

## Research Advances

## Advance in Matrix Effect Study of LA-MC-ICPMS U-Pb Dating on U-Bearing Oxide Minerals

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### Objective

With the development of analytic technologies, in-situ dating on U-bearing oxide minerals (e.g., cassiterite, rutile and baddeleyite) has been widely used in geological chronological researches and has attracted remarkable attention to explore evolution of the earth and obtain age information of various geological processes. Matrix effect related studies are especially important during in-situ U-Pb dating based on Laser Ablation Multiple Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICPMS). However, to our knowledge, only few thorough and systematical matrix effect study of U-bearing oxide minerals has been reported. In this study, we systematically analyzed the matrix effect of U-bearing oxide minerals in order to take place the standards which are difficult to prepare with available standards.

### Methods

U-Pb dating of U-bearing oxide minerals was carried out using a LA-MC-ICPMS system in the Isotopic Laboratory of Tianjin Geological Survey Center. The system consists of a Neptune MC-ICPMS coupled with a 193 nm excimer laser. U-Pb age data were collected by ablating U-bearing oxide minerals with laser beam diameters of 75  $\mu\text{m}$  and repetition rate of 11 Hz. The data was preprocessed with reasonable common Pb correction without element fractionation correction for studying the matrix effects of various minerals. All data were processed by ICPMSDataCal software and Isoplot program. In order to estimate the matrix effects in different kinds of standard substances, Matrix normalization factor  $F_{\text{AVG}}$  was defined as bellow:

$$F_{\text{AVG}} = \frac{{}^{206}\text{Pb}/{}^{238}\text{U}_{\text{known}}}{{}^{206}\text{Pb}/{}^{238}\text{U}_{\text{measured}}}$$

In the equation above,  ${}^{206}\text{Pb}/{}^{238}\text{U}_{\text{known}}$  represents the high resolution isotopic dating results obtained by Isotope Dilution Thermal Ionization Mass Spectrometer (ID-TIMS), and  ${}^{206}\text{Pb}/{}^{238}\text{U}_{\text{measured}}$  represents the results

obtained by LA-MC-ICPMS.

### Results

Cassiterite (AY-4), rutile (12DX01-2) and baddeleyite (Phalaborwa) with known ages were measured by U-Pb dating, and the results were shown in Appendix 1. The  ${}^{206}\text{Pb}/{}^{238}\text{U}$  isochron age by LA-MC-ICPMS for cassiterite (AY-4) was  $146 \pm 2$  Ma (MSWD=0.12,  $n=20$ ). Yuan et al. (2011) acquired the weighted mean  ${}^{206}\text{Pb}/{}^{238}\text{U}$  age by ID-TIMS for cassiterite (AY-4) was  $158.2 \pm 0.4$  Ma (MSWD=0.0882,  $n=3$ ), so the matrix normalization factor  $F_{\text{AVG}}$  was 1.08. The weighted mean  ${}^{206}\text{Pb}/{}^{238}\text{U}$  age by LA-MC-ICPMS for rutile (12DX01-2) was  $1647 \pm 23$  Ma (MSWD=5.3,  $n=13$ ). Zhou Hongying et al. (2013) acquired the weighted mean  ${}^{206}\text{Pb}/{}^{238}\text{U}$  age by ID-TIMS for rutile (12DX01-2) was  $1780 \pm 15$  Ma (MSWD=16,  $n=6$ ), and therefore the matrix normalization factor  $F_{\text{AVG}}$  was 1.08. The weighted mean  ${}^{206}\text{Pb}/{}^{238}\text{U}$  age by LA-MC-ICPMS for baddeleyite (Phalaborwa) was between 1941 and 2212 Ma, and the weighted mean  ${}^{206}\text{Pb}/{}^{238}\text{U}$  age by ID-TIMS was  $2057 \pm 2$  Ma (MSWD=9.9,  $n=59$ ) (Heaman, 2009); the matrix normalization factor  $F_{\text{AVG}}$  was 1.06–0.93. Distribution of the matrix normalization factors of cassiterite (AY-4), rutile (12DX01-2) and baddeleyite (Phalaborwa) was shown in Fig. 1.  $F_{\text{AVGS}}$  of cassiterite (AY-4) and rutile (12DX01-2) were all above 1.0. However, some of  $F_{\text{AVGS}}$  of baddeleyite (Phalaborwa) are below 1.0 which has shown no obvious correlation with that of cassiterite (AY-4) and rutile (12DX01-2). In addition, we determined the cassiterite sample DXH.1 which took cassiterite AY-4 and rutile R10 as external standards by LA-MC-ICPMS U-Pb dating, acquired concordant ages of  $431 \pm 4$  Ma (MSWD=2.0,  $n=48$ ) and  $426 \pm 10$  Ma (MSWD=1.4,  $n=50$ ), respectively. They are identical within a reasonable error range. We also determined the rutile sample 13DB05 which took rutile R10 and cassiterite AY-4 as external standards by LA-MC-ICPMS U-Pb dating, acquired concordant ages of  $208 \pm 2$  Ma (MSWD=3.9,  $n=32$ ) and  $208 \pm 2$  Ma (MSWD=4.0,  $n=39$ ), respectively. They are identical within a reasonable

