



Precise U–Pb and Th–Pb age determination of kimberlitic perovskites by secondary ion mass spectrometry

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ABSTRACT

Perovskite, a common Th- and U-enriched accessory mineral crystallised from kimberlitic magmas, has long been thought to be an important geochronometer for dating the emplacement of kimberlite. However, it also contains variably high levels of common Pb, which makes it difficult to obtain a precise measurement of radiogenic Pb/U and Pb/Th isotopic compositions using microbeam techniques such as SIMS and LA-ICP-MS. We present calibration protocols for *in situ* U–Pb and Th–Pb age determination of kimberlitic perovskite using the large double-focusing Cameca IMS 1280. Linear relationships are found between $\ln(^{206}\text{Pb}^{*+}/\text{U}^{+})$ and $\ln(\text{UO}_2^{+}/\text{U}^{+})$, and between $\ln(^{208}\text{Pb}^{*+}/\text{Th}^{+})$ and $\ln(\text{ThO}^{+}/\text{Th}^{+})$, based on which the inter-element fractionation in unknown samples during SIMS analyses can be precisely calibrated against a perovskite standard. The well-characterized Ice River perovskite is chosen as the U–Pb and Th–Pb age standard in this study. The ^{204}Pb -correction method was used to estimate the fraction of common Pb, which is consistent with the results obtained using the ^{207}Pb -based correction method for the dated perovskites of Phanerozoic age.

A Tazheran perovskite with unusually high U but rather low Th yielded a Concordia U–Pb age of 462.8 ± 2.5 Ma and a Th–Pb age of 462 ± 4 Ma. Two perovskite samples from the Iron Mountain kimberlite have identical Concordia U–Pb ages of 410.8 ± 3.4 Ma and 411.0 ± 2.6 Ma, which are consistent within errors with their corresponding Th–Pb ages of 409.2 ± 7.2 Ma and 412.3 ± 3.3 Ma, respectively. Two perovskite samples from the Wessleton Mine of South Africa yielded indistinguishable $^{206}\text{Pb}/^{238}\text{U}$ ages of 91.5 ± 2.2 Ma and 90.3 ± 2.9 Ma, and Th–Pb ages of 90.5 ± 0.8 Ma and 88.4 ± 1.6 Ma, respectively. Accuracy and precision of 1–2% (95% confidence level) for these measurements have been demonstrated by the consistency of their U–Pb and Th–Pb ages with the recommended U–Pb ages of previous works.

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1. Introduction

Kimberlites, the major source of diamonds, are a clan of volatile-rich potassic ultramafic rocks that originate from the deep lithospheric mantle (e.g., Mitchell, 1986, 1995). During their journey to the surface, kimberlites entrain samples (xenoliths and xenocrysts) from the inaccessible parts of the earth's deep lithosphere. These samples are important for deciphering the composition and structure of the lithosphere, but also introduce uncertainties in dating kimberlites with conventional methods. For example, zircon U–Pb dating may give an age older than the kimberlite emplacement as zircon commonly occurs as xenocrysts (e.g., Kinny et al., 1989; Kinny and Meyer, 1994). K–Ar and Ar–Ar methods are commonly used to date kimberlitic mica, but many factors may affect their reliability including the common alteration, low closure temperature, potential excess Ar, and the xenocrystic origin of

some mica. Similar problems potentially exist for Rb–Sr dating of micas, though some reasonable results were reported (e.g., Heaman et al., 2003, 2004; Li et al., 2005).

Perovskite has long been thought to have great potential for dating kimberlites because (1) it is a groundmass or microphenocryst phase related petrographically to the eruption of the kimberlite (Mitchell, 1972, 1986), (2) it generally has high abundances of U (more than 100 ppm) and especially Th, which makes it suitable for U–Th–Pb dating (e.g., Heaman et al., 2003, 2004), (3) perovskite is relatively abundant in kimberlites and can be dated directly in thin section using secondary ion mass spectrometry (SIMS) or laser ablation (LA)-ICP-MS (e.g., Ireland et al., 1990; Smith et al., 1994; Kinny et al., 1997; Batumike et al., 2008; Simonetti et al., 2008; Yang et al., 2009). However, perovskite in kimberlites sometimes occurs as very fine grains that commonly have overgrowths of other Pb-bearing minerals such as rutile, spinel and ilmenite (Kinny et al., 1997; Chakhmouradian and Mitchell, 2000). It is sometimes difficult to separate pure fractions of fine-grained perovskite for isotope dilution analysis using TIMS. More recently, many researchers have used LA-ICP-MS techniques for dating U–Pb ages of perovskite (e.g., Cox and Wilton, 2006; Batumike et al., 2008; Simonetti et al., 2008;

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Yang et al., 2009). However, due to lack of precise ^{204}Pb measurements by LA-ICP-MS, their U–Pb ages can only be obtained by the ^{207}Pb -correction method, which relies on the assumption of a concordant U–Pb system for the dated perovskites. The LA-ICP-MS method will encounter difficulties when Pb loss happened or for relatively old (Mesoproterozoic or older) samples (e.g., Yang et al., 2009). Thus, precise measurement of ^{204}Pb is required for accurate age determination of perovskite. Moreover, the perovskites that are fine-grained, or contain altered domains or potential micro-inclusions of other minerals still call for analysis within smaller volumes, such as can be provided by high-resolution SIMS.

SIMS U–Th–Pb age determinations of perovskites were first reported about 20 years ago for the Allende and Murchison carbonaceous chondrites (Ireland et al., 1990). However, further applications of SIMS for dating perovskite are very limited (Smith et al., 1994; Kinny et al., 1997). In this study we use the large double-focusing Cameca IMS 1280 for perovskite age determination, with development of calibration protocols to achieve precise radiogenic Pb/U and Pb/Th ratios. This method can yield independent U–Pb and Th–Pb data simultaneously, allowing an internal examination of age concordance in the absence of precise $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{235}\text{U}$ data due to the high abundance of common lead in most perovskite crystals.

2. Instrumentation

U–Th–Pb analyses of perovskites were performed using the Chinese Academy of Sciences Cameca IMS-1280 (CASIMS) at the Institute of Geology and Geophysics in Beijing. The O_2^- primary ion beam was accelerated at 13 kV, with an intensity of ca 10–18 nA. The aperture illumination mode (Kohler illumination) was used with a 200 μm primary beam mass filter (PBMF) aperture to produce even sputtering over the entire analyzed area. The ellipsoidal spot is about $20 \times 30 \mu\text{m}$ in size. Positive secondary ions were extracted with a 10 kV potential.

All samples analyzed in this study were cast in one epoxy mount. The mount was coated with about 30 nm of high-purity gold to reach $<20 \Omega$ resistance. Sample charging effects were minimized by optimizing the energy offset to maximum transmission in a 60 eV energy window at the start of each analysis, using the $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4$ reference peak at mass 200. This peak of $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4$ is a matrix reference for centering the secondary ion beam, energy and mass adjustments, as well as reference for mass 200.5 (background). The instrument was operated in high transmission (Filed aperture = 5000, Max area = 40). Rectangular lenses were activated in the secondary ion optics to increase the transmission at high mass resolution (De Chambost et al., 1996). A mass resolution of ca 5500 (defined at 1% peak height) was used to separate $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4^+$ peaks from isobaric interferences. This mass resolution also is enough to separate U, Th and Pb isotopes from isobaric interferences, such as oxides of rare earth elements (e.g., Williams, 1998). A single electron multiplier was used in ion-counting mode to measure secondary ion beam intensities by a peak jumping sequence (Table 1). Each measurement consists of 10 cycles, and the total analytical time is ca 16 min. The mass fractionations of Pb isotopes and Pb hydrides (requiring a mass resolution $>30,000$) were not considered because a number of studies have shown that these two effects are negligible and there appears to be a mutual cancellation (e.g., Ireland et al., 1990; Whitehouse et al., 1997; Williams, 1998; Ireland and Williams, 2003; Li et al., 2009). Two sessions of analyses were performed on the same mount. The raw data are presented in Appendix A.

3. Standards

As for microbeam techniques, well-characterized homogenous, matrix-matched mineral standards are required. Currently, only two perovskite crystals, the Tazheran (Ireland et al., 1990; Kinny et al., 1997)

Table 1

Run table for perovskite U–Th–Pb analysis by Cameca IMS-1280.

