CHIME monazite dating: Pb analysis on an $R_R = 100$ mm spectrometer and correction of interferences between Th, U, and Pb with natural monazite

Mayuko SHIMIZU*, Kenji SHIBATA*, Kazuhiro SUZUKI**, Shigeru SUEOKA* and Masakazu NIWA*

*Toki Research Institute of Isotope Geology and Geochronology, Japan Atomic Energy Agency, Toki, Gifu 509-5102, Japan

**Institute for Space-Earth Environmental Research, Nagoya University, Nagoya 464-8601, Japan

This paper outlines an advanced procedure involving the chemical Th-U-total Pb isochron method (CHIME) dating of monazite using a field-emission electron probe microanalyzer (FE-EPMA) equipped with spectrometers of 100 mm Rowland circle (R_R) radius. The higher count rate of $R_R = 100$ mm wavelength dispersive spectrometer (WDS) compared to $R_R = 140$ mm WDS enables measurements to be taken in a shorter time. CHIME dating using $R_R = 100$ mm WDS had previously been difficult because of lower resolution compared to that of $R_R = 140$ mm WDS. This problem has been overcome by a new interference correction method using natural monazites.

Keywords: CHIME, Monazite, Rowland circle diameter, Correction of spectral interference

INTRODUCTION

Monazite is a minor but ubiquitous heavy detrital mineral in clastic sediments. It contains sizable amounts of Th, U, and radiogenic Pb. The inter- and intra-grain age variation of monazite, therefore, becomes a powerful measure of provenance analysis (Suzuki et al., 1991). Micron-sized domains in a monazite grain are hard to date with conventional mass spectrometry techniques. An approach using secondary ion mass spectrometry (SIMS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) is capable of obtaining U-Pb ages from micro-domains of a monazite grain, but necessitates matrix-matched standards. An alternative approach to monazite chronology is dating with an electron probe microanalyzer (CHIME; Suzuki et al., 1991; Suzuki and Adachi, 1991). The advantage of this method is the high spatial resolution of an electron probe microanalyzer (EPMA; several μm or less) in terms of the size of age domains in the accessory minerals.

Although variation in EPMA hardware has little ef-

fect on resultant concentrations, higher X-ray counting is desirable for determination of trace Pb in CHIME dating, especially for provenance analyses where many ages are sought in order to identify age populations.

A higher counting rate is achieved by adopting a WDS with a smaller Rowland circle (R_R) and larger analyzing crystals. The disadvantage of a smaller R_R is a reduction in spectral resolution. The JEOL JXA-8530F field-emission electron probe microanalyzer (FE-EPMA), installed at Tono Geoscience Center, Japan Atomic Energy Agency, is equipped with $R_R = 100$ mm and conventional $R_R = 140$ mm WDS. If we can reduce the effect of spectral interferences on $R_R = 100$ mm WDS, we may realize significant shortening of analysis time. This paper summarizes the critical components of Pb analysis on $R_R = 100$ mm WDS together with development of a novel method for correction of interferences between Th, U, and Pb with natural monazite.

EPMA HARDWARE

The JXA-8530F employs a field-emission electron gun, and can achieve beam energies of 1–30 kV in 0.1 kV steps and beam current of 0.01–500 nA with probe diam-

Table 1. Spectrometer configuration and measurement conditions

CH	R _R and counter	Analyzing crystal	X-ray line	Peak position (mm) ^{***}	Measurement time (s)		Offset for BGs (mm) ^{***}	
					Peak	BG (-/+)	BG (-)	BG (+)
1	100mm	TAP(100)H [*]	MgK α	107.54	60	30	5	5
	Ar-flow	[LDE2H] ^{**}	NaK α	129.54	60	30	1.5	0.8
2	140mm	TAP(100)	SiK α	77.38	60	30	3	4
	Ar-flow	[LDE1]	AlK α	90.65	60	30	5	5
3	140mm Xe-sealed	PET(002) [LiF(200)]	CaK α	107.59	40	20	3	3
			KK α	119.87	40	20	3.5	1
			UM β	119.02	100	50	4	2
			ThM α	132.55	60	30	2	2
			SK α	172.1	30	15	6	1.5
4	100mm Xe-sealed	PET(002)H [LiF(200)H]	YL α	206.64	50	25	3.5	7.5
			PbM β	162.61	140	70	1.2	1
			PK α	197.23	60	30	5	5
			LaL α	185.52	30	15	3	3
5	100mm Xe-sealed	PET(002)H [LiF(200)H]	CeL α	178.3	30	15	3	3
			NdL β	150.91	30	15	5	4.6
			PrL β	157.3	30	15	1	12
			SmL β	139.2	30	15	4.5	6.5
			EuL β	133.79	20	10	4.5	4
			GdL β	128.7	30	15	1.5	1
			TbL α	137.7	30	15	3	7.5
			DyL α	133.01	30	15	1	1.5
			ErL α	124.39	20	10	2	3

* High intensity type.

