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Discussion

Reply to Comment on "On the recent bimodal magmatic processes and their rates in the Torfajökull–Veidivötn area, Iceland" by K.M. Cooper

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ABSTRACT

Cooper [Cooper, K.M., 2009. Comment on "On the recent bimodal magmatic processes and their rates in the Torfajökull–Veidivötn area, Iceland" by K.M. Cooper. Earth Planet. Sci. Lett.] argues that pre-eruptive crustal magma residence times of 1.4–3.2 ka determined from ^{226}Ra–^{230}Th disequilibrium in co-eruptive Icelandic rhyolites and basalts are erroneous in Zellmer et al. [Zellmer, G.F., Rubin, K.H., Grönvold, K., Jurado-Chichay, Z., 2008. On the recent bimodal magmatic processes and their rates in the Torfajökull–Veidivötn area, Iceland. Earth and Planetary Science Letters, 269: 388–398]. The core of Cooper's comment is that our not having applied model parameterizations that predict differences in mineral-melt partitioning of Ra (D_{Ra}) and Ba (D_{Ba}) introduce non-equilibrium conditions yielding inaccurate isochron ages. Yet the actual correction arising from the $D_{Ra} \neq D_{Ba}$ model is trivial relative to the $D_{Ra} = D_{Ba}$ model we employed for the two mineral phases upon which most of our age interpretations are based: magnetite (23 years) and clinopyroxene (2 years). Cooper's correction scheme might have a larger effect on our lone plagioclase separate were it possible to accurately predict what D_{Ra}/D_{Ba} to employ (correction with $D_{Ra}/D_{Ba} = 0.15$ proposed by Cooper [op. cit.], results in an impossible age). Yet even using an ad hoc $0.15 < D_{Ra}/D_{Ba} < 1$ that could generate an allowable age would still not change our interpretation of when mineral formation began in these magmas. ^{238}U, ^{232}Th and Ba abundances in our mineral separates are within the range of literature values for those phases. But Cooper [Ibid.] also argues that these phase separates are highly impure, using non-realistic Th, U and Ba distribution coefficients (particularly for rhyolite phases and basaltic titanomagnetites) to estimate equilibrium concentrations relative to their host magmas. The Cooper comment thus also faults us for not correcting our data for the perceived impurities, using the flawed assumption that generic, theoretical D_i values are apparently applicable to any magma composition. Such a correction also introduces ~10× greater uncertainty to age estimates (errors that are not adequately characterized in the comment or prior work using this correction scheme). Cooper subsequently asserts that our extremely well correlated data ($R^2 > 0.99$) on Ba-normalized ^{230}Th–^{226}Ra activity diagrams are mixing arrays without age significance, but this assertion is not supported by careful analysis of the data. Zellmer et al. [Ibid.] discussed the effects of potential impurities and disagree that they disallow or dominate age interpretations of our data. The significant problems associated with the $D_{Ra} \neq D_{Ba}$-and-phase-impurity correction scheme advocated by Cooper result in age estimates that are generally less precise and less accurate when compared to Ra–Th ages determined by the traditional ^{230}Th–^{226}Ra–Ba mineral isochron method, which generates superior results and should be incorporated into future studies, with consideration of $D_{Ra} \neq D_{Ba}$ when minerals are very young (generally <50–300 years, depending on the phase) or when $D_{Ra} >> D_{Th}$.

1. Introduction and background

Our recent study (Zellmer et al., 2008) of the conditions and timing of petrologic processes producing magmas for two historical Icelandic bimodal composition (rhyolite-basalt) eruptions included a component where the timescales of magma crustal residence times were evaluated with mineral-melt internal isochrons using the ^{238}U–^{230}Th and ^{230}Th–^{226}Ra systems. Isochron dating using the ^{226}Ra–^{230}Th system differs somewhat from more common isotope systems (e.g., ^{87}Rb–^{87}Sr, ^{238}U–^{206}Pb), because there is no stable Ra isotope to

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normalize the parent and daughter abundances (e.g., ^{86}Sr in the ^{87}Rb–^{87}Sr system and ^{204}Pb in the ^{238}U–^{206}Pb system). Many papers have thus advocated using the geochemically highly similar element Ba as an imperfect, yet plausible stable analogue for internal and external isochron dating with $^{226}Ra/^{230}Th$ (e.g., Williams et al., 1986; Rubin and Macdougall, 1990; Volpe and Hammond, 1991). Model ages of mineral/whole-rock assemblages are determined analogously to other mineral isochron applications (i.e., by best fit linear regression slope through data on an isochron diagram, where the goodness of fit defines the quality of the age result and indicates if a phase significantly pre- or post-dates the mean age). Notably, mixing of contemporaneous phases occurs along the isochron, so that phase purity affects data dispersion but not the age. Two additional requirements for determining a reliable age with any radiometric dating application are that phase formation occurs over a time scale that is short relative to the controlling radiometric half life, and that individual phases should not represent a mixed assemblage of ages resolvable at the controlling radiometric half life. These issues were assessed in Zellmer et al. (2008), including the possibility that some phases we analyzed contained impurities (a situation common to essentially all natural mineral-melt isochron dating studies).

Theoretical evidence that Ra and Ba might not partition between minerals and melts as exact analogues was presented last decade (Blundy and Wood, 1994), and subsequently refined by Blundy and Wood (2003). Zellmer et al. (2000) have used these theoretical constraints to interpret ^{226}Ra–^{230}Th–Ba systematics in Santorini volcanic rocks. Cooper et al. (2001) presented an alternate ^{226}Ra–^{230}Th–Ba mineral-melt age model that incorporates the Blundy and Wood theory and has subsequently been employed multiple times (as referenced in Cooper's comment). Because this method predicts that Ra and Ba will partition differently between minerals and melts (with each mineral having a characteristic solid-melt partition coefficient ratio, D_{Ra}/D_{Ba}), contemporaneous phases may not be collinear on an isochron diagram using Ba as the normalizing element. This makes it difficult (but not impossible) to calculate a weighted mean assemblage age by curve fitting as in the standard isochron method. Cooper et al. (2001), however, advocates a different method, predicated on independent determination of the age of each mineral in a volcanic rock.