Mass station	Isotopes	Mass (amu)	Times (s)	Delay (s)
1	$^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4$	199.838	3	4
2	Background	200.5	6	1
3	^{204}Pb	203.973	6	1
4	^{206}Pb	205.974	4	1
5	^{207}Pb	206.976	6	1
6	^{208}Pb	207.977	3	1
7	^{232}Th	232.038	4	2
8	^{238}U	238.051	6	2
9	$^{232}\text{Th}^{16}\text{O}$	248.033	2	2
10	$^{238}\text{U}^{16}\text{O}$	254.046	2	2
11	$^{238}\text{U}^{16}\text{O}_2$	270.040	2	2

and the Ice River (Heaman, 2009) perovskites, have been proven to be adequate standards for microbeam U–Pb analysis.

3.1. Tazheran perovskite

This perovskite is from the Tazheran skarn deposit in the Lake Baikal area of eastern Siberia. It has unusually high U contents in excess of 1000 ppm. Chemical analyses show that this perovskite consists of relatively pure CaTiO_3 with minor amounts of Nb, Fe^{2+} , and REE (Ireland et al., 1990; Yang et al., 2009). It has approximately 10 ppm common Pb, with $^{206}\text{Pb}/^{204}\text{Pb}$ ranging from 250 to 1000 (Oversby and Ringwood, 1981; Ireland et al., 1990; Kinny et al., 1997). Based on ID-TIMS analyses, 463 Ma has been recommended as the age of Tazheran perovskite, and a $^{206}\text{Pb}/^{238}\text{U}$ ratio of 0.074465 was used in standardization of SHRIMP measurements (Oversby and Ringwood, 1981; Ireland et al., 1990; Smith et al., 1994; Kinny et al., 1997). Kinny et al. (1997) showed that the Tazheran perovskite has highly variable U and Th concentrations, even within single grains, making it unusable as a concentration standard. In this work, one grain of Tazheran perovskite (ca. 200 μm in diameter) was mounted for SIMS analysis.

3.2. Ice River perovskite

This perovskite came from the Ice River Complex, a small (~30 km²) zoned alkaline ultramafic intrusion located in southeastern British Columbia. The Ice River perovskite is considered as an excellent natural standard and has been used routinely for normalizing LA-MC-ICP-MS analyses of unknown perovskites (Simonetti et al., 2008). Fragments of the Ice River perovskite used in this study are from the same crystal analyzed by Heaman (2009) using the ID-TIMS method. As described by Heaman (2009), the Ice River perovskite has a number of features that make it an ideal natural standard. The chemical composition of this crystal is relatively homogeneous as shown in BSE images (Heaman, 2009). The uranium, thorium, and lead contents are relatively uniform: 141 ± 25 , 1954 ± 270 , and 41 ± 5 ppm, respectively, with Th/U of 14.5 ± 1.3 . This crystal has total common-lead contents ranging from 5.1 to 9.6% of total Pb. The weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 356.5 ± 1.0 Ma based on analyses of eight fractions (Heaman, 2009) is recommended as the best estimate of its crystallization age. In this study, the Ice River perovskite is also used as Th–Pb standard on the assumption that its Th/Pb and U/Pb ages are concordant. Furthermore, the Ice River perovskite contains relatively uniform U content, which makes it usable for calibration of U concentrations.

4. Calibration protocols

4.1. Pb/U calibration

Calibration of inter-elemental fractionation between Pb and U is a fundamental task for SIMS analysis. There are different calibration

protocols in the procedures, parameters, and assumptions used by different workers (Stern and Amelin, 2003). The common approach is to establish the best-fit functional relationship between the desired $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ ratio and an isotopic ratio involving uranium species. As for zircon analyses by SHRIMP, the correlation between $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ and UO^+ / U^+ is most commonly used (e.g., Compston et al., 1984; Hinthorne et al., 1979; Williams, 1998), and that between $^{206}\text{Pb}^+ / \text{UO}^+$ and UO^+ / U^+ is less common (Compston, 2000). For zircon analyses by Cameca SIMS, the correlation between $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ and $\text{UO}_2^+ / \text{U}^+$ appears to have a better linearity than that between $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ and UO^+ / U^+ (Whitehouse et al., 1997; Petersson et al., 2001; Li et al., 2009). The basic assumption used in the SIMS measurements is simply described as:

$$\frac{^{206}\text{Pb}}{^{238}\text{U}} = \frac{^{206}\text{Pb}^+}{^{238}\text{U}^+} \quad (1)$$

at the same $[\text{UO}_x]^+ / [\text{UO}_n]^+ (x=1,2; n=x-1)$, where, u denotes the unknowns and st the standard. The functional relationship between $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ and $[\text{UO}_x]^+ / [\text{UO}_n]^+$ has been treated as linear, quadratic, or power law by different workers on different minerals (e.g., Williams, 1998). A power law ($^{206}\text{Pb}^+ / ^{238}\text{U}^+ = A \times ([\text{UO}_x]^+ / ^{238}\text{U}^+)^E$) is probably the best choice when the exponential E is the same for the unknowns and standard, i.e.,

$$\frac{^{206}\text{Pb}}{^{238}\text{U}} = \frac{^{206}\text{Pb}^+}{^{238}\text{U}^+} = \frac{A_u \times \left(\frac{^{238}\text{UO}_x^+}{^{238}\text{U}^+}\right)^E}{A_{st} \times \left(\frac{^{238}\text{UO}_x^+}{^{238}\text{U}^+}\right)^E} = \frac{A_u}{A_{st}} \quad (2)$$

Eq. (2) has been widely used for zircon U–Pb dating by ion microprobe analyses. For perovskite, however, the U^+ ion yield is too low to get satisfactory counting statistics and hence good precision. Alternatively, the correlation of $^{206}\text{Pb} / \text{UO}^+$ and $\text{UO}_2^+ / \text{UO}^+$ has been used in perovskite analyses by SHRIMP (Ireland et al., 1990; Kinny et al., 1997; Williams, 1998). This calibration protocol is inapplicable in this study because the measured $\text{UO}_2^+ / \text{UO}^+$ varies in a limited range within one session. Therefore, it is difficult to derive a satisfactory calibration curve. According to Ireland et al. (1990), data obtained from the Tazheran perovskite standard over a period of some 18 months were expressed as a quadratic equation.

In this study, U^+ intensity was enhanced by using a strong primary beam ($>10 \text{ nA O}_2^-$). Perovskites in kimberlites usually contain an average of 100 ppm U (Heaman et al., 2003, 2004; Wu et al., in revision). Thus, despite low U^+ ion yields of ca 0.15 cps/ppm/nA O_2^+ (estimate from Ice River perovskite, see Discussion section), a U^+ intensity of more than 100 cps can be obtained by a primary beam exceeding 10 nA O_2^- . A linear relationship is observed between $\ln(^{206}\text{Pb}^* / \text{U}^+)$ (* denotes radiogenic) and $\ln(\text{UO}_2^+ / \text{U}^+)$ (Fig. 1a). The same calibration approach as that used for zircon (Whitehouse et al., 1997; Li et al., 2009) therefore was used for calibrating inter-elemental fractionation. Correction factors were derived from analyses of the Ice River perovskite using an empirical power law relationship (Claoué-Long et al., 1995). The standard deviation of Pb/U values of the reference curve was propagated together with the greater of the observed or Poisson errors from the unknown to give an overall error for the Pb/U ratio of each analysis (Petersson et al., 2001).

