Matrix-independent baddeleyite U/Pb geochronology by femtosecond-LA-ICP-MS?

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Baddeleyite is a key mineral in geochronology because it crystallizes in silica-undersaturated systems that do not grow any zircon. It has been shown that nanosecond (ns-)LA-ICP-MS U/Pb analysis requires matrix-matched calibration due to significantly stronger element downhole fractionation in baddeleyite compared to e.g. zircon. Using zircon as external standard for downhole fractionation correction produces reverse discordant results with low precision intercept ages (≥5%).

In contrast it has been shown that femtosecond (fs-)LA-ICP-MS can produce accurate and precise data for a variety of difficult matrices that require matrix-matching with ns-LA-ICP-MS. Here we compare U/Pb data obtained from ns-LA-ICP-MS (NWR 193 nm excimer LA coupled to a Thermo XSeries 2 quadrupole MS) with fs-LA-ICP-MS (196 nm femtosecond LA coupled to an iCAP-Qc quadrupole MS). We conducted spot as well as raster analyses with both systems applying NIST 610, Plesovice zircon, Duluth zircon and Duluth baddeleyite as reference materials, and the well-characterized Phalaborwa baddeleyite as unknown sample. If the cause for reverse discordance is only downhole isotopic fractionation, then raster analyses should remedy this even with ns-LA-ICP-MS.

Our results show that in contrast to previous observations, fs U/Pb of baddeleyite needs matrix matching to achieve concordant ages. Element fractionation occurs in both fs- and ns-LA-ICP-MS and needs to be corrected by application of baddeleyite as reference material. Although raster analyses are not affected by downhole fractionation, other fractionation processes occur, leading to discordant or in the worst case miscalculated concordia results. This fractionation process might be related to ablation of material deposited from earlier ablation along the raster. As shown in previous studies this ablated material can undergo fractionation during condensation and therefore influence the isotopic composition of the baddeleyite or zircon material ablated later.