Time scale of magma differentiation in arcs from protactinium-radium isotopic data

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ABSTRACT

Absolute chronology of magma differentiation processes has been a long-desired goal, given its importance in understanding magma chamber dynamics and its connection to a fundamental understanding of the style and frequency of volcanic eruptions. Broad estimates of the duration of magma differentiation and overall crustal residence times have been made based on a variety of indirect approaches, such as physical models of magma chamber cooling, rates of crystal growth and settling, and long-lived radiogenic isotopes. In contrast, combined 231Pa-235U data may provide a robust measure of the time scale of magma differentiation. Based on 231Pa-235U, 230Th-238U and 226Ra-230Th data from Taal volcano, Luzon Arc, Philippine Archipelago, we show that 231Pa-235U data may provide a robust direct measure of the time scale of magma differentiation. A closed-system magma fractionation model gives a 231Pa-235U differentiation time scale in the range of 30 k.y., while the 226Ra-230Th time scale is considerably younger. The time scales are reconciled if we consider either fluid-mixing or magma-mixing models. The fluid-mixing model gives a time scale of differentiation similar to the 231Pa-235U closed-system time scale and is supported by the 230Th-238U data. The magma-mixing model gives a considerably longer time, in the range of 55 k.y. The combined observations support the robustness of the 231Pa-235U chronology, indicating a differentiation time scale in the range of 30 k.y., although this time scale for other volcanoes may vary depending on size and thermal state of the magma chamber. The 226Ra-230Th closed-system model ages, which yield much younger estimates for magma differentiation, are not likely to reflect time scales of magma differentiation.

Keywords: time scale, differentiation, 231Pa, 226Ra, magma, uranium series.

INTRODUCTION

The composition of most igneous rocks at the surface is the result of significant modification in crustal-level magma chambers of more primitive mantle melts. This process of differentiation is a fundamental step in generating more chemically evolved lavas. Robust estimation of the time scale of differentiation is important for understanding magma evolution and eruption dynamics of volcanic centers (Sparks, 2003). Previous approaches to constraining magma residence time at crustal chambers and time scale of magma differentiation have included physical methods, such as estimates of crystal growth and settling (e.g., Marsh, 1989; Martin and Nokes, 1988). Long-lived radiogenic isotopes such as Rb-Sr and U-Pb have also been used to estimate residence times of large differentiated systems (e.g., Halliday et al., 1989; Christensen and Geology; August 2005; v. 33; no. 8; p. 633–636; doi: 10.1130/G21638.1; 4 figures; 1 table; Data Repository item 2005120. 633

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1GSA Data Repository item 2005120, Table DR1, complete data and methods, and Appendix 1, complete descriptions on models and parameters, is available online at www.geosociety.org/pubs/fg2005.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.
TABLE 1. PROTACTINIUM, RADIUM, THORIUM, AND URANIUM DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>(^{231}\text{Pa}/^{235}\text{U}) R^2</th>
<th>(^{226}\text{Ra}/^{230}\text{Th}) R^2</th>
<th>(^{230}\text{Th}/^{238}\text{U}) R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB-5 Phil</td>
<td>7.29</td>
<td>1.506 ± 14</td>
<td>1.63 ± 5</td>
<td>0.917 ± 8</td>
</tr>
<tr>
<td>CY-3</td>
<td>6.02</td>
<td>1.464 ± 39</td>
<td>1.34 ± 6</td>
<td>0.936 ± 11</td>
</tr>
<tr>
<td>B-4</td>
<td>5.95</td>
<td>1.451 ± 14</td>
<td>1.34 ± 6</td>
<td>0.945 ± 8</td>
</tr>
<tr>
<td>CAL-1</td>
<td>5.65</td>
<td>1.435 ± 29</td>
<td>1.29 ± 6</td>
<td>0.924 ± 21</td>
</tr>
<tr>
<td>BAL-1-1</td>
<td>1.19</td>
<td>4.043 ± 14</td>
<td>1.19 ± 5</td>
<td>0.946 ± 6</td>
</tr>
<tr>
<td>BAL-1-D</td>
<td>1.19</td>
<td>4.043 ± 14</td>
<td>1.19 ± 5</td>
<td>0.946 ± 6</td>
</tr>
<tr>
<td>BAL-1 Average</td>
<td>1.19</td>
<td>4.043 ± 14</td>
<td>1.19 ± 5</td>
<td>0.946 ± 6</td>
</tr>
<tr>
<td>TML-5</td>
<td>1.00</td>
<td>1.323 ± 11</td>
<td>1.13 ± 4</td>
<td>0.951 ± 12</td>
</tr>
<tr>
<td>TML-4</td>
<td>1.00</td>
<td>1.323 ± 11</td>
<td>1.13 ± 4</td>
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<tr>
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<td>1.00</td>
<td>1.323 ± 11</td>
<td>1.13 ± 4</td>
<td>0.951 ± 12</td>
</tr>
</tbody>
</table>

Note: See footnote 1 in text for complete data table and description of methods.