4.2. Th/U calibration

The Th/U ratio is an important parameter for U- and Th-bearing minerals. For instance, Th/U ratio in zircon can be used as an index to discriminate different genetic types of zircon (e.g., Rubatto et al.,

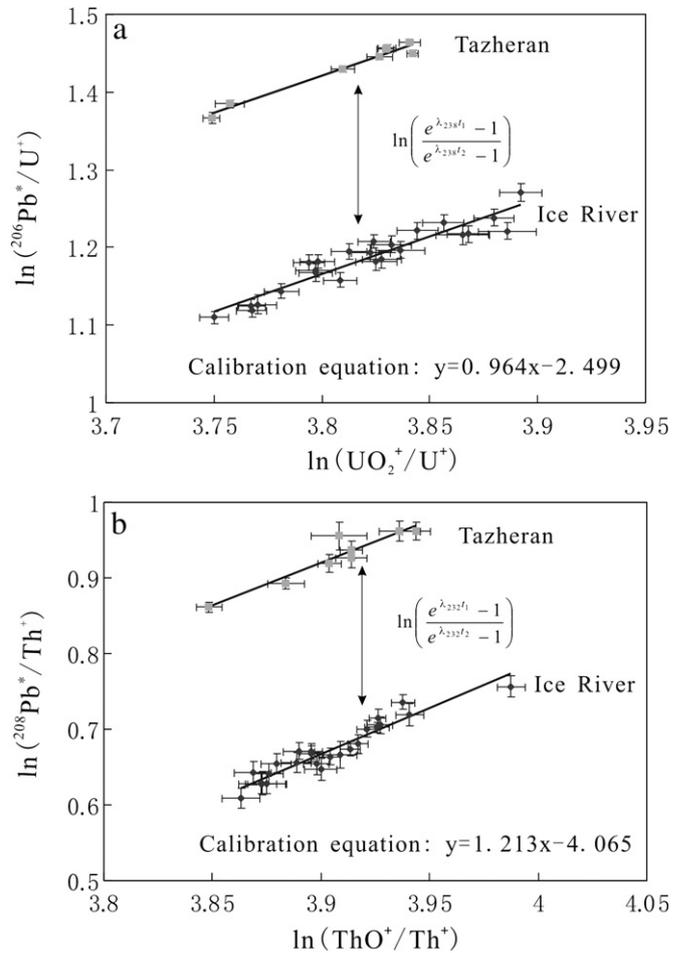


Fig. 1. Logarithmic calibration graphs of (a) $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ vs. $^{270}\text{UO}_2^+ / ^{238}\text{U}^+$ and (b) $^{208}\text{Pb}^+ / ^{232}\text{Th}^+$ vs. $^{248}\text{ThO}^+ / ^{232}\text{Th}^+$ using the data sets from the Tazheran and Ice River perovskites of session 1. Regressions through the data yielded power law exponents of -1 and -1.2 from the slopes for U/Pb and Th/Pb calibration, respectively. The vertical distance between lines is the function of age difference.

1999). Assuming that both the Pb–U and Pb–Th isotopic systems in a mineral are concordant, the radiogenic $^{208}\text{Pb} / ^{206}\text{Pb}$ for any analyzed domain is related to the local $^{232}\text{Th} / ^{238}\text{U}$ by:

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{232}\text{Th}(e^{\lambda_{232}t} - 1)}{^{238}\text{U}(e^{\lambda_{238}t} - 1)} \quad (3)$$

where λ_{232} is the ^{232}Th decay constant ($4.9475 \times 10^{-11} \text{ yr}^{-1}$) and λ_{238} is the ^{238}U decay constant ($1.55125 \times 10^{-10} \text{ yr}^{-1}$) (Steiger and Jäger, 1977). A plot of radiogenic $^{208}\text{Pb} / ^{206}\text{Pb}$ versus $^{232}\text{Th} / ^{238}\text{U}$ defines a straight line with a slope of $(e^{\lambda_{232}t} - 1) / (e^{\lambda_{238}t} - 1)$, which is a constant for a given age (t). This slope varies from 2.47 to 3.19 as a function of age over the full range of geological time. Commonly, Th/U is determined from $\text{ThO}^+ / \text{UO}^+$ by a fixed calibration, for example, $\text{Th} / \text{U} = 1.11 \times \text{ThO}^+ / \text{UO}^+$ for zircon (Compston et al., 1984). A similar calibration, $\text{Th} / \text{U} = 1.02 \times \text{ThO}^+ / \text{UO}^+$, was used for perovskite by Ireland et al. (1990).

Fig. 2 shows the correlation between $\text{ThO}^+ / \text{UO}^+$ and Th/U calculated in terms of $^{208}\text{Pb}^* / ^{206}\text{Pb}^*$ and the corresponding recommended U–Pb ages of previous studies (Kinny et al., 1997; Heaman et al., 2003; Heaman, 2009). These data define a linear correlation ($R^2 = 0.998$). Interestingly, the slope of 1.14 between $\text{ThO}^+ / \text{UO}^+$ and Th/U is almost as same as that (1.11) deduced from zircons (Compston et al., 1984; Williams, 1998), but ca 10% higher than that (1.02) used by Ireland et al. (1990). In this study, Th/U was calculated using a linear relationship given by $\text{Th} / \text{U} = 1.14 \times \text{ThO}^+ / \text{UO}^+$.

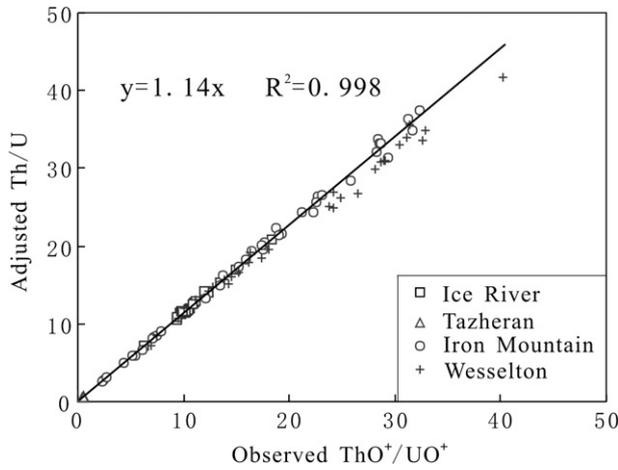


Fig. 2. Linear regression of adjusted Th/U vs. ThO^+/UO^+ for the Tazheran, Ice River, IM21-3 and IM21-10 perovskites. The Th/U data were calculated in terms of their radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ and assigned ages. The data for W7-805 and W2-680b with high proportions of common lead are shown (cross) but not included in the regression.

4.3. Pb/Th calibration

$^{208}\text{Pb}/^{232}\text{Th}$ is calculated in terms of the measured $^{206}\text{Pb}/^{238}\text{U}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and Th/U in SIMS U–Pb zircon analyses (e.g., Williams, 1998). However, this is inapplicable for perovskite, because Th/U in perovskites ranges widely, from 1 to 100, which is much more variable than in zircon. When each sample was treated independently, the corresponding calibration factor of Th/U versus ThO^+/UO^+ can vary by as much as 5%. Therefore, analogous calibration to zircon will result in inaccurate values for Th/U and hence $^{208}\text{Pb}/^{232}\text{Th}$.

As with the Pb/U calibration, a linear relationship is also observed between $\ln(^{208}\text{Pb}^{*+}/\text{Th}^+)$ and $\ln(\text{ThO}^+/\text{Th}^+)$ in this study (Fig. 1b). Thus, a calibration approach analogous to that for Pb/U was used for correction of Pb/Th fractionation. Correction factors were derived from analyses of the Ice River perovskite using an empirical power law relationship (Claoué-Long et al., 1995) with $^{208}\text{Pb}^{*+}/\text{Th}^+ = A \times (\text{ThO}^+/\text{Th}^+)^E$.

