Imprecisions and errors in ²²⁶Ra-²³⁰Th volcanic mineral ages from Ra-Ba partitioning difference estimates

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Mineral isochron dating using 226 Ra- 230 Th (t_{1/2}=1.6 ka) differs somewhat from more common isotope systems (e.g., ⁸⁷Rb-⁸⁷Sr) because there is no stable Ra isotope to normalize parent and daughter abundances (e.g., ⁸⁶Sr in the ⁸⁷Rb-⁸⁷Sr system). Many papers have thus advocated using the geochemically highly similar element Ba as an imperfect, yet plausible stable analogue for ²²⁶Ra-²³⁰Th isochron dating. Various other authors have taken a modified approach, whereby a non-unity solid-melt partition coefficient ratio, D_{Ra}/D_{Ba} , is used to estimate a mineral ²²⁶Ra/²³⁰Th initial ratio, the result generally portrayed as being always both more accurate and more precise (e.g., [1,2]) than age estimates made with the assumption that D_{Ra}=D_{Ba}. Such studies mostly apply a mineral-specific strain parameterization estimate of D_{Ra}/D_{Ba} [3], although recently a small experimental data set has also become available [2]. While we do not question the theoretical framework of D_{Ra}/D_{Ba} variations or the plausibility that some predictied or experimentally determined values can be usefully applied in some circumstances, we caution that in geochronologic applications, where the prediction of initial abundances is paramount for determining an accurate age, the $D_{Ba} \neq D_{Ba}$ model has significant limitations arising from, among other things, (1) the vagaries of natural minerals growing under magmatic conditions; (2) the small number of experiments; (3) incomplete strain parameterizations; (4) mineral impurity or inclusion estimates; and (5) age errors from D_{Ra}/D_{Ba} approximations, which tend to be grossly underestimated in the literature. Age estimates of minerals with $D_{Ra}/D_{Th} > 1$ (e.g., plagioclase) using $D_{Ra} \neq D_{Ba}$, must be viewed and used with extreme caution. However, D_{Ra}/D_{Ba} estimates have generally minor age effects on minerals where D_{Ra}/D_{Th} \ll 1 (such as magnetite and clinopyroxene [4,5]). Nevertheless, adhoc application of poorly constrained D_{Ra}/D_{Ba} in a mineral can lead to variably erroneous ages.

 Cooper et al. (2001) EPSL 184, 703-718. [2] Fabbrizio et al. (2009) EPSL, 280, 137-148. [3] Blundy & Wood (2003) Rev. Min. Geoch. 52, 59-123. [4] Zellmer et al. (2008) EPSL 269, 387-397. [5] Rubin & Zellmer (2009) EPSL., 281, 115-123.

The double spike toolbox

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The double spike technique is a well established method for correcting for instrumental mass fractionation in mass spectrometry [1]. The precision of the technique is controlled by the choices of double spike composition and the proportions in which the double spike and sample are mixed. To make these choices easier, we present a collection of MATLAB codes ("the double spike toolbox") for calculating optimal double spikes for any isotope system. Optimal double spikes are chosen purely on the basis of minimising error propagation on the isotope ratios of the samples, rather than by geometrical methods [2]. In addition, we have produced "cocktail lists" of optimal double spikes for all 33 elements that have 4 or more naturally occurring isotopes, using some sensible default parameters. As examples, we discuss the application of the software to Fe, Pb, and Ca isotopes. The software is freely available at www.johnrudge.com/ doublespike.

[1] Dodson (1963) *J. Sci. Instrum.* **40**, 289-295. [2] Galer (2007) *GCA* **71**, A303.