** Swappable crystals.

*** 'Peak position (mm)' and 'Offset for BGs (mm)' represent the sample-analyzing crystal distance L (mm) on the R_R = 140 mm WDS.

eters adjustable between focus and 300 μ m in 1 μ m steps. It has an energy dispersive spectrometer, three R_R = 100 mm WDS and two R_R = 140 mm WDS. The JEOL WDS refers to X-ray detection position L (mm) such that

$$L = (R_R/d) \times n\lambda,$$

where d is d-spacing (nm) of the analyzing crystal, n is the order of the X-ray line and λ is the wavelength (nm). For the user's convenience, L-values for R_R = 100 mm are always given as L-values for R_R = 140 mm WDS on JEOL EPMA. Individual spectrometers are equipped with two swappable analyzing crystals. The present configuration of crystal and detector on an individual WDS is listed in Table 1. Since the equipment also serves for analysis of light elements, performance of monazite dating is constrained under the present crystal-counter configuration.

Although the spectral resolution of an R_R = 100 mm WDS compares unfavorably with that of an R_R = 140 mm WDS, the former gives a distinctly higher count rate (Fig. 1). The intrinsic responses of two R_R = 100 mm WDS at 15 kV are 2.51 and 2.65 kcps/ μ A wt% Pb for PbM β of crocoite (PbCrO₄) with peak-to-background (P/B) ratios of 89 and 94, respectively, whereas that of the R_R = 140

mm counting system is 0.92 kcps/ μ A wt% Pb with a P/B ratio of 109.

X-RAY LINES USED FOR Th, U, AND Pb ANALYSES

M-lines are used for analyses of Th, U, and Pb of monazite, because the critical excitation energy of the L-shells is higher than 15 kV. The ThM α line can be measured without significant interference for monazite, but the UM α line is hard to discriminate from the strong ThM β line on the both R_R = 140 mm and R_R = 100 mm spectrometers (Fig. 1A). The UM β line is overlapped by ThM γ , ThM3N4 and ThM5P3 lines and ThM5 absorption (Fig. 1A). Although KK α lines potentially affect the UM β line, monazite contains no detectable amounts of K. The combined effect of the Th interferences is corrected through the procedure described in Åmli and Griffin (1975):

$$I_{UM\beta}(\text{net}) = I_{UM\beta}(\text{obs}) - I_{ThM\alpha}(\text{net}) \times f_{ThM\gamma} \quad (\text{Eq. 1}),$$

where $I_{UM\beta}(\text{net})$ is the net UM β intensity, $I_{UM\beta}(\text{obs})$ is the observed intensity at the UM β position, and $I_{ThM\alpha}(\text{net})$ is

Figure 1. Detailed $R_R = 100$ mm and $R_R = 140$ mm WDS intensity step scans around the $\text{ThM}\gamma - \text{ThM}\alpha$ (A) and $\text{PbM}\beta - \text{PbM}\alpha$ (B) regions with PET crystal and sealed Xe detector on a natural monazite, together with step scans around the $\text{PbM}\beta$ region (C) obtained through pulse-height discrimination. The horizontal axis represents the sample-analyzing crystal distance L (mm) on the $R_R = 140$ mm spectrometer.

the net $\text{ThM}\alpha$ intensity of the analyzing spot. $f_{\text{ThM}\gamma}$ represents the correction factor of the interference of $\text{ThM}\gamma$ with $\text{UM}\beta$.

When $I_{\text{ThM}\alpha}(\text{net}) > 0$,

$$\begin{aligned} I_{\text{UM}\beta}(\text{net})/I_{\text{ThM}\alpha}(\text{net}) \\ = I_{\text{UM}\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net}) - f_{\text{ThM}\gamma} \end{aligned} \quad (\text{Eq. 2})$$

Then,

$$\begin{aligned} I_{\text{UM}\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net}) \\ = [1/I_{\text{ThM}\alpha}(\text{net})] \times I_{\text{UM}\beta}(\text{net}) + f_{\text{ThM}\gamma} \end{aligned} \quad (\text{Eq. 3})$$

When $I_{\text{UM}\beta}(\text{net}) = 0$, Eq. 3 shows that

$$f_{\text{ThM}\gamma} = I_{\text{UM}\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net}).$$

Figure 2. (A) Plots of the $I_{\text{UM}\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net})$ X-ray intensity ratio against $I_{\text{UM}\beta}(\text{obs})$ of low-U/Th (Kojaku) and high U/Th (Cooma) monazite grains with limited ranges of $I_{\text{ThM}\alpha}(\text{net})$. Regression lines are drawn by Isoplot 3.75 software (Ludwig, 2012). (B) Plots of $I_{\text{PbM}\beta}(\text{obs})/I_{\text{UM}\beta}(\text{net})$ against $I_{\text{ThM}\alpha}(\text{net})$ for low and high $I_{\text{UM}\beta}(\text{net})$ spots within a chronologically uniform monazite grain with considerable variation in U and Th concentrations. Regression lines are drawn by Isoplot 3.75 software (Ludwig, 2012) using the linear regression model from York (1968).