4.4. Calibration of U, Th and Pb concentrations

The U, Th and Pb concentrations are useful additional pieces of information for characterization and commonly measured during ion

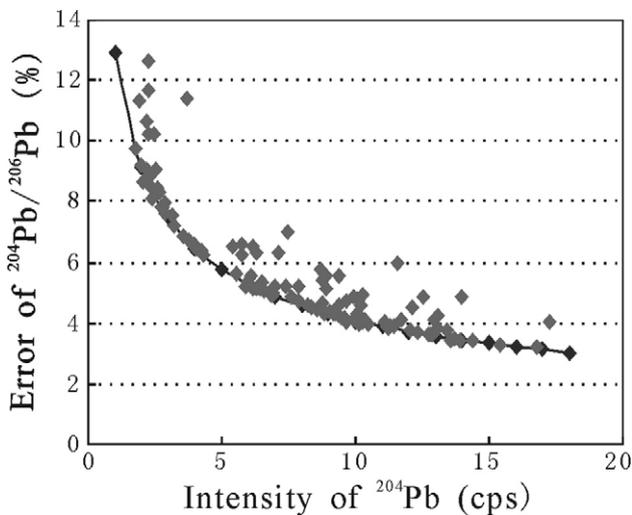


Fig. 3. Correlation between the analytical error on the measured $^{204}\text{Pb}/^{206}\text{Pb}$ ratio and ^{204}Pb intensity for perovskites. The expected uncertainties from the counting statistics, estimated as $1/(\text{total counts})^{1/2}$ are shown as the black curve for comparison.

microprobe analysis for U–Th–Pb geochronology. Pb and Th concentrations can be calculated from $^{206}\text{Pb}/^{238}\text{U}$, Th/U and the Pb isotopic composition. Thus, precise determination of U concentration is fundamental. Ireland et al. (1990) calculated U concentrations using an empirical relationship between $\text{CaTi}_2\text{O}_4^+/\text{UO}^+$ and $\text{UO}_2^+/\text{UO}^+$ for the standard Tazheran perovskite over a long period. Such a long-term calibration was not applicable in this study. Alternatively, we observed that the $\text{UO}_2^+/\text{CaTi}_2\text{O}_4^+$ for the Ice River perovskite with relatively uniform U content is nearly constant within one session ($\pm 3\%$, 1 SD, excluding a few obvious outliers, Appendix A), a sensitivity factor can be obtained in terms of its U content (141 ± 25 ppm) measured by TIMS (Heaman, 2009). The U concentrations for each analysis within one session were determined based on $\text{UO}_2^+/\text{CaTi}_2\text{O}_4^+$ using this linear calibration. However, this calibration may suffer from matrix effects when CaO and TiO_2 contents of the unknowns are significantly different from those of the Ice River perovskite.

4.5. Common-Pb correction

Perovskite contains variably high common lead ranging from a few to tens of percent levels of total Pb (e.g., Kinny et al., 1997). Therefore, common-Pb correction in the perovskite analyses is crucial to U–Pb and Th–Pb age calculations. For ion microprobe analyses, common Pb in the measured minerals can be derived from the initial Pb incorporated into the mineral, the anti-charging coating on the target surface, and contaminants derived from the sample preparation (Williams, 1998). The contribution from surface Pb can be reduced significantly by pre-sputtering of the primary ion beam over each target area prior to analysis. During U–Pb analyses of zircon, total ^{204}Pb ion intensities are usually as low as ~ 0.1 cps (e.g., Li et al., 2009), indicating that the contribution from surface Pb is very minor. Thus, common Pb from surface contamination is negligible for perovskite analyses in terms of their high ^{204}Pb intensities, which range mostly from 2 to 20 cps (Fig. 3). Therefore, common Pb in perovskite is dominated by initial Pb derived from the kimberlitic magma. In this study, the ^{204}Pb - and ^{207}Pb -based methods (Williams, 1998) are used for common-Pb correction on the U–Pb system using the terrestrial Pb (Stacey and Kramers, 1975) appropriate to the age of the unknowns as the common-Pb compositions with assigned absolute errors of 0.5 on $^{206}\text{Pb}/^{204}\text{Pb}$, 1 on $^{208}\text{Pb}/^{204}\text{Pb}$ and 0.05 on $^{207}\text{Pb}/^{206}\text{Pb}$. As for Th–Pb system of perovskite analyses, the ^{204}Pb -based correction is adequate because f_{208} values (the percentage of common ^{208}Pb in total ^{208}Pb) of most analyses, except for the Tazheran perovskite, are smaller than the corresponding f_{206} values (the percentage of common ^{206}Pb in total ^{206}Pb) as shown in Fig. 4.

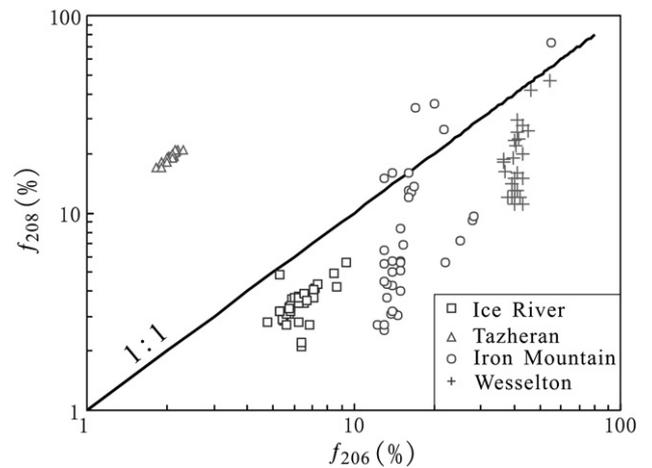


Fig. 4. Comparison between the f_{206} and f_{208} values, the percentage of common ^{206}Pb and ^{208}Pb in total ^{206}Pb and ^{208}Pb , respectively, of the perovskites analyzed in this study. The plot shows that most perovskites, except for Tazheran perovskite, have much lower f_{208} than f_{206} values.

Table 2
Summary of age results for perovskite dated in this study.

Sample	Tera–Wasserburg plot		Terrestrial Pb correction		Th–Pb age (Ma)	Accepted age (Ma)
	Lower intercept age (Ma)	Common $^{207}\text{Pb}/^{206}\text{Pb}$	^{207}Pb -corr. age (Ma)	^{207}Pb -corr. age (Ma)		
Tazheran	458 ± 44	0.60 ± 0.94	458 ± 7.6	462.2 ± 2.5	462.8 ± 2.5	463 (1, 2)
Ice River	346 ± 10	0.61 ± 0.08	346.4 ± 1.8	356.9 ± 1.5	357.5 ± 1.7	356.5 (3)
IM21-3	409.4 ± 5.7	0.85 ± 0.02	409.4 ± 2.8	410.5 ± 3.5	410.8 ± 3.4	409.2 ± 7.2
IM21-10	411 ± 12	0.86 ± 0.06	411.0 ± 3.0	411.0 ± 3.0	411.0 ± 2.6	412.3 ± 3.3
W7-805	85 ± 10	0.77 ± 0.05	85.4 ± 2.4	90.9 ± 2.3	91.5 ± 2.2	90.5 ± 0.8
W2-680b	96 ± 12	0.87 ± 0.08	95.5 ± 2.7	92.3 ± 2.4	90.3 ± 2.9	88.4 ± 1.6

(1) Oversby and Ringwood (1981); (2) Kinny et al. (1997); (3) Heaman (2009); (4) Heaman et al. (2003); (5) Smith et al. (1989); (6) Batumike et al. (2008).

5. Analytical results

Considering that most kimberlitic perovskites dated in this study are young (i.e., Phanerozoic) and have low abundances of ^{235}U , the accumulation of radiogenic ^{207}Pb is very small. Consequently, the high proportion of common lead will have a large effect on the uncertainties associated with the $^{207}\text{Pb}/^{235}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Only $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages are reported here. All ages were calculated using the decay constants recommended by Steiger and Jäger (1977) and the calculation routines of Isoplot/Ex (Ludwig, 1999). The resulting regression and weighted average ages are quoted at the 95% confidence interval. The age results are summarized in Table 2 and detailed data are presented in Appendix A.

5.1. Standards

The Tazheran and Ice River perovskites have been used as U–Pb standards by microbeam techniques (e.g., Ireland et al., 1990; Smith et al., 1994; Kinny et al., 1997; Simonetti et al., 2008), and their U–Th–Pb dating results are described below.

5.1.1. Tazheran perovskite

A total of 18 analyses, including 8 in session 1 and 10 in session 2, were performed on a single grain of the Tazheran perovskite. As shown in Appendix A, this grain shows uniform uranium, thorium and common-lead contents: 1410 ± 48 ppm U, 802 ± 32 ppm Th, 7.3 ± 0.5 ppm Pb (1 SD), and a consistent Th/U of 0.58 ± 0.02 (1 SD) (Appendix A). The ^{204}Pb -based f_{206} and f_{208} are ca 2% and 18%, respectively (Fig. 4). The U–Th–Pb isotopic compositions were calibrated against the Ice River perovskite as standard. Due to the tight clustering of data points, a Tera–Wasserburg plot gave an imprecise lower intercept age at 458 ± 44 Ma (Fig. 5a), and an imprecise upper intercept of common $^{207}\text{Pb}/^{206}\text{Pb}$ composition at 0.60 ± 0.94 as well. Using terrestrial Pb (Stacey and Kramers, 1975) as an estimate of common-lead composition, a Concordia U–Pb age can be calculated at 462.8 ± 2.5 Ma (Fig. 5b). Despite relatively higher f_{206} values of ca 2% relative to zircons, a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 471 ± 13 Ma (MSWD = 1.11) can be obtained, consistent within errors with its U/Pb ages.

