Capability of Cameca SXFive Field Emission EPMA in Acquiring High-precision and High-accuracy Minor and Trace Elemental Data at High Spatial Resolution

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1. Introduction

With increasing attention being paid to micro-scale geochemical information, *in-situ* analytical techniques including EPMA, LA-ICP-MS and SIMS are being further developed. The detailed geochemical information within complexly zoned grains can reveal fine-scale mineral growth details and provide insights into tectonic evolution. However, due to the generally large beam size (i.e., 10-60μm) of SIMS and LA-ICP-MS, such techniques are not optimal to use when thin rims or tiny zones (<5μm) are present (**Fig.1**). EPMA, with its exceptional high resolution down to sub-micron scale, makes it possible to accurately analyze these tiny zones. Our study goals are to (1) develop protocols for high-precision, high-accuracy minor and trace element analyses under high spatial resolution, using the recently installed Cameca SXFive field emission (FE) EPMA at University of Florida, and to (2) make applications to metamorphic and magmatic systems so as to address various geologic problems.

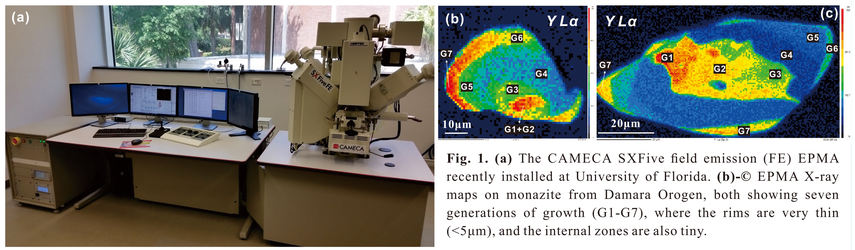


Fig. 1. (a) The CAMECA SXFive field emission (FE) EPMA recently installed at University of Florida. **(b)-(c)** EPMA X-ray maps on monazite from Damara Orogen, both showing seven generations of growth (G1-G7), where the rims are very thin (<5μm), and the internal zones are also tiny.

2. Exploring the preicision and spatial resolution

Monazite U-Th-Pb and zircon/quartz Ti major, minor and trace elements were analyzed to explore the precision (detection limits) and spatial resolution under different parameters (**Figs. 2-3**). Results indicate that beam size does not affect the precision of data. The detection limits of Th, U, Pb and Ti have been reduced to ~90 ppm, ~50 ppm and ~35 ppm and 6 ppm, respectively. Regarding the spatial resolution, under 200nA, 15kV and 480s peak counting, an 1μm dimension interactive volume is generated, such spatial resolution is sufficiently high to analyze tiny zones (<5μm). Lower detection limits and higher spatial resolution can be achieved if lower backgrounds are attained and lower accelerating voltage is applied (the FE source allows high beam intensity while at lower voltage).

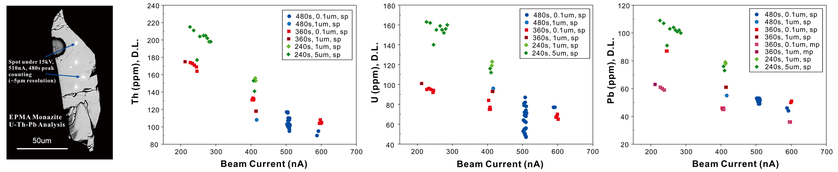


Fig. 2. The detection limits and spatial resolution of Th, U and Pb analyses in monazite using different EPMA parameters. These parameters include the beam current (nA), peak counting time (s), beam size (μm), and selection of one single spectrometer or multiple spectrometers integration. "480s, 0.1μm, sp" means peak counting time at 480s (plus 240s*2 on backgrounds), beam size at 0.1μm (a focused beam, at 100nm), and single spectrometer; "mp" means multiple spectrometers (SP2+SP4) simultaneously collecting Pb peaks.

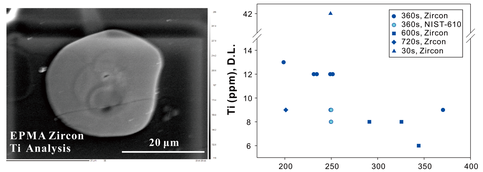


Fig. 3. The detection limits of Ti in zircon and NIST-610 with different parameters. All the Ti analyses were done using "multiple spectrometer" (SP1+SP2+SP4).

