Earth Evolution Sciences, Vol. 16, pp. 14–18, March 1, 2022

Age error estimation for electron microprobe dating of monazite based on approximation

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Abstract

The age errors of electron microprobe dating of monazite were estimated using approximation. Each error was used to calculate weighted mean ages and their errors. The results are consistent with the CHIME ages calculated using the isochron method. The calculation procedures discussed in this study are useful particularly for obtaining ages from small and/or homogeneous domains without constructing isochrons.

Keywords: Age error; Electron microprobe dating; Monazite; Approximation

Introduction

Chemical Th–U–Pb dating using electron microprobe allows *in-situ* dating with high spatial resolution. Therefore, this technique has been used to reveal thermal history of metamorphic terranes combined with mineral textures. Suzuki and Adachi (1991, 1994) proposed the regression-based approach by constructing isochrons (CHIME method) based on the following equation assuming that domains and/or grains of a single generation have the same amounts of common (initial) Pb:

$$Total\ n_{Pb} = n_{Pb,initial} + n_{Th}\left(e^{\lambda_{232}t} - 1\right) + n_U\left(\frac{e^{\lambda_{235}t} + 137.88e^{\lambda_{238}t}}{138.88} - 1\right) \quad (1)$$

where n is the amount of substance, λ is the decay constant: $\lambda_{232} = 4.9475 \times 10^{-11}/y$, $\lambda_{235} = 9.8485 \times 10^{-10}/y$, and $\lambda_{238} = 1.55125 \times 10^{-10}/y$ (Steiger and Jäger, 1977), and t is the time (y). The disadvantage of this approach is that many points with constant ages and variable ThO_2 and PbO contents are necessary to obtain a reasonable isochron. On the other hand, Montel et al. (1996) proposed the following equation assuming that common Pb is negligible:

$$Pb = \frac{Th}{232}\left[e^{\lambda_{232}t} - 1\right]208 + \frac{U}{238.04}0.9928 \times \left[e^{\lambda_{238}t} - 1\right]206 + \frac{U}{238.04}0.0072 \times \left[e^{\lambda_{235}t} - 1\right]207 \quad (2)$$

where Pb, U, and Th are the contents in ppm. This method enables to obtain single-point ages. In order to calculate age errors, the standard error of the mean of repeated measurements (e.g., Bell and Welch, 2002; Williams and Jercinovic, 2002) or the error propagation of the Poisson statistics of electron microprobe analysis have been used. However, because the age (t) cannot be calculated directly from the equations (1) and (2), the error propagation from analytical to age errors cannot be traced precisely. Therefore, unpublished procedures (e.g., Montel et al., 1996) and several approaches including the two-term Taylor expansion (e.g., Williams et al., 1999; Williams and Jercinovic, 2002), the second-degree Taylor-Maclaurin expansion (e.g., Vlach, 2010), the Monte Carlo simulation (e.g., Lisowiec, 2006; Vlach, 2010), and the multiple polynomial regression and mathematical programming for the correction functions applied to the first-order Maclaurin expansion (Săbău, 2012) have been adopted using the equation (2) to calculate age errors through the error propagation. Hokada and Motoyoshi (2006) also estimated age errors based on the simplified equation and its error propagation as follows:

$$T\ (Ma) = \frac{n_{Pb}}{n_U + 0.36n_{Th}} \times 7600 \quad (3a)$$

$$Age\ error\ (Ma) = \left[\left\{-\left(\frac{w_{PbO}}{M_{PbO}}\right)\Big/\left(\frac{w_{UO_2}}{M_{UO_2}} + 0.36 \times \frac{w_{ThO_2}}{M_{ThO_2}}\right)^2\right\} + \left\{-\left(\frac{w_{PbO}}{M_{PbO}}/0.36\right)\Big/\left(\frac{w_{UO_2}}{M_{UO_2}}/0.36 + \frac{w_{ThO_2}}{M_{ThO_2}}\right)^2\right\} + \left\{1\Big/\left(\frac{w_{UO_2}}{M_{UO_2}} + 0.36 \times \frac{w_{ThO_2}}{M_{ThO_2}}\right)^2\right\}\right]^{1/2} \quad (3b)$$

where w is the oxide contents (wt.%), and M is the molecular weight of oxide. They calculated ages using the equation (1) assuming that common Pb ($n_{Pb,initial}$) is negligible. This study then attempts to estimate ages and their errors of each analysis using approximation of the equation (1) assuming that common Pb is negligible, and calculate weighted mean ages and their errors. This study particularly focuses on monazite, which is a common Th-rich mineral in metamorphic rocks.