As for Th–Pb ages, till now there are no reported Th–Pb ages on Tazheran and Ice River perovskites. In this study, it is assumed that Ice River perovskite has consistent U–Th and Th–Pb age. Thus, using Ice River perovskite as Th–Pb standard, an independent $^{208}\text{Pb}/^{232}\text{Th}$ age of 462.0 ± 4.2 Ma (Fig. 5d, MSWD = 1.17) is obtained. This Th–Pb age is well consistent with its U–Pb age and the recommended $^{206}\text{Pb}/^{238}\text{U}$ age of 463 Ma by ID-TIMS (Oversby and Ringwood, 1981; Kinny et al., 1997). This agreement indicates that the Tazheran and Ice River perovskite should be concordant in both U–Pb and Th–Pb systems.

5.1.2. Ice River perovskite

The U–Th–Pb results ($n = 37$), including 24 in session 1 and 13 in session 2 for the Ice River perovskite are presented on a U–Pb Concordia diagram (Fig. 5f). All but one spot (Ice_River@6 with U = 182 ppm) have very uniform uranium contents of 141 ± 4.5 ppm (1 SD, 141 ppm is the recommended value by Heaman, 2009). However, Th contents and Th/U ratios are highly variable, ranging from 1278 to 2769 ppm and from 7.2 to 20.8, respectively. The common-lead contents are also relatively uniform at 1.7 ± 0.3 ppm (1 SD, Appendix A). The ^{204}Pb -based f_{206} value of this perovskite ranges from 4.7% to 9.4% (Fig. 4), comparable with those (5.1–9.6%) determined by ID-TIMS (Heaman, 2009). As in the Tazheran perovskite, the U–Pb data points are tightly clustered on the Tera–Wasserburg plot, resulting in imprecise lower and upper intercepts (Fig. 5e). The U–Pb isotopic compositions are calibrated against the Tazheran perovskite standard. A Concordia U–Pb age of 357.5 ± 1.7 Ma (Fig. 5f) was obtained. This age is in good agreement with the ID-TIMS U–Pb age of 356.5 ± 1.0 Ma (Heaman, 2009). Owing to the high concentrations of Th and hence high levels of radiogenic ^{208}Pb , the ^{204}Pb -based f_{208} value of this perovskite is fairly lower, ranging from 2.2% to 5.6% (Fig. 4). The Th–Pb ages were “internally” calibrated by treating each analysis in turn as an unknown with the remainder as standards, yielding an uncertainty of 1.7 Ma (2 SE) which indicates a homogenous Th–Pb system (Fig. 5h, MSWD = 0.81).

5.2. Applications

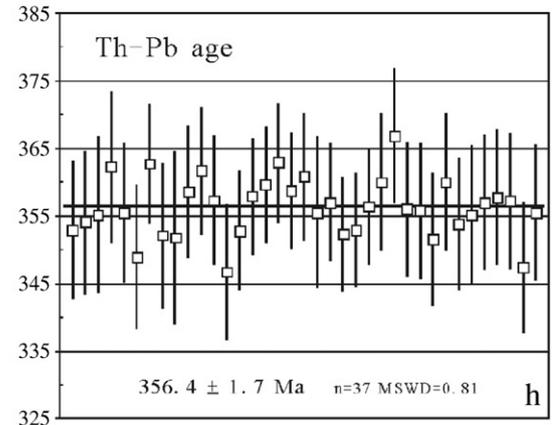
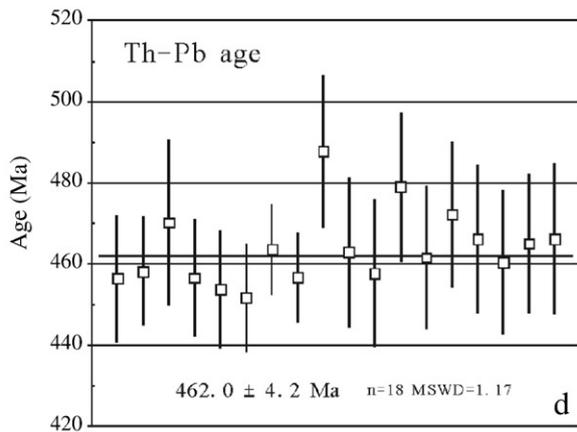
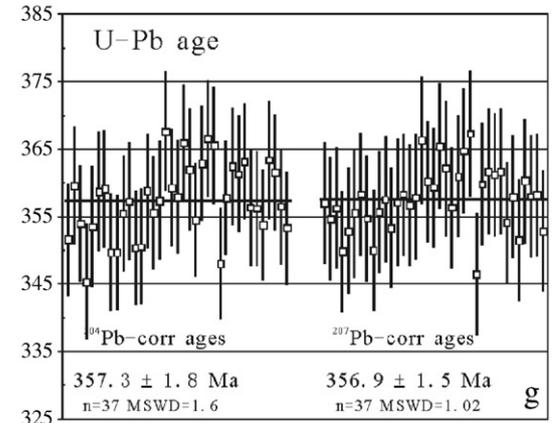
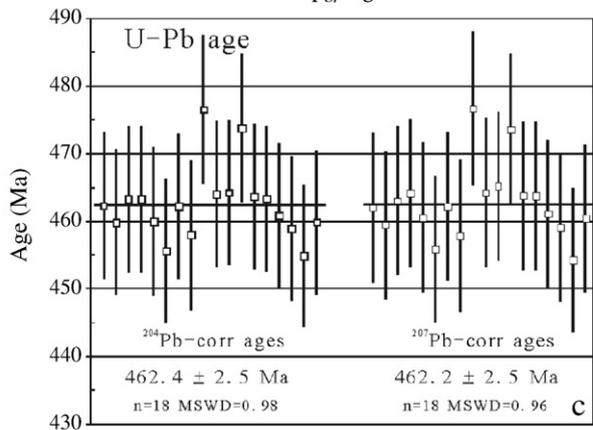
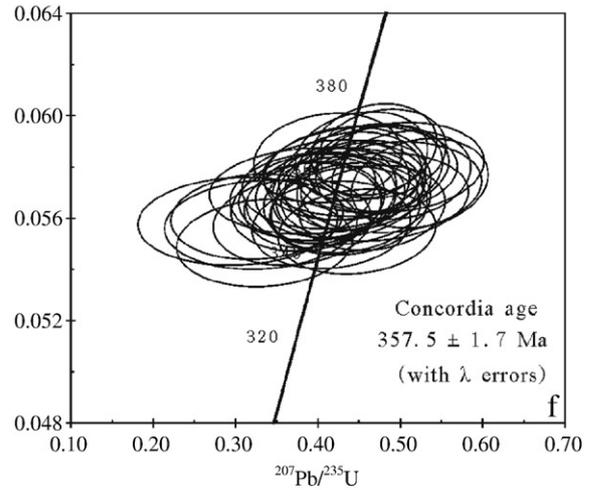
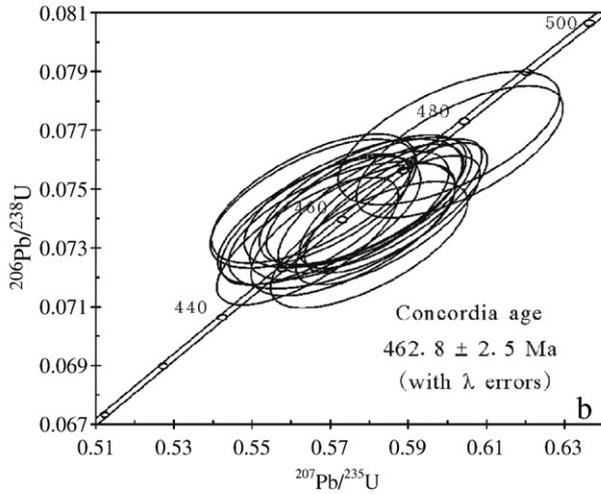
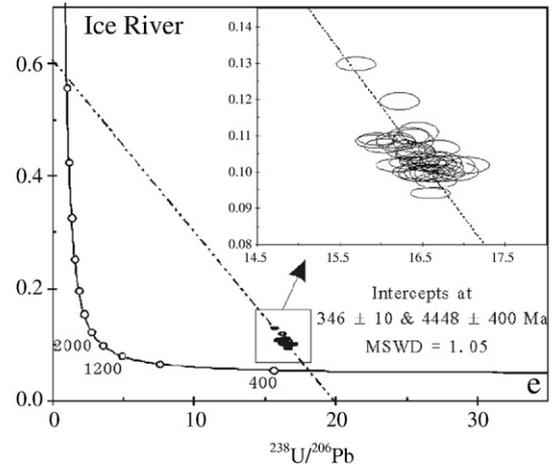
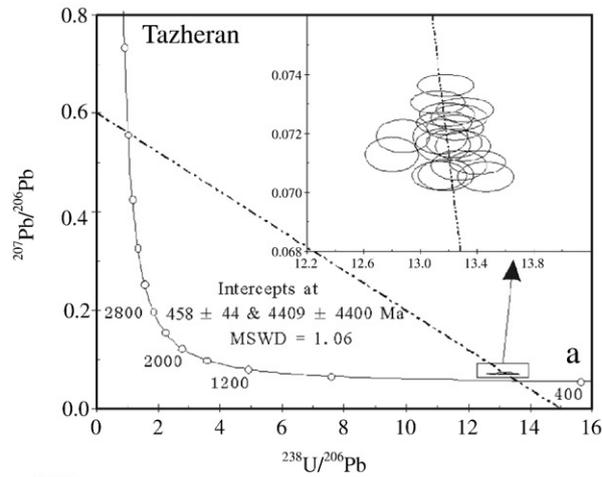
Four perovskite samples from two locations with known U–Pb ages were analyzed in this study to test our analytical procedures. The $^{206}\text{Pb}/^{238}\text{U}$, $^{208}\text{Pb}/^{232}\text{Th}$ ages and elemental abundances were calibrated relative to the Ice River perovskite standard.

