Re-evaluating the $^{238}U/^{235}U$ ratio of zircon and accessory minerals

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U-Pb geochronology requires knowledge of an accurate and precise $^{238}U/^{235}U$ ratio of any mineral being dated by this method. The only previous systematic study of zircon by [1] recommended a value of 137.818 ± 0.045 (2SD) for U-Pb geochronology of zircon despite several zircon analyses with U isotopic compositions outside this uncertainty. To re-evaluate the range of U isotopic compositions in zircon, we analysed 28 bulk zircon samples from rocks with a wide range of ages (from 13 to 3465 Ma) and geographical distributions using refined analytical methods. We find true variation between different zircon populations and determine an average $^{238}U/^{235}U$ ratio of 137.816 ± 0.033 (normalized to CRM-145 ratio of 137.829 ± 0.022 [1]) with the uncertainty including the full range of the 28 zircon samples analysed and the uncertainty on CRM-145. This value is indistinguishable from that of [1] but with a full range approximately 30% smaller than their calculated two standard deviation uncertainty around the average of their main cluster and with no outliers. This result suggests that the uncertainty proposed by [1] is an acceptable, if not, conservative estimate that can be added in quadrature to other sources of error. We also find variability in the $^{238}U/^{235}U$ ratio of coexisting phases within single samples of up to 2.9 ε-units (parts per 10,000). In addition, the average U isotopic composition of zircon is heavier than that reported for bulk continental crust in general and most granitoid intrusive rocks specifically [2]. We attribute this and the existence of an offset of zircon relative to cogenetic phases to different coordination environments of U in minerals relative to their source magmas (e.g. [3]) and predict that other phases not yet analysed must host isotopically lighter U to ensure mass balance in single samples. Finally, the existing zircon data appears to define a trend towards greater diversity in the U isotope composition with time (mainly expanding the range to lighter isotopic signatures), starting with a value that is approximately 4 ε-units heavier than the bulk Solar System initial [4]. If correct, this trend may reflect increasing diversity of U reservoirs through time, possibly driven by progressive sequestration of isotopically heavy U in Earth's crust through time.

[1] Hiess J., *et. al.* (2012) *Science* 335, 1610. [2] Tissot F. L. H. and Dauphas N. (2015) *Geochim. Cosmochim. Acta* 167, 113. [3] Tissot F.L. *et. al.* (2017) *Geochim. Cosmochim. Acta* 213, 593. [4] Connelly *et. al.* (2012) *Science* 338, 651.