Thus the interference correction factor can be calculated easily from X-ray intensity data of U-free and Th-rich material. Without U-free and Th-rich material, we employ an estimation of the correction factor by measuring natural monazites with variable $I_{\text{UM}\beta}(\text{obs})$. Figure 2A shows the X-ray intensity at $\text{UM}\beta$ position [$I_{\text{UM}\beta}(\text{obs})$] on

Table 2. Representative analyses of monazite from Kojaku granite and Cooma Granodiorite

	Kojaku Granite					Cooma Granodiorite				
	1	2	3	4	5	1	2	3	4	5
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	2.17	1.76	1.86	2.16	1.99	0.00	0.03	0.06	0.00	0.00
CaO	0.07	0.06	0.07	0.08	0.08	1.46	1.42	1.23	1.36	0.80
UO ₂	0.32	0.22	0.27	0.35	0.27	1.03	1.00	0.63	0.85	1.26
ThO ₂	9.04	7.45	7.84	9.23	8.67	5.82	5.73	5.03	5.59	2.33
PbO	0.028	0.020	0.023	0.026	0.027	0.163	0.163	0.129	0.147	0.121
SO ₃	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.00	0.00
Y ₂ O ₃	0.88	1.00	1.10	0.96	0.76	2.21	2.19	2.40	2.63	2.27
La ₂ O ₃	12.81	12.31	12.22	11.94	13.28	12.55	12.08	12.29	11.72	13.45
Ce ₂ O ₃	30.90	31.01	30.55	29.88	31.57	27.65	27.28	27.34	27.05	29.14
Pr ₂ O ₃	3.28	3.47	3.38	3.34	3.28	3.07	3.05	3.12	3.01	3.18
Nd ₂ O ₃	10.99	12.24	11.95	11.78	10.69	11.33	11.79	12.00	11.80	12.09
Sm ₂ O ₃	1.91	2.12	2.24	2.25	1.66	1.52	2.21	2.16	2.20	2.32
Eu ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.09
Gd ₂ O ₃	1.07	1.22	1.41	1.32	0.87	1.54	1.70	1.89	1.79	1.65
Tb ₂ O ₃	0.13	0.14	0.16	0.16	0.10	0.00	0.16	0.00	0.18	0.24
Dy ₂ O ₃	0.26	0.29	0.37	0.32	0.18	0.46	0.53	0.61	0.64	0.56
Er ₂ O ₃	0.10	0.11	0.12	0.12	0.10	0.05	0.15	0.16	0.20	0.12
P ₂ O ₅	25.71	26.45	26.33	25.72	26.77	29.71	29.86	29.82	29.69	29.70
Total	99.68	99.88	99.90	99.65	100.31	98.60	99.38	98.88	98.86	99.33
Ca+Si										
Th+U+Pb+S	1.04	1.04	1.04	1.02	1.02	0.97	0.99	1.03	0.97	1.01
Age (Ma)	66	58	63	60	67	417	426	429	413	439

the horizontal axis and $I_{UM\beta}(\text{obs})$ for net $\text{ThM}\alpha$ intensity [$I_{\text{ThM}\alpha}(\text{net})$] on the vertical axis. Eq. 3 shows, under condition of constant X-ray intensity of $\text{ThM}\alpha$, that the value of $f_{\text{ThM}\gamma}$ is equal to the value of y when $I_{UM\beta}(\text{net}) = 0$. This is because $I_{UM\beta}(\text{obs})$ is the sum of $I_{UM\beta}(\text{net})$ and [$I(\text{obs})$ at $UM\beta$ detected position]. However, $I_{UM\beta}(\text{obs})$ when $I_{UM\beta}(\text{net}) = 0$ cannot be clarified by EPMA measurement for natural monazites that generally contain minor amounts of U (Table 2). Hence, the authors assume that the detection limit of the $UM\beta$ line ($DL_{UM\beta}$) represents the $I_{UM\beta}(\text{obs})$ at $I_{UM\beta}(\text{net}) = 0$. $DL_{UM\beta}$ is defined as 3σ : triplication of the standard deviation (σ) of the background intensity at the $UM\beta$ position. $f_{\text{ThM}\gamma}$ is calculated by assigning $DL_{UM\beta}$ to the equation of the approximate line of $I_{UM\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net})$ versus $I_{UM\beta}(\text{obs})$. To draw the approximate line, we selected the data that meet the following requirements: (1) $I_{UM\beta}(\text{obs})$ is high and has variation, (2) $I_{\text{ThM}\alpha}(\text{net})$ is similar, and (3) the ratio of $I_{UM\beta}(\text{obs})$ to $I_{\text{ThM}\alpha}(\text{net})$ is high. We plotted the selected data as the difference between the maximum and minimum of $I_{\text{ThM}\alpha}(\text{net})$, which in the plotted data group falls within $\pm 5\%$ of the mean of the group in order to fit similar

$I_{\text{ThM}\alpha}(\text{net})$ (Fig. 2A). The approximate line was drawn by linear regression using Isoplot 3.75 software (Ludwig, 2012) from both measured X-ray intensities and their errors. The linear regression model used is from York (1968). Although approximate lines from two data groups (monazite grains from Kojaku granite and Cooma Granodiorite; details of these samples are shown in subsequent sections) were drawn, we first adopted the $DL_{UM\beta}$ determined by analyses of monazites from Cooma Granodiorite ($DL_{UM\beta} = 0.0807$) to calculate $f_{\text{ThM}\gamma}$. This was done because spots of low Th intensity in monazite grains were collected more often from Cooma Granodiorite than from Kojaku granite. As $I_{\text{ThM}\alpha}(\text{net})$ increases, the slope of the approximate line of $I_{UM\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net})$ versus $I_{UM\beta}(\text{obs})$ becomes steep, and interference of $\text{ThM}\gamma$ on the $UM\beta$ line is not negligible. The slope of the approximate line drawn from data on Cooma Granodiorite is steeper than that of Kojaku granite. Let y be $I_{UM\beta}(\text{obs})/I_{\text{ThM}\alpha}(\text{net})$, and let x be $I_{UM\beta}(\text{obs})$. Then, the regression line for Cooma Granodiorite monazites is given by:

