

Quantification of excess ^{231}Pa in late Quaternary igneous baddeleyite

YI SUN^{1,*}, AXEL K. SCHMITT¹, LUCIA PAPPALARDO², AND MASSIMO RUSSO²

¹Institute of Earth Sciences, Heidelberg University, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany
²Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, via Diocleziano 328, 80124 Naples, Italy

ABSTRACT

Initial excess protactinium (^{231}Pa) is a frequently suspected source of discordance in baddeleyite (ZrO_2) geochronology, which limits accurate U/Pb dating, but such excesses have never been directly demonstrated. In this study, Pa incorporation in late Holocene baddeleyite from Somma-Vesuvius (Campanian Volcanic Province, central Italy) and Laacher See (East Eifel Volcanic Field, western Germany) was quantified by U-Th-Pa measurements using a large-geometry ion microprobe. Baddeleyite crystals isolated from subvolcanic syenites have average U concentrations of ~200 ppm and are largely stoichiometric with minor abundances of Nb, Hf, Ti, and Fe up to a few weight percent. Measured $(^{231}\text{Pa})/(^{235}\text{U})$ activity ratios are significantly above the secular equilibrium value of unity and range from 3.4(8) to 14.9(2.6) in Vesuvius baddeleyite and from 3.6(9) to 8.9(1.4) in Laacher See baddeleyite (values within parentheses represent uncertainties in the last significant figures reported as 1σ throughout the text). Crystallization ages of 5.12(56) ka (Vesuvius; MSWD = 0.96, $n = 12$) and 15.6(2.0) ka (Laacher See; MSWD = 0.91, $n = 10$) were obtained from $(^{230}\text{Th})/(^{238}\text{U})$ disequilibria for the same crystals, which are close to the respective eruption ages. Applying a corresponding age correction indicates average initial $(^{231}\text{Pa})/(^{235}\text{U})_0$ of 8.8(1.0) (Vesuvius) and 7.9(5) (Laacher See). For reasonable melt activities, model baddeleyite-melt distribution coefficients of $D_{\text{Pa}}/D_{\text{U}} = 5.8(2)$ and 4.1(2) are obtained for Vesuvius and Laacher See, respectively. Speciation-dependent (Pa^{4+} vs. Pa^{5+}) partitioning coefficients (D values) from crystal lattice strain models for tetra- and pentavalent proxy ions significantly exceed $D_{\text{Pa}}/D_{\text{U}}$ inferred from direct analysis of ^{231}Pa for Pa^{5+} . This is consistent with predominantly reduced Pa^{4+} in the melt, for which D values similar to U^{4+} are expected. Contrary to common assumptions, baddeleyite-crystallizing melts from Vesuvius and Laacher See appear to be dominated by Pa^{4+} rather than Pa^{5+} . An initial disequilibrium correction for baddeleyite geochronology using $D_{\text{Pa}}/D_{\text{U}} = 5 \pm 1$ is recommended for oxidized phonolitic melt compositions.

Keywords: Baddeleyite, accessory mineral, Uranium series, protactinium, geochronology, trace elements