Protocol and pitfalls of CHIME dating

Kazuhiro SUZUKI

Center for Chronological Research, Nagoya University, Japan

CHIME dating originated by the research group of Nagoya University (Suzuki et al., 1991: Suzuki and Adachi, 1991) is a novel method for micron-scale dating of monazite, zircon and other Th- and U-bearing minerals on the basis of the EPMA analyses. It consists in measuring many spots within constant age domains showing sufficient compositional variation, and in constructing an "pseudo-isochron" from which an age can be obtained by regression.

Analyses were carried out on a JEOL JXA-733 EPMA equipped with 4 wavelength-dispersive (WD) spectrometers (radius of Rowland circle = 140 mm). The instrument was operated at 15 kV accelerating voltage, 200 nA probe current and defocused 3-6 μm probe diameter. $ThM\alpha$, $UM\beta$, $PbM\alpha$ ($PbM\beta$) and $YL\alpha$ lines were measured simultaneously with PET crystals and sealed Xe X-ray detectors. $CaK\alpha$, $SK\alpha$, $PK\alpha$. $SiK\alpha$, $KK\alpha$, ($ZrL\alpha$) and $NbL\beta1$ lines were also measured. For the analyses of Th, U, Pb and Y, X-ray intensity was integrated over 400s period for the line peak position and over 200s period for two optimum background positions. To ensure that possible changes of the sample surface had only a minimal effect on the results, we repeated measurement of peak and background positions five times for each analysis. For the analyses of other elements, X-ray intensities were integrated over 40s on each line peak position and 20s on two background positions. The background value for each line was estimated by linear interpolation of two readings, because WD step spectra examined prior to spot analyses suggests few discrepancies between linear and exponential fits. The standards were euxenite provided by Smellie et al. (1978) for Th, U and Nb, synthesized glass provided by Suzuki and Adachi (1998) for Pb, Si and Ca, synthesized Y-glass (Y_2O_3= 10 wt% and K_2O= 2 wt%) for Y and K, barite for S, zircon for Zr, and xenotime for P. Standards for rare earth element, when analyzed, are synthesized glass provided by Drake and Weill (1972). A high Th monazite with little U and a high U xenotime with little Th are used to determine the X-ray interference correction factors. The correction factors for Nb and Y interferences were estimated by using inhomogeneous columbite (Nb_2O_5= 31-36 wt%) and the synthesized Y-glass, respectively. The X-ray intensity data were converted into concentrations by the Bence and Albee's method using analyses of natural minerals as the matrix composition. The small difference in the matrix between analyzed and reference minerals has little effect on the ThO_2, UO_2 and PbO determinations. The detection limits at a 2σ confidence level are 0.009, 0.011 and 0.006 wt. % for ThO_2, UO_2 and PbO, respectively. Relative errors are about 10% for 0.03 wt.% PbO, 2% for 0.6 wt.% UO_2 and 0.5% for 7.0 wt.% ThO_2. The construction of "pseudo-isochron", coupled with discrimination of possibly concordant age data by chemical criteria like S content (<0.005 wt.%) and (Ca+Si)/(Th+U+Pb) ratio (0.95-1.05) for monazite and Ca and S contents (< 0.01 and 0.005 wt. %, respectively) for zircon, has the potential advantage of significant precision, and the ability to work with minerals having substantial initial Pb, and can identify two or more homogeneous domains that are separated by an age gap smaller than the error on individual spot analyses of age.

Many features that are insignificant in major element analysis can have major manifestation in

acquired trace elements. Critical comments include the roles of collimator slit, detector gas, accelerating voltage, probe current, X-ray interferences and count-rate in affecting the accuracy, and a way to access the Th and U interference correction without pure Th- and U-oxides or synthesized pure $ThSiO_4$. The $PbM\alpha$ line as measured on the JCXA-733 is approximately 25 % intense than the $PbM\beta$ line. Further the $PbM\beta$ line has a demerit in evaluation of background because the high-energy side of the $PbM\beta$ peak is occupied by a series of ThM-, UM- and PbM-lines. The $PbM\alpha$ line is preferable for the Pb determination of monazite and zircon. The interferences are corrected by:

$$I_{PbM\alpha}(net) = I_{PbM\alpha}(obs) - I_{NbL\alpha}(obs) \times f_{NbL\beta} - I_{YL\alpha}(obs) \times f_{YL\gamma} - I_{ThM\alpha}(obs) \times f_{ThM\zeta}$$

where $f_{NbL\beta}, f_{YL\gamma}$ and $f_{ThM\zeta}$ are the correction factor and are defined as:

$f_{NbL\beta} = $ I(obs) at $PbM\alpha$ detected position / $I_{NbL\alpha}$(obs)   (in columbite)

$f_{YL\gamma} = $ I(obs) at $PbM\alpha$ detected position / $I_{YL\alpha}$(obs)   (in synthesized Y-bearing glass)

$f_{ThM\zeta} = \{I_{PbM\alpha}$(obs, mz-std) $- (I_{PbM\beta}$(obs, mz- std) $\times I_{PbM\alpha}$ (obs, Pb-std)/$I_{PbM\beta}$(obs,Pb- std))/ $I_{ThM\alpha}$(obs, mz-std)

(in a high Th and low U monazite standard and in a U- and Th-free Pb-standard)

Because $YL\gamma$ interference with $PbM\alpha$ is severe for xenotime and polycrase, the $PbM\beta$ line was used for Pb determination in these minerals. The $NbL\gamma$ and $UM\zeta2$ interferences on the $PbM\beta$ line are corrected by,

$$I_{PbM\beta}(net) = I_{PbM\beta}(obs) - I_{NbL\alpha}(obs) \times f_{NbL\gamma} - I_{UM\alpha}(obs) \times f_{UM\zeta}$$

where $f_{NbL\gamma}$ and $f_{UM\zeta}$ are the correction factor and are defined as:

$f_{NbL\zeta} = $ I(obs) at $PbM\beta$ detected position / $I_{NbL\alpha}$(obs)   (in columbite)

$f_{UM\zeta} = \{ I_{PbM\alpha}$(obs, xe-std) $- (I_{PbM\beta}$(obs, xe-std) $\times I_{PbM\alpha}$ (obs, Pb-std)/$I_{PbM\beta}$(obs, Pb-std)$\}/$ $I_{UM\alpha}$(obs, xe-std)

(in a high U and low Th xenotime standard and in a U- and Th-free Pb-standard)

The age-mapping procedure for young monazite and zircon includes acquirering $PbM\alpha$ (or $PbM\beta$) intensity of individual pixels with multiple spectrometers, correcting background with background map computed from a measured background intensity through the intensity relationships determined in advance of the measurement, calibrating of intensity with standard and calculating of ages from the Th, U and Pb concentrations. This technique provides age maps showing difference in age domains on the order of 20 Ma with in monazite as young as 100 Ma. Consideration of sample damage by irradiation of intense probe was briefly shown.

Rerefences

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