$$y = 0.1148x - 0.0030.$$

When $DL_{UM\beta} = 0.0807$ is substituted for x , we have $f_{ThM\gamma} = 0.00626$, similar to values obtained in previous studies (e.g., Suzuki and Kato, 2008; Grand'Homme et al., 2016; Jercinovic and Williams, 2005). The error margin of the inclination is ± 0.0049 and that of the intercept is ± 0.0049 . Therefore, considering error propagation, $f_{ThM\gamma}$ has an error margin of ± 0.00492 . To evaluate the validity of the correction factor, we also calculated $f_{ThM\gamma}$ using $DL_{UM\beta} = 0.0807$ and the approximate line drawn from data on Kojaku granite; the calculated value was 0.00621. In this case, an error margin reflecting error propagation is ± 0.00201 . The error margin of the inclination is ± 0.0032 and that of the intercept is ± 0.0020 .

Figure 1B shows a wavelength step scan including the PbM β to PbM α region of monazite. Both PbM lines are subject to first order interferences from coexisting major elements. The PbM α line is overlapped or affected by ThM ζ 1, YL γ 2,3, NbL β 3, SsK α 4, ThM ζ 2 and SsK α 3 lines. Although the NbL β 3 line also exists between YL γ 2,3 and SsK α 4, monazite generally contains little Nb, therefore correction of NbL β 3 interference is insignificant (Suzuki and Kato, 2008). Intensity of Nb was lower than the detection limit in all samples. Sulfur hampers Pb determination, but is intrinsic in monazite to form the CaSO₄ component; S content varies from a barely detectable amount to as high as 1 wt% (Suzuki and Kato, 2008). PbM α is overlapped by ThM ζ 1, ThM ζ 2 and YL γ 2,3. PbM β line is overlapped by UM ζ 2 line and is possibly affected by SK β 1 and SK β x lines. The $R_R = 100$ mm spectrometer appears to favor the M β line for Pb determination through pulse-height discrimination (Fig. 1C). The interferences from UM ζ 2 and SK β are corrected by the following:

$$I_{PbM\beta}(\text{net}) = I_{PbM\beta}(\text{obs}) - I_{UM\beta}(\text{net}) \times f_{UM\zeta} - I_{SK\alpha}(\text{net}) \times f_{SK\beta} \quad (\text{Eq. 4}),$$

where $f_{UM\zeta}$ and $f_{SK\beta}$ are correction factors. Since S-rich monazites are eliminated by the chemical criteria (Ca + Si)/(Th + U + Pb + S), the last term in Eq. 4 can be negligible. Therefore Eq. 4 is equal to:

$$I_{PbM\beta}(\text{net}) = I_{PbM\beta}(\text{obs}) - I_{UM\beta}(\text{net}) \times f_{UM\zeta} \quad (\text{Eq. 5}).$$

When $I_{UM\beta}(\text{net}) > 0$,

$$\begin{aligned} I_{PbM\beta}(\text{net})/I_{UM\beta}(\text{net}) \\ = I_{PbM\beta}(\text{obs})/I_{UM\beta}(\text{net}) - f_{UM\zeta} \end{aligned} \quad (\text{Eq. 6}).$$

When $I_{PbM\beta}(\text{net}) = 0$,

$$f_{UM\zeta} = I_{PbM\beta}(\text{obs})/I_{UM\beta}(\text{net}) \quad (\text{Eq. 7}),$$

where $f_{UM\zeta}$ is $I_{PbM\beta}(\text{obs})/I_{UM\beta}(\text{net})$ in Pb- and Th-free U-rich material and $f_{SK\beta}$ is $I_{PbM\beta}(\text{obs})/I_{SK\alpha}(\text{net})$ in Pb-free and S-rich material. Without pure U or Pb- and Th-free U standards, we employ an estimation of the correction factor $f_{UM\zeta}$ from age-known monazite. Figure 2B shows $I_{ThM\alpha}(\text{net})$ on the horizontal axis and $I_{PbM\beta}(\text{obs})$ for net UM β intensity [$I_{UM\beta}(\text{net})$] on the vertical axis. In the case of monazite, the observed intensity at the PbM β position [$I_{PbM\beta}(\text{obs})$] is the sum of X-rays for Pb from the decay of U [$I_{PbM\beta}(\text{net})$ from U] and Th [$I_{PbM\beta}(\text{net})$ from Th], and the interference from UM ζ 2 [$I(\text{obs})$ at PbM β detected position]. In an aged monazite grain, $I(\text{obs})$ at the PbM β detected position is negligibly small compared with $I_{PbM\beta}(\text{net})$ from U and $I_{PbM\beta}(\text{net})$ from Th at low U spots. The approximated value of the y -intercept at Figure 2B is:

$$y_1 = [I_{PbM\beta}(\text{net}) \text{ from U}]/I_{UM\beta}(\text{net}).$$

In contrast, at high U spots $I(\text{obs})$ at the PbM β detected position contributes a large part of $I_{PbM\beta}(\text{obs})$ and the y -intercept is:

$$\begin{aligned} y_2 = \{[I_{PbM\beta}(\text{net}) \text{ from U}] \\ + [I(\text{obs}) \text{ at PbM}\beta \text{ detected position}]\} \\ /I_{UM\beta}(\text{net}). \end{aligned}$$