*Activity ratios and 2σ errors; activity is equal to the number of atoms multiplied by the decay constant for that nuclide.

Initial activity ratios; uncertainties in initial ratios (values at time of eruption) reflect uncertainties in age estimates, 0.250 ka, and analytical uncertainty, except for the 1968 eruption (MB-5). For historical lavas initial corrections for U, Pa, and Th are insignificant. Values for the secular equilibrium standard and for Table Mountain Latite (TML) are measured values.

The salient feature of our Pa and Ra data is that the enrichments correlate with MgO content, an index of magma differentiation, with wt% MgO = \(^{231}\text{Pa}/^{235}\text{U}) R^2 value of 0.995 (Fig. 1A). If these lavas had crystallized from the same parental magma (Miklius et al., 1991), there would be no variation in their \(^{231}\text{Pa}/^{235}\text{U}) and \(^{226}\text{Ra}/^{230}\text{Th}) data. It is more likely that they differentiated from different batches of magma that were similar in composition, and that variations in \(^{231}\text{Pa}/^{235}\text{U}) and \(^{226}\text{Ra}/^{230}\text{Th}) reflect the time scale of magma differentiation.

**DISCUSSION AND CONCLUSIONS**

In Figure 1A, we show results of a differentiation age model. If each of the lavas started from a distinct batch of magma that had a \(^{231}\text{Pa}/^{235}\text{U}) value similar to the least differentiated sample (basalt), their position on the curve shows the time of differentiation from the parent magma. Similarly, the MgO-\(^{226}\text{Ra}/^{230}\text{Th}) variations are shown in Figure 1B, including results from an age model starting from the \(^{226}\text{Ra}/^{230}\text{Th}) of the least-differentiated sample. The \(^{231}\text{Pa}/^{235}\text{U}) chronology shows that differentiation from basaltic composition to the most evolved end member took 27 k.y. (Fig. 1A). In contrast, significantly shorter durations are implied by \(^{226}\text{Ra}/^{230}\text{Th}) data. If the two chronometers were concordant, based on the \(^{231}\text{Pa}/^{235}\text{U}) chronology, the most differentiated and second-most differentiated sample would have secular equilibrium \(^{226}\text{Ra}/^{230}\text{Th}) values. Yet the most differentiated sample (BAL-8) has a slightly measured \(^{226}\text{Ra}) excess outside of its 2σ error range, \(^{226}\text{Ra}) 1.025 ± 16, which, when age corrected to the time of eruption, corresponds to an initial \(^{226}\text{Ra}) of 1.13 ± 3. The second-most differentiated sample shows measurable enrichment, \(^{226}\text{Ra}) = 1.071 ± 43, 2σ, with an initial ratio of 1.18 ± 6. The \(^{231}\text{Pa}/^{235}\text{U}) differentiation chronology for the intermediate composition sample ranges from 5 to 7 k.y. (Fig. 1A), while the \(^{226}\text{Ra}/^{230}\text{Th}) chronology varies from 1 to <2.0 k.y. (Fig. 1B).

Given the coupling of the two uranium decay series, the Pa and Ra may be combined to construct a \(^{231}\text{Pa}/^{235}\text{U})-^{226}\text{Ra}/^{230}\text{Th}) concordia diagram (Fig. 2A), allowing for the graphical analysis of the two chronologies. A similar diagram can also be constructed for the \(^{231}\text{Pa}/^{235}\text{U})-^{226}\text{Ra}/^{230}\text{Th}) system (Fig. 2B). Concordant samples should fall on the solid lines in each diagram. All of our samples fall off the line on the \(^{231}\text{Pa}/^{235}\text{U})-^{226}\text{Ra}/^{230}\text{Th}) diagram, except for one sample that is within 2σ analytical error. The most primitive lava by definition has to be on the concordia line. In contrast, all the samples except one fall on the \(^{231}\text{Pa}/^{235}\text{U})-^{226}\text{Ra}/^{230}\text{Th}) concordia line, within analytical error. The broad concordance between the Pa-U and Th-U data and the lack of concordance between the Pa-U and Ra-Th data show that other processes likely affect Ra during differentiation. Although there are few samples with combined Pa and Ra data, no one has ever reported concordant Pa and Ra chronologies.