5.2.1. Iron Mountain perovskite

Two perovskite samples, IM21-3 and IM21-10, came from the Iron Mountain kimberlite in the Wyoming craton. The analyzed perovskite has contents of U (114–117 ppm), Th (796–1380 ppm) and Th/U (7.0–11.8) (Heaman et al., 2003). Three ID-TIMS analyses yielded $^{206}\text{Pb}/^{238}\text{U}$ ages of 408.1 ± 3.8, 408.8 ± 3.8 and 412.9 ± 3.6 Ma. Two slightly younger, consistent measurements yield a weighted average $^{206}\text{Pb}/^{238}\text{U}$ date of 408.4 ± 2.6 Ma, which is considered as the best estimate for the emplacement age of the Iron Mountain kimberlite (Heaman et al., 2003).

Based on 16 analyses in session 1, the IM21-3 perovskite has relatively uniform uranium contents of 124 ± 13 ppm (1 SD). In contrast, the thorium contents vary significantly from 252 to 3675 ppm and Th/U ratios vary between 2.8 and 25.7 (Appendix A). This perovskite contains common lead ranging from 4 to 15 ppm, and the ^{204}Pb -based f_{206} value from 15% to 55% (Fig. 4). The scattered data

Fig. 5. U–Th–Pb dating results for the Tazheran (a)–(d) and the Ice River (e)–(h) standard perovskites. (a) and (e), Tera–Wasserburg inverse concordia plots; (b) and (f), conventional concordia diagrams; (c) and (g), weighted average age from ^{204}Pb - and ^{207}Pb -corrections for common lead; (d) and (h), weighted average Th–Pb ages. Data-point error ellipses, weighted age uncertainties and error bars are at the 2 σ level.



points on the Tera–Wasserburg plot give a lower intercept age at 409.4 ± 5.7 Ma (Fig. 6a) and the upper intercept of common-Pb composition at 0.85 ± 0.02 , which is consistent with the terrestrial Pb of Stacey and Kramers (1975). A weighted average $^{206}\text{Pb}/^{238}\text{U}$ age derived by the ^{204}Pb -based common-Pb correction is 410.8 ± 3.4 Ma (MSWD = 1.4), identical to the average $^{206}\text{Pb}/^{238}\text{U}$ age of 410.5 ± 3.5 (MSWD = 0.34) given by the ^{207}Pb -based common-Pb correction (Fig. 6c). The large range in Th contents results in highly variable ^{204}Pb -based f_{208} values ranging from 4.3% to 73% (Fig. 4). A weighted average of independent $^{208}\text{Pb}/^{232}\text{Th}$ ages is 409.2 ± 7.2 Ma (MSWD = 4.4, Fig. 6d). Although this Th–Pb age is consistent within errors with the U–Pb age, the high MSWD indicates that either the Th–Pb system was disturbed by later thermal events or there may be a weak matrix effect due to the highly variable Th contents.

Twenty-one measurements were conducted on the IM21-10 perovskite, with 9 and 12 measurements in session 1 and 2, respectively. This perovskite shows similar characters to the IM21-3 sample, with uniform uranium contents (125 ± 10 ppm, 1 SD), large variation in Th contents ranging from 548 to 5177 ppm and Th/U from 5.1 to 31.5. Common-lead contents vary from 3.6 to 8.3 ppm (Appendix A). The ^{204}Pb -based f_{206} of this sample varies between 12% and 28%, mostly around 15% (Fig. 4). A weighted average $^{206}\text{Pb}/^{238}\text{U}$ age given by the ^{204}Pb -based common-Pb correction is 411.0 ± 2.6 Ma (MSWD = 1.14), in good agreement with the average $^{206}\text{Pb}/^{238}\text{U}$ age of 411.0 ± 3.0 (MSWD = 0.98) given by the ^{207}Pb -based common-Pb correction (Fig. 6g). The ^{204}Pb -based f_{208} values of this sample are between 2.5% and 27% (Fig. 4). Independent $^{208}\text{Pb}/^{232}\text{Th}$ ages yielded a weighted average of 412.3 ± 3.3 Ma (MSWD = 1.5, Fig. 6h), excluding one analysis of spot @10 in session 2.

Overall, the U–Pb and Th–Pb ages (409.2 ± 7.2 Ma to 412.3 ± 3.3 Ma) of these two perovskites from Iron Mountain are in good agreement with each other, and also consistent with ID-TIMS results of 408–412 Ma (Heaman et al., 2003).

5.2.2. Wesselton perovskite

Two perovskite samples, W7-805 and W2-680b, were collected from the hypabyssal kimberlite phases of the Wesselton Mine in the Kimberley area of southern Africa. The perovskites are euhedral and 20–60 μm across. Previous dating work on kimberlitic perovskites from this area has given an age span between 88 and 94 Ma (Smith et al. 1989; Batumike et al., 2008; Wu et al., in review).

A total of 16 measurements were performed on the W7-805 perovskite in session 1. This perovskite has fairly uniform uranium contents (178 ± 18 ppm, 1 SD) and common-lead contents (3.6 ± 0.2 ppm, 1 SD), but high and variable thorium contents ranging from 1008 to 6620 ppm, and Th/U from 7.2 to 41.6 (Appendix A). The ^{204}Pb -based f_{206} value is between 38% and 46% (Fig. 4). The weighted average $^{206}\text{Pb}/^{238}\text{U}$ age derived by the ^{204}Pb -based common-Pb correction is 91.5 ± 2.2 Ma (MSWD = 0.18), which is in good agreement with the result of 90.9 ± 2.3 (MSWD = 0.09) given by the ^{207}Pb -based common-Pb correction (Fig. 7b). The ^{204}Pb -based f_{208} value of this sample varies mostly between 11% and 26%, apart from one analysis (spot @15) that has a significantly higher value of 42% (Fig. 4). Independent $^{208}\text{Pb}/^{232}\text{Th}$ ages yielded a weighted average of 90.5 ± 0.8 Ma (MSWD = 0.5, Fig. 7c), which is well consistent with its U–Pb age.