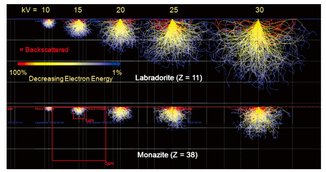


Fig. 4. Spatial resolution in monazite and labradorite, illustrating the Montel Carlo simulation of electron scattering as a function of beam voltage. Figure credit: *Jercinovic et al. (2012)*

3. Exploring the accuracy

In order to evaluate the accuracy of the EPMA data, standards like Moacyr monazite, FC-1 zircon, Sri Lanka zircon gemstones, and NIST-610 were tested. In terms of major element component (Th), the accuracy is good, but for those minor and trace elements (i.e., U, Pb and Ti), their contents are underestimated or overestimated (**Figs. 5-6**). These problems can be solved by improving the accuracy for background acquisition (see section 4).

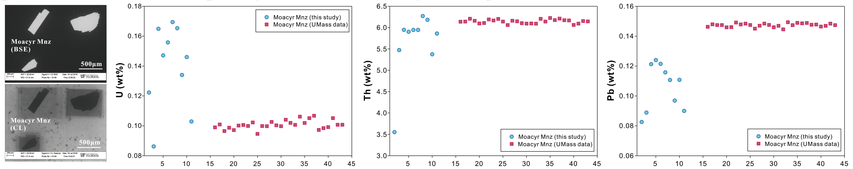


Fig. 5. Evaluation on the accuracy of U, Th, Pb analyses in Moacyr monazite standard. Note that all three Moacyr monazite grains are relatively homogeneous (BSE & CL). The U content was overestimated, whereas the Pb concentration was underestimated. Th content is generally consistent to the UMass data.

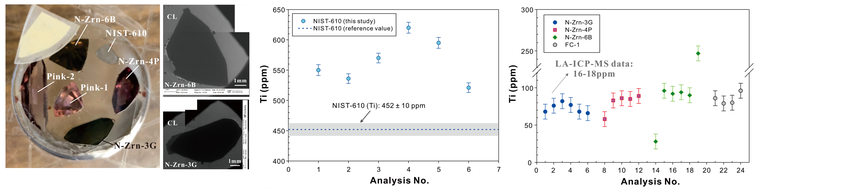


Fig. 6. Evaluation on the accuracy of Ti analyses in NIST-610 glass and FC-1 zircon standards, and a test for the homogeneity of Sri Lanka zircon gemstones (N-Zrn). The obtained Ti contents for NIST-610 and N-Zrn-3G are systematically higher. Among the zircon gemstones, N-Zrn-3G and N-Zrn-4P show some degrees of homogeneity in terms of Ti concentrations.

4. Data accuracy improvements

In order to improve the monazite U-Th-Pb data accuracy, we repolished the sample and did a plasma cleaning before the experiment, performed detailed WDS step scans (cf. Jercinovic and Williams, 2005), applied the exponential regression background method during the data acquisition, and also completed the post-analyis background modeling (**Figs. 7-8**) to correct the Quanti data by applying the Savitsky-Golay (S-G) filtered background models. The data accuracy have been significantly improved (**Figs. 9-10**) following the aforementioned procedures.

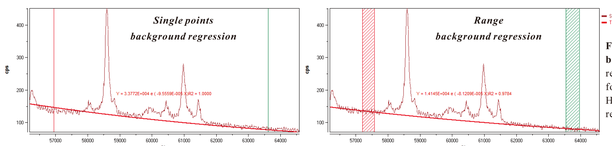


Fig. 7. A comparison of "single spots" and "range" background regression. Note that the "single spots" regression could generate notable changes in models for just a slight shift of the background offsets. However, the "range" regression would allow more reliable and consistent models.

