the course of Pb isotope analyses of zircon from Early Proterozoic granitoids from the Flin Flon area, Canada (Ansdell and Kyser, 1991). At the filament temperatures attained during a typical Pb-evaporation analysis, the ^{180}Hf intensity was only marginally above background levels on the secondary electron multiplier, but significant signals were obtained by increasing the evaporation and ionization filament temperatures to about 2000–2300 °C. However, electron microprobe analyses of reacted zircon samples (Table 1) indicate that some Hf is retained within the zirconium oxide phase that forms during the breakdown of zircon. In addition, measurement of ^{176}Hf using the evaporation technique is intractable without prior element separation because of mass interferences from ^{176}Lu and ^{176}Yb.

IMPLICATIONS FOR DATING ZIRCON USING THE Pb-EVAPORATION TECHNIQUE

Zircons are often internally heterogeneous and may contain growth zones, resorption features, cores, overgrowths, metamict zones, alteration zones, and mineral and fluid inclusions. Radiogenic Pb that accumulates within the zircon as a result of decay of U may be held in, or associated with, all of these internal features, although they have different capacities to retain Pb (Kober, 1986). For example, Pb is more easily removed from metamict zones than crystalline domains in zircon. Conventional dissolution and analysis of zircon that contains both domains result in discordant U-Pb ages. In most conventional U-Pb laboratories, painstaking but fruitful attempts are made to reduce the likelihood of analyzing zircon containing domains that have undergone later Pb loss in order to obtain high-precision, concordant U-Pb ages. The methods employed include abrasion (Krogh, 1982a), magnetic susceptibility (Krogh, 1982b), and hand picking. In contrast, the Pb-evaporation technique relies on temperature to separate Pb from different domains within the zircon, i.e., Pb adsorbed onto the surface or along cracks is driven off at low temperatures, Pb from metamict domains at intermediate temperatures, and Pb from crystalline portions of the zircon at high temperatures (Kober, 1986, 1987).

The observations made in this study indicate that the breakdown of zircon preferentially takes place from the margin inwards. Thus, any Pb adsorbed on the surface of the zircon would be removed during the lowest temperature step. This Pb is assumed to be analogous to that removed during abrasion and acid leaching, prior to dissolution in conventional U-Pb geochronology.

In an internally homogeneous zircon (e.g., Fig. 2A), subsequent higher temperature steps result in the inward migration of the reaction front from the margins of the zircon, and each step should yield the same $^{207}Pb/^{206}Pb$ ages. In zircon that is cracked and contains inclusions but is otherwise relatively homogeneous (e.g., Fig. 2C), the age spectrum may be more complex. The reaction front migrates from the internal heterogeneities, as well as the margins of the zircon, and the last aliquot of Pb is derived from the most crystalline portions of the zircon that are also the farthest away from both the margin and any internal heterogeneities. In these cases, the highest temperature evaporation step yields the most accurate $^{207}Pb/^{206}Pb$ age for that zircon. Inclusion-rich zircon exhibiting magmatic growth zoning (e.g., Fig. 2D) reacts preferentially around the margins and inclusions, as well as along specific growth zones. In zircon exhibiting magmatic growth zoning in which specific growth zones have not preferentially undergone Pb loss, $^{207}Pb/^{206}Pb$ ages obtained from growth zones that react at lower temperature do not differ from those that react at higher temperature, since the zircon grew over a relatively short time during the crystallization of the magma.

The development of metamict zones in zircon commonly includes the formation of microfractures that crosscut the more crystalline portions of the zircon and radiate away from the metamict zones (Chakoumakos et al., 1987). This phenomenon is likely related to the volume expansion of the metamict zones. The location of these metamict or cracked crystalline zones within the zircon controls the temperature at which Pb is derived from them. Zones connected to the surface by cracks lose Pb at relatively low temperatures, and the crystalline, most crack-free internal portions of the zircon lose Pb at higher temperatures, unless the metamict domains are located toward the center of the zircon and are not connected to the surface by cracks. Characterization of the internal structure and composition of a zircon grain are thus important in properly interpreting age spectra obtained using the Pb-evaporation technique.

Overall, the observations made on partially analyzed zircon support the general hypothesis of Kober (1986) that Pb is derived from locations within the zircon at different temperatures, with the Pb from the most retentive sites being released only at the highest temperature. These domains are the least likely to have undergone alteration and Pb loss. Accordingly, the $^{207}Pb/^{206}Pb$ ratio derived from the higher temperature steps are considered to be an accurate indicator of the age of the zircon.

The observations made during this study also shed light on the process by which Pb is released from zircon. In experiments performed at atmospheric pressure, Butterman and Foster (1967) showed that zircon breaks down to form zirconium oxide and silica at 1676 °C. Kober (1987) suggested that this breakdown reaction was unlikely to be the dominant source of silica because this temperature is higher than the temperature of the evaporation filament during the Pb-evaporation technique. However, it appears that under vacuum (10^{-8} bar), the zircon structure breaks down to zirconium oxide, releasing silica and other trace elements, such as Pb, at temperatures as low as 1400 °C. The zircon thus provides its own silica bed on the ionization filament, which results in a stable Pb^+ ion beam. We suggest that the viability of the single-zircon Pb-evaporation technique is dependent upon the release of silica from the zircon and the formation of the silica bed. Bogomolov (1991) assumed that volume diffusion was the main mechanism of lead migration between approximately 1200 and 1650 °C for various ground and unground single zircon grains. However, the textural evidence reported here suggests that the release of Pb is likely related to the progression of the reaction front through the zircon.

APPLICATION TO OTHER MINERALS

Attempts to use the Pb-evaporation technique to determine the age of single crystals of other U- and Pb-bearing minerals were unsuccessful. Titanite from the Phantom Lake granite, Saskatchewan, Canada, which has been dated at 1840 ± 7 Ma using the Pb-evaporation technique on zircon (Ansdell and Kyser, 1991), was heated progressively from about 1200 to about 2000 °C. Detectable bursts of ^{206}Pb were obtained at about 1250, 1300, and 1800 °C, but none produced a measurable Pb signal after a 10 min evaporation period at these temperatures. Apatite from the Annabel Lake pluton (1860 ± 6 Ma; Ansdell and Kyser, 1991) yielded a ^{206}Pb signal only slightly above background up to about 1500 °C and nothing at higher temperatures. At these temperatures the apatite had melted. Baddeleyite from the Phalaborwa complex, South Africa (2047 + 11 or −8 Ma; Eriksson, 1984) yielded a small but consistent ^{206}Pb signal as the temperature of the evaporation filament was raised from 1200 to 2000 °C.

The lack of success in obtaining $^{207}Pb/^{206}Pb$ ages for U-bearing minerals other than zircon implies that the silica released by zircon during breakdown may play an important role in the production of a stable Pb^+ ion beam. To test this theory, 12 μL of silica gel was dried on Re filaments prior to loading apatite and baddeleyite. For both minerals, the filaments were heated to 1500–1700 °C and allowed to evaporate for 20 min. Although there was no improvement in the overall Pb signal obtained from the apatite, a significant ^{206}Pb signal was attained for a very short period from the baddeleyite. Higher temperature evaporation steps yielded ^{206}Pb intensities barely above background intensities. The addition of silica gel to the filaments containing the minerals may improve the beam stability, but the silica is removed completely during the first evaporation step. Therefore, the lack of silica in baddeleyite and apatite indicates that successful analysis of these minerals by the Pb-evaporation technique is unlikely. Successful analysis of titanite requires detailed documentation of the temperatures at which breakdown reactions occur, and successful analysis will only be possible if there is coincidental release of both Pb and silica.

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