Perovskite W2-680b, with 12 measurements in session 2, shows relatively uniform uranium and common-lead contents averaging at 233 ± 25 ppm and 4.5 ± 0.3 ppm (1 SD), respectively, but a large range of thorium contents from 1382 to 4678 ppm and Th/U ratio from 8.4 to 19.5 (Appendix A). The ^{204}Pb -based f_{206} value of this sample is between 37% and 54% (Fig. 4). The weighted average of

$^{206}\text{Pb}/^{238}\text{U}$ age given by the ^{204}Pb -based common-Pb correction is 90.3 ± 2.9 Ma (MSWD = 0.52), which is consistent with the result of 92.3 ± 2.4 (MSWD = 0.31) given by the ^{207}Pb -based common-Pb correction (Fig. 7e). The ^{204}Pb -based f_{208} value of this sample is between 16% and 47% (Fig. 4). Independent $^{208}\text{Pb}/^{232}\text{Th}$ ages yielded a weighted average of 88.4 ± 1.4 Ma (MSWD = 0.91, Fig. 7f), which is consistent within errors with the U–Pb ages. The previous U–Pb dating results for the kimberlites from this area summarized by Batumike et al. (2008) have a range between 86 and 92 Ma, consistent with our results from 88.4 ± 1.4 Ma to 92.3 ± 2.4 .

6. Discussion

6.1. Calibration protocols and standards

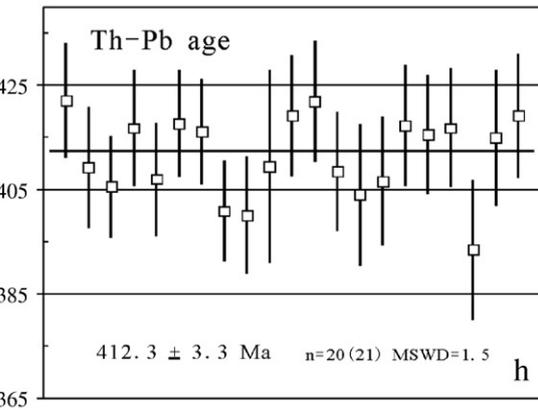
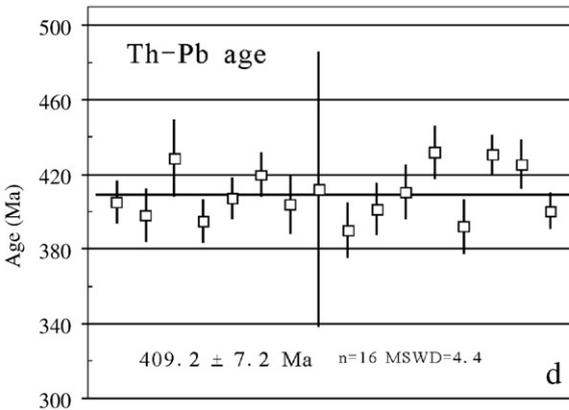
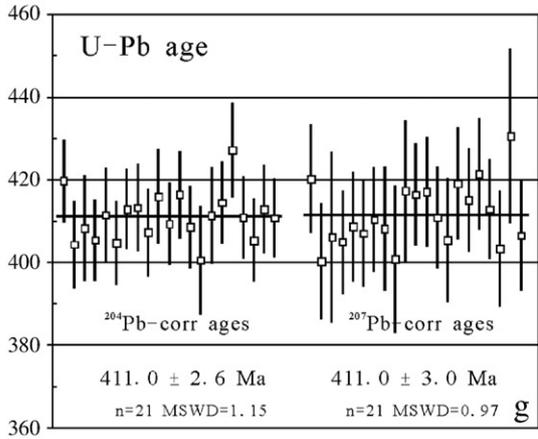
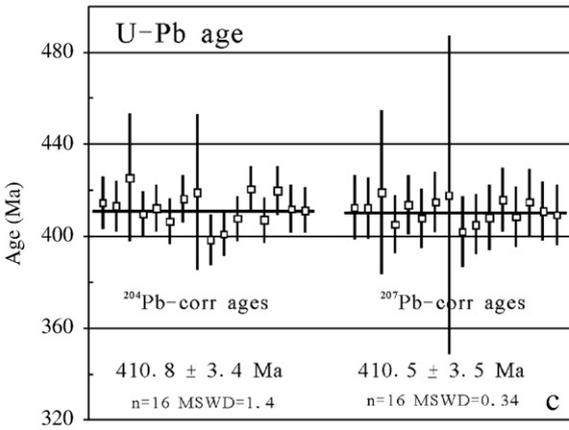
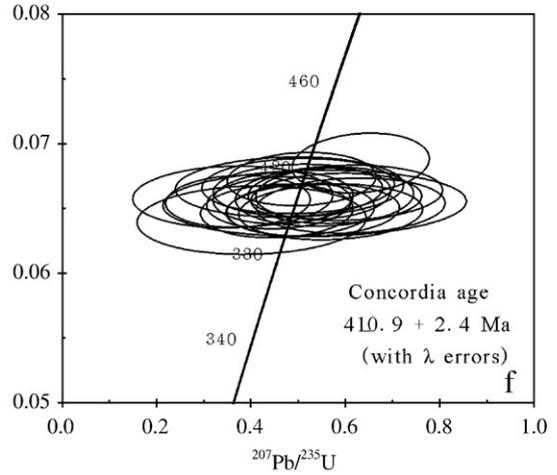
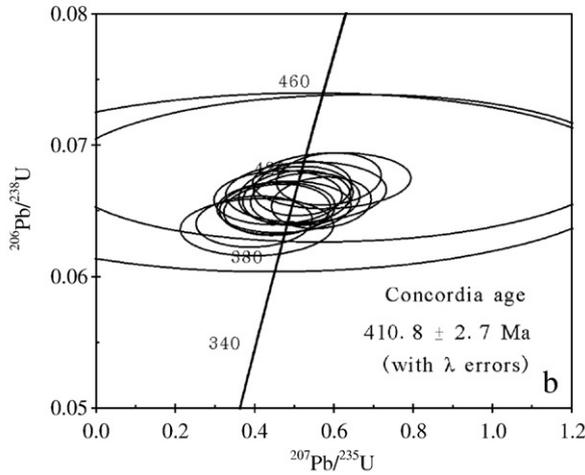
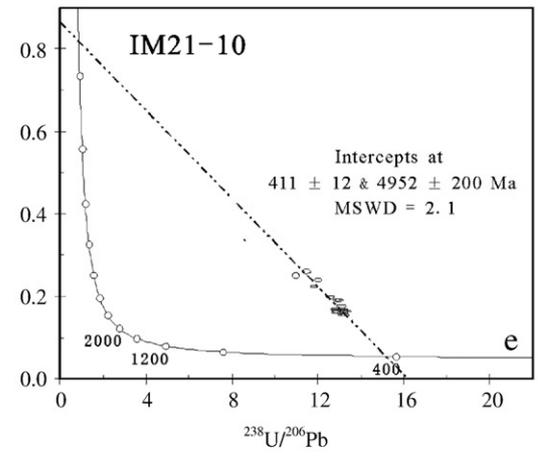
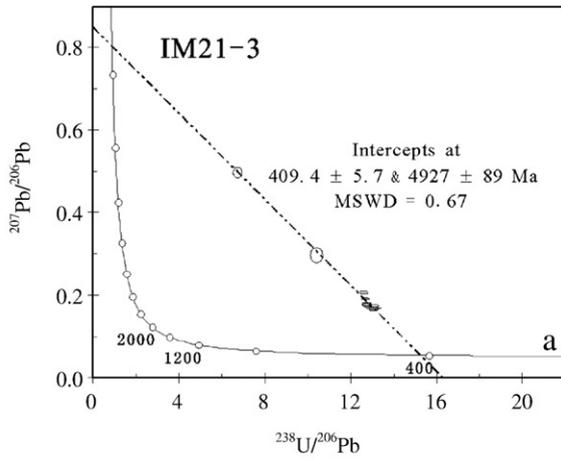
For U–Th–Pb age determination of minerals using ion microprobe, the primary task is to deduce the true $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ratios from large inter-elemental fractionations. The observed relationships between $^{206}\text{Pb}^{*+}/^{238}\text{U}^{+}$ and $\text{UO}_2^{+}(\text{UO}^{+})/\text{U}^{+}$, and between $^{208}\text{Pb}^{*+}/^{232}\text{Th}^{+}$ and $\text{ThO}^{+}/\text{Th}^{+}$ have been applied to calibration of inter-elemental fractionation for many minerals (e.g., Williams, 1998; Ireland and Williams, 2003). Therefore, the calibration protocol for inter-elemental fractionation between Pb^{*} , U and Th may be independent of the matrix. The empirical power law relationship has been applied to different minerals, such as zircon, monazite, xenotime, apatite and allanite (e.g., Claoué-Long et al., 1995; Williams, 1998; Sano et al., 1999; Gregory et al., 2007). Our work demonstrates that the same method also is applicable for perovskite.