The $[I_{PbM\beta}(\text{net}) \text{ from U}]/I_{UM\beta}(\text{net})$ and $[I_{PbM\beta}(\text{net}) \text{ from Th}]/I_{ThM\alpha}(\text{net})$ values remain constant irrespective of variation in U and Th within a single-age monazite grain. Therefore, $f_{UM\zeta}$ is calculated by subtracting y_1 from y_2 . In order to estimate y_1 and y_2 , we drew two regression lines using two plot groups of low and high U spots from a single monazite grain. Data requirements to draw better regression lines are summarized as follows: (1) The plotted data must be of chronologically uniform domains in a single monazite grain, (2) There is considerable variation in $I_{ThM\alpha}(\text{net})$ within the selected spots, and (3) $I_{UM\beta}(\text{net})$ is similar within each data group of low and high U spots but is significantly different between the two groups. In this study, a monazite grain of 420 ± 20 Ma from Hikami granite in the South Kitakami terrane, Northeast Japan (Suzuki and Adachi, 1991), is used for calculation of $f_{UM\zeta}$. The plotted data of low-U and high-U domains were chosen in order that the difference between the two extreme values (maximum minus minimum) in each dataset fell within $\pm 5\%$ of the mean. Two approximate lines for each of the low and high U data groups were drawn using Isoplot (Fig. 2B). The $f_{UM\zeta}$ calculated by subtracting y_1 (0.083) from y_2 (0.0836) is nearly zero (0.0006; an error margin reflecting error propagation is ± 0.00092 and error margins of the intercept are ± 0.029 for low-U domains and ± 0.0089 for high-U domains). The value of $f_{UM\zeta}$ by Suzuki

and Kato (2008) is also very low (0.00186). Thus, we determined $f_{\text{UM}\zeta} = 0$ when calculating Pb concentration for CHIME dating in this study.

OFFSET POSITION FOR BACKGROUND MEASUREMENT

Monazite contains La and Ce as major constituents. The wavelengths of the second order $\text{LaL}\beta_1$ and $\text{CeLa}_{1,2}$ interfere with the spectral region around $\text{PbM}\beta$. Although the energies of Ar escape peaks from LaLa and CeLa partly overlap the energy of $\text{PbM}\beta$, the Xe escape peaks from second order $\text{LaL}\beta$ and CeLa are largely excluded by the pulse-height window occupied by $\text{PbM}\beta$. This provides us with a wide interference-free window on the low energy side of $\text{PbM}\beta$. The high energy side, however, is occupied by $\text{SK}\beta_1$, $\text{SK}\beta_x$, SK_{abs} , PbM4O2 , PbM5_{abs} , $\text{UM}\zeta_1$, ThM4N3 , ThM1O3 . Further, the region between PbM4O2 and PbM5_{abs} corresponds to one of the background holes for PET(002) analyzing crystals (Kato and Suzuki, 2014), which is an intensity depression on X-ray spectra due to diffraction by additional lattice planes. This suppresses background intensity by approximately 4%. In this study, the measurement positions of $\text{PbM}\beta$ background are set at -1.2 and $+1$ mm (Table 1). The position on the high energy side is decided based on a spectrum from qualitative analysis of a monazite, in order to confirm that the position does not overlap with the X-ray peaks mentioned above. Although sulfur behaves as an intrinsic component in monazite, most grains contain little S; the $\text{SK}\alpha$ count is usually below 0.1 kcps/ μA . The corresponding $\text{SK}\beta_1$ and $\text{SK}\beta_x$ counts, around 0.05 of $\text{SK}\alpha$, are negligibly small compared to the intensity of continuous X-rays around $\text{PbM}\beta$. If this is the case, the spectral region between $\text{UM}\zeta$ and the background hole can be selected for the offset position on the high-energy side. In the case of a high $\text{SK}\alpha$ count, the measurement at the offset position should be corrected as follows:

$$I_{\text{offset}}(\text{net}) = I_{\text{offset}}(\text{obs}) - I_{\text{SK}\alpha}(\text{net}) \times f_{\text{SK}\beta},$$

where $f_{\text{SK}\beta}$ is the correction factor for the combined $\text{SK}\beta_1$ and $\text{SK}\beta_x$ interferences and is defined as $I_{\text{offset}}(\text{obs}) / I_{\text{SK}\alpha}(\text{net})$ in Pb-free S standard.

ANALYZING ELEMENTS, STANDARDS AND ANALYTICAL CONDITIONS

Measurements were carried out on polished thin sections and mounts of separated monazite grains. The analyzing elements are Th, U, Pb, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, P, Si, Ca, S, Na, K, Al, and Mg (22 elements).

The non-monazite components, Na, K, Al, and Mg, were measured to provide a control of the interference of adjacent minerals and subsurface inclusions. They should fall below the detection limits of the EPMA.