Method

As the common (initial) Pb abundances in monazite are generally small relative to radiogenic Pb (e.g., Parrish, 1990; Montel et al., 1996; Jercinovic and Williams, 2005), if the common Pb is assumed to be negligible, the equation (1) can be rewritten as follows:

$$\frac{w_{PbO}}{M_{PbO}} = \frac{w_{ThO_2}}{M_{ThO_2}}\left(e^{\lambda_{232}t} - 1\right) + \frac{w_{UO_2}}{M_{UO_2}}\left(\frac{e^{\lambda_{235}t} + 137.88e^{\lambda_{238}t}}{138.88} - 1\right). \quad (4)$$

The molecular weights (M) of Th and U are 264 and 270, respectively, and the molecular weight of Pb is 224 for Th-rich minerals and 222 for U-rich minerals (Suzuki and Adachi, 1991, 1994). Based on the Maclaurin expansion, $e^{\lambda t}$ is written as follows:

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \cdots. \quad (5)$$

Therefore, using the first-order approximation, the equation (4) is rewritten as:

$$t_1 \approx \frac{n_{Pb}}{n_{Th}A + n_U B} \quad (6a)$$

where A and B are defined as:

$$A \equiv \lambda_{232} \quad (6b)$$

$$B \equiv \frac{\lambda_{235} + 137.88\lambda_{238}}{138.88}. \quad (6c)$$

Using the second-order approximation, the equation (4) is also rewritten as:

$$t_2 \approx \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (7a)$$

where a, b, and c are defined as:

$$a \equiv n_{Th}\frac{(\lambda_{232})^2}{2} + n_U\frac{(\lambda_{235})^2 + 137.88(\lambda_{238})^2}{2 \times 138.88} \quad (7b)$$

$$b \equiv n_{Th}\lambda_{232} + n_U\frac{\lambda_{235} + 137.88\lambda_{238}}{138.88} \quad (7c)$$

$$c \equiv -n_{Pb}. \quad (7d)$$

Based on the error propagation assuming that all covariance terms are zero, the age error (σt) can be calculated as follows:

$$\sigma t = \sqrt{\left(\frac{\partial t}{\partial w_{ThO_2}}\right)^2 \left(\sigma w_{ThO_2}\right)^2 + \left(\frac{\partial t}{\partial w_{UO_2}}\right)^2 \left(\sigma w_{UO_2}\right)^2 + \left(\frac{\partial t}{\partial w_{PbO}}\right)^2 \left(\sigma w_{PbO}\right)^2} \tag{8}$$

where σw is the analytical error of oxide contents (wt.%). As for the first-order approximation (equation (6a)), each partial derivative can be calculated as follows:

$$\frac{\partial t_1}{\partial w_{ThO_2}} \approx -\frac{n_{Pb}A}{M_{ThO_2}(n_{Th}A+n_U B)^2} \tag{9a}$$

$$\frac{\partial t_1}{\partial w_{UO_2}} \approx -\frac{n_{Pb}B}{M_{UO_2}(n_{Th}A+n_U B)^2} \tag{9b}$$

$$\frac{\partial t_1}{\partial w_{PbO}} \approx \frac{1}{M_{PbO}(n_{Th}A+n_U B)}. \tag{9c}$$

As for the second-order approximation (equation (7a)), each partial derivative can be calculated as follows:

$$\frac{\partial t_2}{\partial w_{ThO_2}} \approx \left[-\frac{b_1}{M_{ThO_2}} + \frac{1}{2\sqrt{Y}}\left(\frac{2bb_1-4a_1c}{M_{ThO_2}}\right)\right]\Big/Z + \left(X+\sqrt{Y}\right)\left(-\frac{2a_1}{Z^2 M_{ThO_2}}\right) \tag{10a}$$

$$\frac{\partial t_2}{\partial w_{UO_2}} \approx \left[-\frac{b_2}{M_{UO_2}} + \frac{1}{2\sqrt{Y}}\left(\frac{2bb_2-4a_2c}{M_{UO_2}}\right)\right]\Big/Z + \left(X+\sqrt{Y}\right)\left(-\frac{2a_2}{Z^2 M_{UO_2}}\right) \tag{10b}$$

$$\frac{\partial t_2}{\partial w_{PbO}} \approx \frac{4a}{2\sqrt{Y}M_{PbO}}\Big/Z \tag{10c}$$

where X, Y, Z, a_1, a_2, b_1, and b_2 are defined as:

$$X \equiv -b \tag{10d}$$

$$Y \equiv b^2 - 4ac \tag{10e}$$

$$Z \equiv 2a \tag{10f}$$

$$a_1 \equiv \frac{(\lambda_{232})^2}{2} \tag{10g}$$

$$a_2 \equiv \frac{(\lambda_{235})^2+137.88(\lambda_{238})^2}{2\times 138.88} \tag{10h}$$

