

$^{206}\text{Pb}/^{238}\text{U}$ matrix induced bias in LA-ICP-MS: A multivariate study

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Many studies acknowledge the occurrence of systematic discrepancies between the $^{206}\text{Pb}/^{238}\text{U}$ ratios measured by LA-ICP-MS and TIMS across different reference materials (e.g. [1, 2]). In order to investigate these effects further high-precision morphology and volume determinations of laser ablation pits, obtained in several zircon materials under varying ablation conditions, have been achieved by confocal laser scanning microscopy (CLSM 700, Carl Zeiss). These provide detailed information on subtle differences in ablation behaviour between different zircon matrices. We demonstrate that small but significant differences in pit dimensions and laser penetration rates exist between zircons. Subsequent evaluation of the $^{206}\text{Pb}/^{238}\text{U}$ values reveals an association between ablation behaviour and deviations in the $^{206}\text{Pb}/^{238}\text{U}$ downhole fractionation patterns observed during ablation - a finding that has major ramifications for studies of U-Pb geochronology employing laser ablation.

The differences in ablation behaviour between zircons, however, cannot be ascribed to a single variable. Based on our initial observations the measured laser penetration rates may also be partially dependent on the crystallographic orientation of the crystals. Multivariate analysis of all possible parameters involved in the ablation process (zircon chemistry, crystallographic orientation, accumulated radiation damage, topographical and morphological data, and ablation cell spatial variations) will be used to identify the most important causes of these artifacts, and thus hopefully provide a means of correcting the results. Our ultimate goal is to offer researchers a method for producing high-accuracy U-Pb ratio measurements by LA-ICP-MS.

[1] Klötzi *et al.* (2009) *Geostand. Geoanal. Res.* 33, 5-15. [2] Allen & Campbell (2012) *Chem. Geol.* 332-333, 157-165.

Fe, S isotope systematics of the 3.24 Ga old Mendon-Mapepe Formations, Kaapvaal Craton, South Africa

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Variations of Fe and S isotope compositions of sedimentary pyrites have placed important constraints on the chemistry and redox evolution of the Earth's ocean and atmosphere over geological time. In order to better constrain the paleo-environmental conditions and potential biological role on these pyrite formations, we developed coupled Fe and S isotope and trace element compositions analyses in 28 samples from the Barberton Barite Drilling Project (BBDP). The BBDP intercepted the transition from deep-water black cherts and komatiitic basalts of the Mendon Formation to shallow-water sulfate deposits and terrigenous and volcanoclastic sediments of the 3.24 Ga old Mapepe Formation. In situ Fe and S isotope compositions of pyrite were measured with ims 1280 HR2 at CRPG, with a reproducibility better than 0.2 ‰ (2σ) in both $\delta^{56}\text{Fe}$ and $\delta^{34}\text{S}$. Iron and S isotopes of bulk-rocks were analysed at IPGP, with a reproducibility better than 0.1 ‰ (2σ) in $\delta^{56}\text{Fe}$, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$.

In situ and bulk-rock analyses reveal a large range of variation from -4.3 ‰ to +3.2‰ for $\delta^{56}\text{Fe}$, from -6.6 ‰ to +3.5 ‰ for $\delta^{34}\text{S}$ and from -3.5‰ to 1.8‰ for $\Delta^{33}\text{S}$. Although mean in situ pyrite Fe and S isotope compositions are generally well correlated with bulk-rock values, there are some offset depending on the presence of other Fe and S mineralogical phases (sulfates, carbonates, clays). This is well illustrated by co-variations between Fe and S isotope compositions with some major and trace elements (SiO₂, Al, U...). Pyrites of all samples show a clear correlation between in situ $\delta^{56}\text{Fe}$ and $\Delta^{33}\text{S}$ values. Pyrite from sedimentary rocks display a rough trend between negative $\delta^{56}\text{Fe}$ and $\Delta^{33}\text{S}$ values and positive $\delta^{56}\text{Fe}$ and $\Delta^{33}\text{S}$ values (mostly in BIFs). These large Fe and S isotope variations may reflect a mixing between different sources and record pyrite formation pathways. Coupled S and Fe isotope composition at μm-scale provides new insights into the origin of isotope variations in Archaean pyrites and its link to ocean chemistry.