Here, two alternative models are considered to explain the discrepancy between the \(^{231}\text{Pa}) and \(^{226}\text{Ra}) chronologies. Model I is a magma replenishment model, based on the formulations of Hughes and Hawkesworth (1999). In this model, fresh magma with initial composition of the parent magma is added in an amount equal to the fraction of magma that
crystallizes out, until the initial magma is completely replaced (F degree of crystallization = 1). The model takes into account isotopic fractionation due to crystal fractionation and decay and magma mixing. Crystal fractionation and decay are implemented in alternating small steps in order to approximate a continuous process (Appendix 1 has details of parameters and implementation; see footnote 1). Best-fitting parameters were identified iteratively. The model that best fits the data, Figure 3, has the following values: \((^{226}\text{Ra}/^{230}\text{Th})_{\text{Melt}} = 10\), \((^{231}\text{Pa}/^{235}\text{U})_{\text{Melt}} = 1.57\), degree of crystallization of 0.36% per batch, and replenishment frequency of 200 yr and a duration of crystallization of 56 k.y. As can be seen in Figure 3A, the model fits the data well, but it requires that the magma added has a \((^{226}\text{Ra}/^{230}\text{Th})\) of 10. The \((^{226}\text{Ra}/^{230}\text{Th})\) value in Philippine lavas, even of basalts, are very low, e.g., BM-5 (Table 1). A value of 10 is almost twice the value observed even in lavas with the highest reported \((^{226}\text{Ra}/^{230}\text{Th})\) values (Turner et al., 2000).

Model II is similar to Model I, except it assumes fluid rather than magma replenishment. Fluid replenishment is carried out exactly as in Model I, taking into account the effects of fractional crystallization, radioactive decay, and fluid addition on the \((^{226}\text{Ra}/^{230}\text{Th})\) and \((^{231}\text{Pa}/^{235}\text{U})\) values. The model best fits the data (Figure 3B) with the following parameters: low concentration of Ra (1% of magma) but high \((^{226}\text{Ra}/^{230}\text{Th})\) of 70 and \((^{231}\text{Pa}/^{235}\text{U})\) of 1.528, degree of crystallization of 0.01% per replenishment cycle, replenishment frequency of 370 yr, and a duration of crystallization of 37 k.y. The fluid addition model has many attractive features. The time interval between the time of crystallization and the most differentiated sample is similar to that arrived at from the simple closed-system model obtained from \((^{231}\text{Pa}/^{235}\text{U})\) chronology (Fig. 1A) and \((^{230}\text{Th}/^{238}\text{U})\) chronology (Fig. 2B). See text and Appendix 1 (see footnote 1) for details on model.

The apparent high \((^{226}\text{Ra}/^{230}\text{Th})\) required by the fluid addition model is justifiable on many grounds. Given the high diffusivity and fluid mobility of Ra (Cooper, 2001), it is unlikely that the Ra-Th will remain a closed system during the differentiation process in a fluid-dominated system such as an arc crustal magma chamber. In Figure 4 we show diffusivities for Ra and Pa calculated based on the elastic strain diffusion models described by Van Orman et al. (2001). The Ra values are similar to those reported by Saal and Van Orman (2004). We also show U and Th diffusivities from numerical calculation. The eventual fate of the fluids involved during magma differentiation is not clear. One possibility is that magmatic fluids may be eventually lost as a vapor, leaving the melt enriched in fluid-mobile elements, such as Ra.

Although both the melt replenishment and fluid replenishment models take the effect of crystal fractionation into consideration, using bulk distribution coefficients for Pa, Ra, U, and Th, the potential effect of some important minerals, such as plagioclase with respect to Ra and accessory minerals with respect to U and Th, is difficult to assess. Ra is more compatible than U, Th, and likely Pa in plagioclase (Cooper, 2001; Cooper and Reid, 2003), suggesting that significant plagioclase fractionation could potentially deplete a given evolved melt with respect to Ra, as suggested by Zellmer et al. (2000). However, the effect on U-Th and Pa should be minimal; \(D_u\) and \(D_p\) based on phenocryst data (Cooper and Reid, 2003) are low and of similar magnitude. Decrease in the Ra/Th ratios from ~55 (for the intermediate lavas) to 42 for the most differentiated lavas may indicate late-stage plagioclase removal. In contrast, the U/Th ratios of all the lavas are remarkably similar (0.28–0.29; Table 1), despite nearly a fourfold increase in concentration from basalt to the most differentiated lavas.

The global coherence in igneous rocks between \((^{230}\text{Th}/^{238}\text{U})\) and \((^{231}\text{Pa}/^{235}\text{U})\) and the apparent difficulty of reconciling the \((^{226}\text{Ra}/^{230}\text{Th})\) has been suggested as evidence for selective \(^{226}\text{Ra}\) mobilization (Saal and Van Orman, 2004). Our results showing the lack of coherence between \((^{231}\text{Pa}/^{235}\text{U})\) and \((^{226}\text{Ra}/^{230}\text{Th})\) chronologies (Figs. 1A, 1B, and 2A) and the coherence between \((^{231}\text{Pa}/^{235}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\) chronologies (Fig. 2B) are in line with the global observations. Although we are not as pessimistic about the global igneous \(^{226}\text{Ra}\) data, the numerical data reinforce our conclusions concerning the open-system nature of the \(^{226}\text{Ra}\) chronology.

Although we think that the Ra data do not provide the full time scale of differentiation, they could provide a very useful constraint for postdifferentiation magma chamber residence time. In addition, as pointed out by Turner et