Considering that the calibration of Pb/U and Pb/Th for perovskites uses radiogenic Pb, rather than the total Pb, precise common-lead correction for the standards is important for constructing the calibration line. In this regard, a useful U–Th–Pb standard mineral should have not only a homogenous U–Pb system, but also a low proportion of common lead. The Tazheran perovskite, with its high uranium concentration and relatively low proportion of common lead ($f_{206} \approx 2\%$) is an ideal U–Pb standard. However, its relatively low Th content limits its usefulness as a Th–Pb standard. In contrast, the Ice River perovskite has moderate uranium content and moderate f_{206} value of ca 5–10%, which makes it a useful U–Pb standard. Moreover, it has fairly high Th contents, making it also a good Th–Pb standard, on the assumption that its Th/Pb and U/Pb ages are concordant. This assumption is supported by the concordant Th/Pb (462 ± 4 Ma) and U/Pb (462.8 ± 2.5 Ma) ages of the Tazheran perovskite determined using the Ice River perovskite as a standard.

6.2. Th–Pb vs. U–Pb ages

It is well known that the concordant U–Pb age is much more significant than the apparent $^{206}\text{Pb}/^{238}\text{U}$ age for geological interpretations. However, the high proportion of common lead in most Phanerozoic perovskites makes it difficult to obtain precise $^{207}\text{Pb}/^{235}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Consequently, an estimate of U–Pb age concordance is not possible. In general, the U–Pb and Th–Pb dates are concordant only if the samples satisfy the conditions for age determination, including (a) the mineral has remained closed to U, Th, Pb, and all intermediate daughters throughout its history; (b) correct values are used for the initial Pb isotope ratios; and (c) all analytical results are accurate and free of systematic errors (Faure and Mensing, 2005). Thus, to a certain degree, the concordance of $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages may shed light on the behaviour of the U–Th–Pb system.

Because perovskite is mostly much richer in Th than in U and the relative amount of common ^{208}Pb is much less than common ^{206}Pb



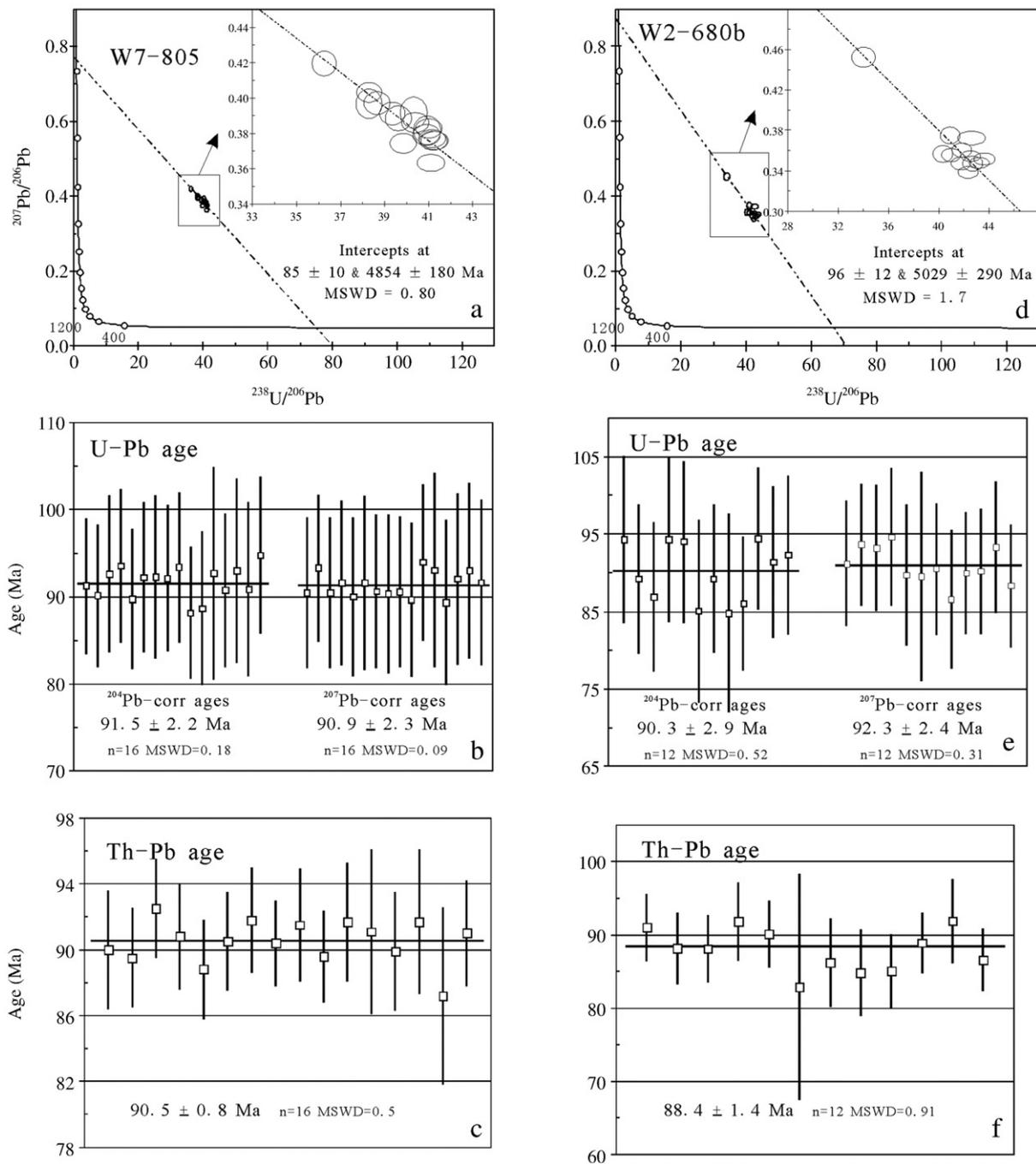


Fig. 7. U–Th–Pb dating results for Wesselton perovskite. (a)–(c), W7-805 perovskite, (d)–(f), W2-680b perovskite. Data-point error ellipses are 1σ . Weighted age uncertainties and error bars are at the 2σ level.

(Fig. 4), precise Pb/Th ages should be easier to be obtained than Pb/U ages. This is also the case for many other Th-rich minerals, such as monazite and allanite (e.g., Williams, 1998; Gregory et al., 2007). The f_{208} values are mostly less than 30% for the dated perovskites in this study (Fig. 4), hence the common-Pb correction propagates insignificant errors to the radiogenic Th/Pb ratios. Our work demonstrates that independent U–Pb and Th–Pb perovskite ages can be obtained simultaneously. In addition, all perovskites dated in this study show concordant Th–Pb and U–Pb ages by common-lead correction using the terrestrial Pb compositions (Stacey and Kramers, 1975); this in turn supports the reliability of the ^{207}Pb -based common-Pb correction method, and the effectiveness of using the terrestrial Pb as common-lead compositions.

7. Conclusions

Perovskite, a common Th- and U-enriched accessory mineral crystallised from kimberlitic magmas, has long been thought to be an important geochronometer for dating the emplacement of kimberlite. However, it contains variably high levels of common Pb, which makes it difficult to check if it is concordant on U–Pb system using microbeam techniques such as SIMS and LA-ICP-MS. We developed calibration protocols to precisely measure radiogenic Pb/U and Pb/Th ratios for dating perovskites using the large double-focusing Cameca IMS 1280. This method is capable of giving perovskite U–Pb and Th–Pb ages simultaneously, allowing an internal examination of U–Th–Pb

isotopic concordance. The accuracy and precision of 1–2% (95% confidence level) for these measurements have been demonstrated by their consistent U–Pb and Th–Pb ages, which are in good agreement with the recommended U–Pb ages obtained by previous studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2009.10.014](https://doi.org/10.1016/j.chemgeo.2009.10.014).

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