The responses of the $R_R = 100$ mm counting system at 15 kV are 2.13 kcps/ μA wt% PbO for $\text{PbM}\beta$ and 1.37 kcps/ μA for background on monazite. To measure 300 ppm PbO at 1σ , with a counting uncertainty of 10% and 200 nA probe current, a counting duration of 150 s is needed. By adopting 100 s counting duration, analysis of 0.2 wt% PbO at an uncertainty of 5% is achieved with 50 nA probe current. Since almost all the energy of the incident electrons is dissipated in the form of heat, irradiation of a focused 400 nA beam may potentially cause significant damage to samples, especially those rich in U and Th. With a lower beam current, the X-ray count remains relatively constant for an exposure time over 85 m (Suzuki and Kato, 2008). Present monazite dating prefers a long duration for X-ray integration under optimized probe currents. The integration times and background positions for measurement of monazite, partly different from those for calibration on standards, are listed in Table 1. The total time for a single run is about 15 m. The detection limit of PbO at 1σ confidence level is 30 ppm for 200 nA probe current and 140 s counting duration.

Standards used in monazite dating are: monazite provided by Astimex Scientific Ltd. For Th ($\text{ThO}_2 = 11.80$ wt%), euxenite provided by Smellie et al. (1978) for U, crocoite for Pb, Y-Al garnet for Y and Al, quartz for Si, anhydrite for Ca and S, periclase for Mg, orthoclase for K, albite for Na, apatite for P, and elemental substances, synthesized phosphates or fluorides for the rest of the rare earth elements.

The instrument operating conditions were 15 kV accelerating voltage and 50 – 200 nA probe current. Higher probe currents were adopted to analyze low Pb in young monazites. Probe diameter was 3 – 5 μm for lower probe currents and around 10 μm for higher probe currents. To ensure the accuracy of analyses of Pb in young monazites, we normally repeated the measurement on a single spot twice or three times, and took the arithmetic mean as a reliable estimate.

After correction of background and interference, X-ray intensities were calibrated with those of standards. The relative intensities were converted into concentrations through ZAF matrix correction. Analyses with substantial K, Na, Al, or Mg, as noted above, were excluded. Also excluded were analyses giving the sum of analyzed oxides smaller than 98% or larger than 101% . Th and U in monazite form huttonite $[(\text{Th,U})\text{SiO}_4]$ and cheralite $[(\text{Th,U})\text{Ca}(\text{PO}_4)_2]$ substitutions. Moreover, some monazite grains show coupling of Ca and S in the form of

CaSO₄ (Suzuki and Kato, 2008). The (Ca + Si)/(Th + U + Pb + S) ratio, being unity in ideal monazite, deviates from unity for analyzing spots in metamict portions and on or around inclusions (Suzuki and Kato, 2008). We adopt chemical features for practical discrimination of analyses on possibly discordant domains from those on concordant domains.

MONAZITE DATING

Reliability of Pb analyses on the R_R = 100 mm spectrometer was tested through dating of monazite grains of known age from late Cretaceous Kojaku granite and Silurian Cooma Granodiorite. Kojaku granite, exposed on the Tsuruga Peninsula, central Japan, is a fine- to coarse-grained granite (syenogranite to monzogranite; Sawada et al., 1997). The monazite grains used for dating were separated from the sample code KGR-Mj, for which zircon U–Pb age was determined to be 68.5 ± 0.7 Ma (2 σ) by using LA-ICPMS (Sueoka et al., 2016). This sample is monzogranite consisting of quartz, plagioclase, K-feldspar, biotite, and trace muscovite with accessory apatite, zircon, allanite, monazite, chlorite, magnetite, and titaniferous magnetite. Monazite grains form short prisms of 90–120 μ m in length. The Cooma Granodiorite forms a 3 $\times$ 6 km pluton in the Lachlan Fold Belt of southeastern Australia (Vernon et al., 2001). The analyzed sample is medium-grained cordierite- and sillimanite-bearing two-mica monzogranite. Monazite forms subhedral to anhedral grains of around 50 μ m in size, with some exceptionally large grains of over 150 μ m. Monazite in the Cooma Granodiorite was dated by SHRIMP as 432.8 ± 3.5 Ma (Williams, 2001) and by CHIME as 436 ± 16 Ma (Suzuki and Dunkley, 2003).

Monazite from Kojaku granite contains 16.14–5.74 wt% ThO₂, 0.58–0.05 wt% UO₂, and 0.049–0.014 wt% PbO. Representative analyses are listed in Table 2. The high SiO₂ content (3.74–1.29 wt%), coupled with a positive correlation between SiO₂ and ThO₂ + UO₂, suggests a monazite-huttonite substitution. A total of 27 screened analyses are plotted on the PbO versus ThO₂* diagram (ThO₂*: measured ThO₂ plus ThO₂ equivalent of measured UO₂; Suzuki and Adachi, 1991) (Fig. 3). Data points are arrayed linearly, and are approximated by an isochron of 69 ± 8 Ma.

Monazite from the Cooma Granodiorite contains 6.37–2.32 wt% ThO₂, 1.36–0.30 wt% UO₂, and 0.177–0.069 wt% PbO. The high CaO (1.54–0.66 wt%) and low SiO₂ (below 0.25 wt%) concentrations suggest a monazite-cheralite substitution. A total of 84 screened analyses are plotted linearly on the PbO versus ThO₂* diagram, and yield an isochron of 432 ± 26 Ma (Fig. 3).

Figure 3. Plots of PbO against ThO₂* for monazite grains from Kojaku granite (solid circles) and Cooma Granodiorite (open circles). Relative error (1 σ) for PbO determination is approximated by $0.4983X^{-0.933}$, where X represents PbO concentration in wt%. Relative error for ThO₂* is around 3 wt%.

