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Research Advances

Types and Correction Methods of Matrix Effect during Zircon LA-ICP-MS U-Pb Dating

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Matrix effect primarily impacts the accuracy and precision of zircon LA-ICP-MS U-Pb data. This paper describes three types of matrix effect in zircon LA-ICP-MS U-Pb dating, i.e., the element matrix effect, high D_{dpa} or uranium matrix effect and alpha dose matrix effect, and illustrates the correction of these three effects. In addition, we point out the limitation and possible problems of the existing correction methods.

The element matrix effect shows a positive linear correlation between some trace elements and $^{206}Pb/^{238}U$ age offset (the difference between LA-ICP-MS $^{206}Pb/^{238}U$ age and TIMS $^{206}Pb/^{238}U$ "true" age), and this effect is likely to relate with the size distribution of aerosol and plasma conditions or the lattice strain induced by xenotime coupled substitution. There is a quantitative correction formulae established by formers for the element (REE+P, etc.) matrix effect: $^{206}Pb/^{238}U_{corrected\ age}$= ($^{206}Pb/^{238}U_{measured\ age}$)×(1-$C$/100), where C=[1.17±0.58]×[μg/g Nd]-[3.8±1.8]-[% Offset]. However, It is worth questioning this formulae for the very small age spread (<3Ma) of young standard zircons (Age<1.0Ga) and the narrow range of trace element contents (P, Sm, Nd, etc). Also, it needs efforts to testify the existence of the element (Ca, Al, Fe, Mg) matrix effect which is a deduction based on other studies; more experimental data are needed to support it.

The alpha dose matrix effect exhibits a log-linear relationship between alpha dose and $^{206}Pb/^{238}U$ age offset, which arises from the alpha dose difference between standard and unknown zircons. Previous workers have established the correlation equation as: $y=407.89e^{0.8461x}$, where y is alpha dose and x is $^{206}Pb/^{238}U$ age offset. Alpha dose (D_a) is defined as the total number of alpha decays the zircon has undergone per gram since crystallization, and is calculated by formula as follows: $D_\alpha=8\times N_{238}[\exp(t/\tau_{238)}-1]+7\times N_{235}[\exp(t/\tau_{235)}-1]+6\times N_{232}[\exp(t/\tau_{232)}-1]$, where N_{238}, N_{235}, and N_{232} are the measured numbers of atoms/g of ^{238}U, ^{235}U and ^{232}Th, respectively; τ_{238}, τ_{235}, and τ_{232} are their respective half-lives; t is the geological age. The theoretical D_a represents the highest degree of radiation damage, and is commonly not identical with the actual alpha dose. This is because the crystal structure of zircon can be restored and the radiation damage will not be recorded or even erased when the environment temperature is higher than the self-annealing temperature (250±50℃). It is difficult to confirm whether zircons have suffered self-annealing incidents and how much radiation damage has been restored. As a result, we can not obtain the exact D_a of the zircons. Hence, the correlation equation is incapable of correcting the alpha dose matrix effect. Alternatively, it seems that we may estimate the actual alpha dose of zircon using the empirical equation between the preserved alpha dose and the full width at half-maximum (FWHM) of the B_{1g} Raman band at about 1008 cm^{-1}: FWHM (cm^{-1})≈1.2+1400×D_α(10^{15}/mg). Nevertheless, it has been proved to be a very limited usable range (FWHM lower than10cm^{-1} and D_α lower than 2×10^{15} /mg). Comparing with the methods above, restoring the zircon structure by annealing experiments before dating can eliminate the alpha-dose-induced differences between the standard and unknown zircons, which is expected to be an effective way to avoid the alpha dose matrix effect. Pretreatment of zircons by thermal annealing has been proved to yield more accurate age with noteworthy less dispersion.

The high D_{dpa} matrix effect was initially defined as a high uranium matrix effect, which shows a strongly positive correlation between the uranium and SIMS $^{206}Pb/^{238}U$ age when uranium concentrations in zircon are higher than the threshold value. It is frequently mentioned by *in-situ* U-Pb micro analysis, but no common belief has been reached on the threshold value of this matrix effect. As the radiation damage accumulated over time, the threshold value is dependent on the zircon age. It is therefore not appropriate to judge this effect on zircons of different ages using the same uranium concentrations. Actually, it is essential to use the degree of radiation damage (like D_{dpa}) instead of uranium concentrations to describe this matrix effect. The screening criteria (D_{dpa}<0.08) is a robust discriminant proposed by formers for reliable U-Pb dating. D_{dpa} is the radiation dose in dpa

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and is a function of alpha dose. We can use the following formula to quantitatively estimate the amount of radiation damage: $D_{dpa} \approx 9.40 \times 10^5 \times D_\alpha \times M/(N_A \times 6)$, where N_A is Avogadro's number, M is the molecular weight of zircon, and D_α is the radiation dose in unit of α-decays/mg. Similarly, it is the theoretical D_{dpa} calculated by the formula that ignores the self-annealing effect on D_α. Consequently, the screening criteria ($D_{dpa}<0.08$) may mistakenly get rid of the zircons with actual $D_{dpa}<0.08<$theoretical D_{dpa}, thereby losing the age message and geological meanings of these zircons. Additionally, this D_{dpa} screening criteria is incapable of lowering the labor and cost of dating experiments, and may filter the Pb/U data after dating, resulting in lack of predictability.

Both the high D_{dpa} matrix effect and alpha dose matrix effect are essentially related with the radiation damage induced physical difference between standard and unknown zircons, which lead to the system error (i.e. $^{206}Pb/^{238}U$ age offset, even $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ age offset) resulted from the external standard correcting method. Therefore, thermal annealing is also supposed to be an effective way to eliminate the high D_{dpa} matrix effect.

What worth thinking are how to confirm the annealed zircons have completely restored their crystal structure, and whether the same annealing conditions (temperature, time, etc.) are suitable for all zircons?