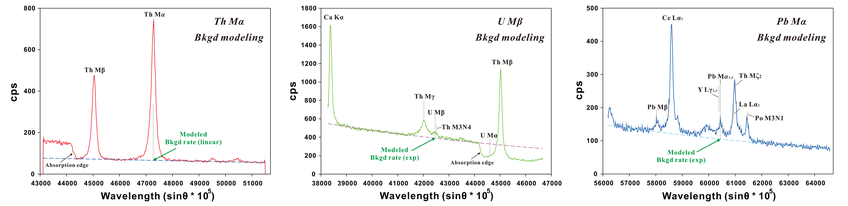


Fig. 8. The U, Th and Pb "range" background modeling on S-G filtered detailed WDS step scans. Note that the models presented are selected as they can best fit the continuum spectrum. The modeled intensity (cps) at the peak position is considered as the background rate and is applied to the Quanti data for correction. Also note that there are existing interfering peaks surrounding Pb Mα and U Mβ, such as Y $L\gamma_{2,3}$ and Th Mζ$_2$, interferences on Pb Mα, and Th Mγ and Th M3N4 on U Mβ

5. Further improvements

Despite the improvements of data accuracy, the Moacyr monazite U-Th-Pb ages are still statistically younger than reference values (475 ± 22 Ma vs. ~506 Ma) (**Figs. 9-10**). This can be explained by the complex age calculation process that even 10s of ppm changes of Pb and/or U can contribute to 10s of Ma age difference. Considering the surrounding peak interferences on Pb Mα and U Mβ (**Fig. 8**), further improvements can be done by performing detailed interferences corrections on these X-ray lines.

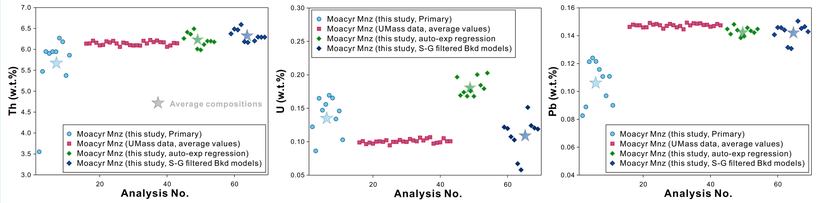


Fig. 9. The accuracy improvements of monazite U-Th-Pb analyses using detailed WDS scan, S-G filtering and exponential background modeling. The data accuracy has been stably improved. Note that the UMass data are the daily average values; the star marks also indicate the average values for our three comparative experiments.

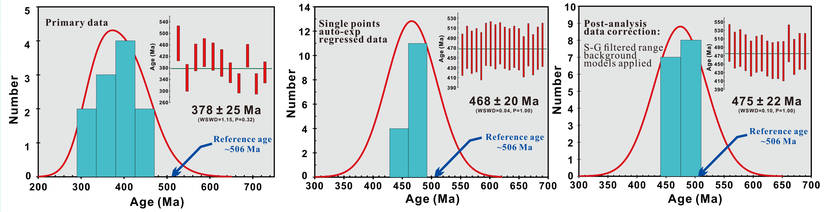


Fig. 10. The calculated weighted mean apparent monazite U-Th-Pb ages and age probability distribution curves.

Apart from interference corrections, a complete analysis of all the major, minor and trace elements in monazite will be done to allow matrix correction by using the built-in *"Matrix Definition and Stoichiometry"* analysis mode in the EPMA software. Furthermore, primary standards for monazite U-Th-Pb analyses need to be updated due to their uneven surface and compositional heterogeneity (**Fig. 11**). By completing all these steps, the Cameca SXFive FE EPMA is very promising to obtain both precise and accurate EPMA data while under high spatial resolution.

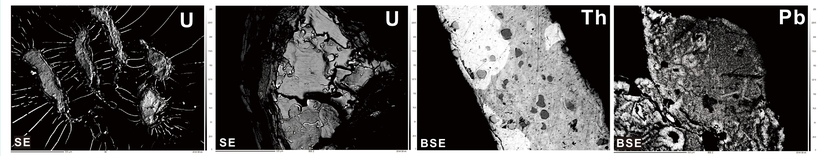
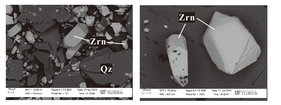


Fig. 11. The uneven surface and compositional heterogeneity of the primary U, Th and Pb standards for monazite EPMA analysis. Note that the U standards show obvious decay traces (U decayed to Pb, leading impure U standards?), and exhibit uneven surface; the Th standard shows obvious mineral inclusions and reveal heterogeneous BSE compositions. Pb standard also shows some degrees of BSE heterogeneity.

References

1. MJ Jercinovic et al., IOP Conference Series: Materials Science and Engineering 32 (2012), p. 1–22.
2. MJ Jercinovic and ML Williams, American Mineralogists 90 (4) (2005), p. 526-546.



Synthetic Ti-free zircons and quartz for EPMA Ti analysis. May be a good "blank" test for Ti!

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