A primary basis of the Cooper (2009) comment is an opinion that meaningful age results cannot be generated from the Zellmer et al. (2008) data using the $D_{Ra}=D_{Ba}$ isochron model, and that only the $D_{Ra}\neq D_{Ba}$ methodology she proposes produces meaningful age estimates. Importantly, the application of Cooper's method requires either high phase purity, due to D_{Ra}/D_{Ba} differences between phases, or significant data manipulation to infer such values for an impure phase separate. It also requires the assumption of a specific D_{Ra}/D_{Ba} for each mineral, a value with considerable uncertainty.

After evaluating chemical, radiometric and mineralogical trends in our data on the aforementioned Icelandic lavas, we concluded that the most reliable age constraints arise from a $D_{Ra}=D_{Ba}$ isochron interpretation based on two main observables: a) the contemporaneousness of mineral separates in each rock and excellent goodness of fit to an isochron using this method, and b) the equality of magnetite (mt)–whole-rock (WR) two point isochron ages with the multi-mineral–WR isochron ages. We noted that Ba and Ra were so incompatible in mt that a difference in their partitioning behavior would not have a measurable effect on this two point isochron age.

Cooper (2009) states that our logic is flawed with respect to these observations, resulting in incorrect data interpretations. Cooper asserts that asynchronous mineral formation is the norm, thereby invalidating our arguments about contemporaneous phase formation in the Torfajökull–Veidivötn magmas, yet does not consider our other evidence that is at least permissive of coeval phase formation. Cooper also argues that Ra–Ba fractionation during mt formation is so significant that it invalidates any age arguments we make from this mineral and the weight we place on those results. Yet we will demonstrate here that the age predictions of our age model and Cooper's are nearly identical for mt, as well as for clinopyroxene (px), because of the radiometric in-growth systematics of a highly incompatible daughter element in a mineral phase (i.e., ^{226}Ra grows in from effectively zero abundance at zero age), thus invalidating her assertions regarding these minerals.

Cooper (2009) goes on to assert that the only way to produce highly correlated linear mineral-melt ^{226}Ra–^{230}Th–Ba data of the type we observe is not by contemporaneous phases with D_{Ra}/D_{Ba} ~1, but rather by mixing of impure phases, producing arrays without age significance. However, (a) contemporaneous phases will mix along a traditional isochron; (b) contemporaneous phases are not *a priori* disallowed for one or another volcanic system by any age-dating model; and (c) contemporaneous phases are consistent with the simple, small, euhedral, equilibrium mineral assemblages in our samples. Furthermore, our evaluation of the phase compositions in our samples demonstrates that no simple mixtures can account for the ^{226}Ra–^{230}Th–Ba–U–Th phase compositions we observed.

A third argument of Cooper (2009) is that observables on natural phenocrysts need to be "corrected" to pure phase values in order to date them with the $D_{Ra}\neq D_{Ba}$ model of Cooper et al. (2001). This critical component of that model relies on an ad hoc "contamination" correction scheme utilizing untested assumptions about contaminant compositions and distributions within a phase separate to calculate so called pure phase ^{226}Ra–^{230}Th–Ba abundances for dating purposes (e.g., Cooper et al., 2001; Cooper and Reid, 2003). The correction scheme in those papers and in Cooper (2009) relies upon comparing observations in natural materials to means of experimentally derived mineral-melt partition coefficients that are an oversimplification of the extant literature of individual experiment values often ranging by as little as factors of five to as much as multiple orders of magnitude, and likewise differing substantially from distribution coefficients determined on natural minerals (cf., discussion in Blundy and Wood, 2003). The Blundy and Wood (2003) study also provides useful insights into mineral structural and chemical controls on elemental partitioning between volcanic minerals and melts, yet the leap to using their generalized parameterizations of relative partition coefficient ratios as literal predictions of both chemical partitioning and anticipated pure phase equilibrium compositions is a large one, introducing roughly an order of magnitude higher uncertainties (or more in some cases) into ^{226}Ra–^{230}Th–Ba model ages of individual minerals by the Cooper et al. (2001) method than those authors chose to acknowledge. We return to each of the main points of Cooper's comment in more detail below.

2. Discussion

2.1. Geochronological constraints of Ra–Ba partitioning behavior

There are multiple implications of the assertion (e.g., Cooper, 2009) that specific (and different) values of D_{Ra} and D_{Ba} are required to conduct mineral-melt geochronology using Ba-normalized ^{226}Ra–^{230}Th data, including uncertainties associated with D_{Ra}, D_{Ba} and D_{Th} estimates. Th, U and Ba partition coefficients have been historically quite difficult to measure, commonly with factors of 2 to >100 range in literature D_i values for specific minerals such as px and garnet (and somewhat narrower, ca. 2× to 10×, ranges in D_U/D_{Th} and D_U/D_{Ba} ratios); almost all D_{Ra} values are estimated from D_{Ba}. Such variations complicate petrogenetic and geochronologic interpenetrations of U-series disequilibria data sets on natural volcanic rocks (cf. Pietruszka et al., 2001). D_i estimation errors do not however factor into traditional isochron age determinations assuming $D_{Ra}=D_{Ba}$ (e.g., Zellmer et al., 2008).

Early efforts to rationalize and provide predictability to mineral-melt partitioning into specific mineral lattice sites used isoelectronic