$$b_1 \equiv \lambda_{232} \tag{10i}$$

$$b_2 \equiv \frac{\lambda_{235}+137.88\lambda_{238}}{138.88}. \tag{10j}$$

Application and discussion

In this study, the ages and their errors were calculated using the data measured by Kadowaki and Tsunogae (2020). The ages were estimated using the equation (4), and the weighted mean ages and MSWD values were calculated using the Isoplot 4.15 software (Ludwig, 2012). Only X-ray counting statistics of sample analysis was used to calculate age errors in this study, although that of standard analysis has been considered in previous studies (e.g., Pyle et al., 2005; Lisowiec, 2006; Vlach, 2010). The equation used to calculate the analytical error (standard deviation) of the net intensity (σI_{net}) is as follows:

$$\sigma I_{net} = \sqrt{\frac{I_{peak}}{t_{peak}} + \left(\frac{\overline{L_{PBH}}}{\overline{L_{PBH}}+\overline{L_{PBL}}}\right)^2 \frac{I_{PBL}}{t_{PBL}} + \left(\frac{\overline{L_{PBL}}}{\overline{L_{PBH}}+\overline{L_{PBL}}}\right)^2 \frac{I_{PBH}}{t_{PBH}}} \tag{11}$$

where t is the measurement time (s), I is the intensity (cps), and $\overline{L}$ is the distance from a peak position (mm). Other parameters such as $peak$, PBH, and PBL represent the peak, high background, and low background positions, respectively. The relative error (εI_{net}) is then calculated as:

$$\varepsilon I_{net} = \frac{\sigma I_{net}}{I_{net}}. \tag{12}$$

The CHIME isochron ages were recalculated using the computer program in Kato et al. (1999) with York (1966) method. The results are summarized in Supplementary Table 1.

The results of a monazite in khondalite from the Trivandrum Block in southern India (sample KP5H; N=9) were 535.8±8.1 Ma (MSWD=2.7) using the first-order approximation and 535.8±8.1 Ma (MSWD=2.9) using the second-order approximation. These ages are consistent with the CHIME isochron age of 544±17 Ma (MSWD=2.8). Application to monazites in pelitic granulite from the Limpopo Complex in Zimbabwe (samples C25A and C54D; N=76) gave Paleoproterozoic ages of 1977.8±9.4 Ma (MSWD=21) using the first-order approximation and 1979.2±9.5 Ma (MSWD=28) using the second-order approximation. These ages are slightly older than but broadly consistent with the CHIME isochron age of 1928±19 Ma (MSWD=20). The age differences could be due to an excess of Pb possibly because Pb was overestimated or the monazites contain a certain amount of common Pb.

The age errors were also calculated using the equation (3b) from Hokada and Motoyoshi (2006). Although the equation (3a) is similar to the first-order approximation (equation (6a)), large age errors of each analysis and the resultant low MSWD values were obtained (536±25 Ma and MSWD=0.070 for sample KP5H; 1975.8±8.1 and MSWD=1.1 for samples C25A and C54D). The large age errors of each analysis also caused the large error of the weighted mean age of sample KP5H (25 Ma) because of the small number of analyses. The differences of errors are because of the mistakes of the equation (3b), and application of corrected partial derivatives below gave consistent results of 535.9±8.1 Ma (MSWD=2.4) for sample KP5H and 1977.1±9.3 Ma (MSWD=19) for samples C25A and C54D:

$$\frac{\partial T}{\partial w_{ThO_2}} = -\frac{0.36 n_{Pb} \times 7600}{M_{ThO_2}(0.36 n_{Th} + n_U)^2} \tag{13a}$$

$$\frac{\partial T}{\partial w_{UO_2}} = -\frac{n_{Pb} \times 7600}{M_{UO_2}(0.36 n_{Th} + n_U)^2} \tag{13b}$$

$$\frac{\partial T}{\partial w_{PbO}} = \frac{7600}{M_{PbO}(0.36 n_{Th} + n_U)}. \tag{13c}$$

The ages and their errors calculated using the method and spreadsheet by Săbău (2012) also gave similar ages of 536.1±8.3 Ma (MSWD=2.6) for sample KP5H and 1985±11 Ma (MSWD=18) for samples C25A and C54D.

It is important to note that the results obtained using the first-order approximation and second-order approximation are very similar, suggesting that the higher-order terms of the Maclaurin expansion could be negligible particularly for young monazites. Therefore, both the methods can be applicable to the electron microprobe dating of natural monazites in high-grade metamorphic rocks, although the second-order approximation should give more precise errors. The methods in this study are useful particularly for obtaining ages from small and/or homogeneous domains without constructing isochrons.

Acknowledgements

This study was partly supported by the Grant-in-Aid for JSPS Fellows from Japan Society for the Promotion of Science (JSPS) (No. 19J20534). The author thanks Prof. T. Tsunogae for his review comments. Prof. T. Tsunogae is also acknowledged for offering the electron microprobe data presented in Kadowaki and Tsunogae (2020).

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