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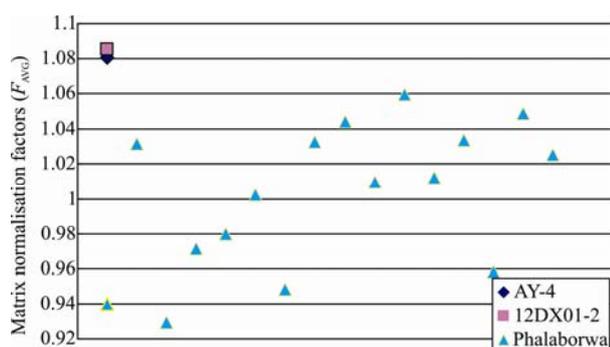


Fig. 1. Distribution of the matrix normalization factors of cassiterite (AY-4), rutile (12DX01-2) and baddeleyite (Phalaborwa).

error range, too. In summary, these phenomena indicate that cassiterite and rutile can replace each other in the dating of cassiterite sample DXH.1 and rutile sample 13DB05, while, whether they can replace each other in a wide range still need a further insight study.

## Conclusions

Our results indicate that  $^{206}\text{Pb}/^{238}\text{U}$  ages obtained by fractional distillation correction based on different mineral standards have shown differences. Thus, matrix effect in different U-bearing oxide minerals indeed exists. However,

family minerals rutile and cassiterite with similar crystal structure but different chemical element have not shown apparent matrix effect. To reveal the influence of matrix effect further, ID-TIMS U-Pb dating for U-bearing oxide minerals is thus necessary in the future.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (grants No. 41503052 and 41373053) and the National Science and Technology Infrastructure (grant No. DDK14-39).

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## Appendix 1 $^{206}\text{Pb}/^{238}\text{U}$ ages of cassiterite (AY-4), rutile (12DX01-2) and baddeleyite (Phalaborwa)

Sample	U (ppm)	Pb (ppm)	$^{206}\text{Pb}/^{238}\text{U}$ age (Ma)	Methods	Literature sources
AY-4	30–33	1.4–3.6	158.2±0.4	ID-TIMS	Yuan et al., 2011
			146±2	LA-MC-ICPMS	This work
12DX01-2	3.0–5.3	1.0–1.1	1780±15	ID-TIMS	Zhou Hongying et al., 2013
			1647±23	LA-MC-ICPMS	This work
Phalaborwa	51–2124	19–782	2057±2	ID-TIMS	Heaman, 2009
			1941–2212	LA-MC-ICPMS	This work