DISCUSSION

Analyses of Pb for EPMA monazite dating are delicate and time consuming. The 300 mm collimator setting on R_R = 140 mm WDS barely achieves an intrinsic response of 0.32–0.37 kcps/ μ A wt% PbO with a background rate of 0.12–0.18 kcps/ μ A (Suzuki and Kato, 2008). It requires 600–800 s to measure 300 ppm PbO at a 1 σ counting uncertainty of 10% with 200 nA probe current. The R_R = 100 mm WDS, providing the same determination within 140 s, has the advantage of significantly shortening analysis time.

Monazite ages calculated by CHIME are quite sensitive to Pb determination on EPMA, especially for younger samples. The good agreement of 69 ± 8 Ma with the 68.5 ± 0.7 Ma isotopic zircon age (Sueoka et al., 2016) demonstrates that the interference and background corrections adopted for UM β and PbM β measurement on R_R = 100 mm WDS are highly accurate. The accuracy of the interference correction is largely determined by the accuracy of the correction factors. The correction factor for ThM γ on UM β ($f_{\text{ThM}\gamma}$) is determined without difficulty through the use of U-free Th standard and Pb- and Th-free U standard. Utilization of pure Th and U standards, however, is not easy in Japan due to legal regulations. Alternatively, Kato et al. (2005) developed a working standard technique that includes calibration of natural minerals with well-characterized primary Th and U stand-

ards. Suzuki and Kato (2008) proposed use of high Th ($\text{ThO}_2 > 25 \text{ wt\%}$) monazite with hardly detectable amounts of U for f_{ThM} determination and for f_{UM} a combination of high U and low Th ($\text{ThO}_2/\text{UO}_2 < 0.1$) xenotime and U- and Th-free Pb standard. However, adoption of this technique is not easy because extremely high Th monazite and high U xenotime are uncommon. On the other hand, monazites with moderate and variable Th and U concentrations are not uncommon, especially in pegmatite samples. These natural minerals coupled with the methodology proposed above result in a reliable f_{ThM} estimate.

The present achievement of Pb analyses on $R_R = 100 \text{ mm}$ WDS was supported by careful selection of background positions. Since the high and low energy sides of the $\text{PbM}\beta$ line are occupied by closely-spaced X-ray lines including the second-order REE-L lines, it is sometimes preferable to use global rather than local background positions (e.g., Williams, 1996; Jercinovic and Williams, 2005; Williams et al., 2007). Scherrer et al. (2000) showed experimentally that it is best for elements from Pr to U to measure of upper and lower backgrounds on two closest overlap-free positions surrounding the peaks. Pyle et al. (2005) placed the background position for the high-energy side of $\text{PbM}\beta$ at around PbM4O2 . Their placement largely avoids the effect of $\text{SK}\beta$ but is subjected to inevitable depression by the background hole and the rise in PbM4O2 . The background for the low energy side of $\text{PbM}\beta$ is often placed at the window between the second-order CeLa and PbM5O3 (e.g., Pyle et al., 2005; Suzuki and Kato, 2008). Some selection techniques of background-measurement positions based on theoretical calculations have also been developed (Jercinovic et al., 2012; Allaz et al., 2014), which achieve high background precision. The trough between $\text{PbM}\beta$ and the second-order CeLa also provides an interference-free window. A large offset potentially causes a depression in count rate through discrimination by pulse-height analyzer, and forces exponential fitting for estimation of the background. Without a facility for exponential fitting, a small offset provides a better estimation by linear interpolation.

The important assumption for EPMA monazite dating is the closed-system behavior in the Th-U-Pb system. The linear arrangement of screened data on the PbO-ThO_2^* diagram strongly suggests that the chemical criteria reasonably discriminates concordant analyses from discordant ones. Each screened single date, 52–70 Ma for Kojaku granite and 383–477 Ma for Cooma Granodiorite, accords with the isotopic ages of $68.5 \pm 0.7 \text{ Ma}$ (Sueoka et al., 2016) and $432.8 \pm 3.5 \text{ Ma}$ (Williams, 2001) within the uncertainty of EPMA counting. The single date appears to properly represent the grain or domain age. This

is particularly interesting in the study of sedimentary rocks where monazite grains are chronologically inhomogeneous and many age data points are required to characterize populations.

CONCLUSION

This paper describes CHIME dating of monazite on EPMA with $R_R = 100 \text{ mm}$ WDS, together with a way to assess Th and U interference correction with natural monazite. This study overcame the low spectral resolution peculiar to $R_R = 100 \text{ mm}$ WDS through interference corrections and suitable selection of background positions. Although the precision of this method might not be beyond that of dating methods using LA-ICPMS, the significant shortening of analysis time provides a new opportunity for deciphering geologic histories.

ACKNOWLEDGMENTS

We thank Dr. K. Umeda, Dr. K. Yasue, and Mr. T. Ishimaru for their encouragement throughout the study, Ms. N. Sano for helping with data processing, and Mr. K. Yoshikawa for his excellent sample preparation. Thanks are extended to Mr. G.F. McCrank for helping with English language. Constructive comments by an anonymous reviewer and Dr. T. Shimura, and handling by Dr. T. Kato are much appreciated. The FE-EPMA at Tono Geoscience Center was introduced under a contract with the Ministry of Economy, Trade and Industry of Japan as part of its R&D supporting program for developing geological disposal technology for development of advanced technique for provenance analyses.

REFERENCES

- Allaz, J., Jercinovic, M.J., Williams, M.L. and Donovan, J.J. (2014) Trace element analyses by EMP: Pb-in-monazite and new multipoint background method. *Microscopy and Microanalysis*, 20, 720–721.
- Ämli, R. and Griffin, W. (1975) Microprobe analysis of REE minerals using empirical correction factors. *American Mineralogist*, 60, 599–606.
- Grand'Homme, A., Janots, E., Seydoux-Guillaume, A.M., Guillaume, D., Bosse, V. and Magnin, V. (2016) Partial resetting of the U-Th-Pb systems in experimentally altered monazite: Nanoscale evidence of incomplete replacement. *Geology*, 44, 431–434.
- Jercinovic, M.J. and Williams, M.L. (2005) Analytical perils (and progress) in electron microprobe trace element analysis applied to geochronology: Background acquisition, interferences, and beam irradiation effects. *American Mineralogist*, 90, 526–546.
- Jercinovic, M.J., Williams, M.L., Allaz, J. and Donovan, J.J. (2012) Trace analysis in EPMA. In *IOP Conference Series*:

- Materials Science and Engineering, 32, 012012, IOP Publishing.
- Kato, T., Cho, D.L. and Suzuki, K. (2005) Determination of interference correction factors and preparation of standard materials using “working standard” technique for CHIME dating. *Bulletin of the Nagoya University Museum*, 21, 43–49.
- Kato, T. and Suzuki, K. (2014) ‘Background holes’ in X-ray spectrometry using a pentaerythritol (PET) analyzing crystal. *Journal of Mineralogical and Petrological Sciences*, 109, 151–155.
- Ludwig, K.R. (2012) User’s Manual for Isoplot 3.75: A geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication, 5, 75.
- Pyle, J.M., Spear, F.S., Wark, D.A., Daniel, C.G. and Storm, L.C. (2005) Contributions to precision and accuracy of monazite microprobe ages. *American Mineralogist*, 90, 547–577.
- Sawada, K., Yoshida, G. and Fujii, R. (1997) Granitic masses around Lake Biwa, southwest Japan: the Koujyaku granite pluton. *Earth Science*, 51, 401–412.
- Scherrer, N.C., Engi, M., Gnoss, E., Jakob, V. and Liechti, A. (2000) Monazite analysis; from sample preparation to microprobe age dating and REE quantification. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 80, 93–105.
- Smellie, J.A.T., Cogger, N. and Herrington, J. (1978) Standards for quantitative microprobe determination of uranium and thorium with additional information on the chemical formulae of davidite and euxenite—Polycrase. *Chemical Geology*, 22, 1–10.
- Sueoka, S., Umeda, K., Yasue, K., Niwa, M., Shimada, K., Ishimaru, T., Danhara, T., Iwano, H. and Yagi, K. (2016) Cooling and denudation history of the Tsuruga body of the Kōjaku granite, southwest Japan, constrained from multi-system thermochronology. *Journal of Geography*, 125, 201–219.
- Suzuki, K. and Adachi, M. (1991) Precambrian provenance and Silurian metamorphism of the Tsubonosawa paragneiss in the South Kitakami terrane, Northeast Japan, revealed by the chemical Th–U–total Pb isochron ages of monazite, zircon and xenotime. *Geochemical Journal*, 25, 357–376.
- Suzuki, K., Adachi, M. and Tanaka, T. (1991) Middle Precambrian provenance of Jurassic sandstone in the Mino Terrane, central Japan: Th–U–total Pb evidence from an electron microprobe monazite study. *Sedimentary Geology*, 75, 141–147.
- Suzuki, K. and Dunkley, D.J. (2003) CHIME monazite ages of the Cooma Granodiorite, southeastern Australia. Abstracts of 110th Annual Meeting of the Geological Society of Japan, 177, O-353.
- Suzuki, K. and Kato, T. (2008) CHIME dating of monazite, xenotime, zircon and polycrase: protocol, pitfalls and chemical criterion of possibly discordant age data. *Gondwana Research*, 14, 569–586.
- Vernon, R.H., Richards, S.W. and Collins, W.J. (2001) Migmatite–granite relationships: origin of the Cooma granodiorite magma, Lachlan Fold Belt, Australia. *Physics and Chemistry of the Earth, Part A: Solid Earth and Geodesy*, 26, 267–271.
- Williams, C.T. (1996) Analyses of rare earth minerals. In *Rare Earth Minerals: Chemistry, origin and deposits* (Jones, A.P., Wall, F. and Williams, C.T. Eds.). Chapman and Hall, London, 327–348.
- Williams, I.S. (2001) Response of detrital zircon and monazite, and their U–Pb isotopic systems, to regional metamorphism and host-rock partial melting, Cooma Complex, southeastern Australia. *Australian Journal of Earth Sciences*, 48, 557–580.
- Williams, M.L., Jercinovic, M.J. and Hetherington, C.J. (2007) Microprobe monazite geochronology: understanding geologic processes by integrating composition and chronology. *Annual Review of Earth Planetary Sciences*, 35, 137–135.
- York, D. (1968) Least squares fitting of a straight line with correlated errors. *Earth and planetary science letters*, 5, 320–324.

Manuscript received July 19, 2016

Manuscript accepted March 18, 2017

Manuscript handled by Takenori Kato