Mafic–felsic magma mixing limited by reactive processes: A case study of biotite-rich rinds on mafic enclaves

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ABSTRACT

Mafic enclaves in felsic plutons are often used to argue that intermediate magmas are formed by mafic–felsic magma mixing, but the extent and nature of mixing remains unclear. Here, we examine biotite-rich rinds on mafic enclaves from the Cretaceous Bernasconi Hills Pluton in the Peninsular Ranges Batholith of southern California to gain insight into magma mixing processes. Rinds differ from the enclave interior and the host monzogranite in being more fine-grained and more mafic and potassic. Rinds are also 2–5 times more enriched in rare earth elements than the host monzogranite and up to 3 times more enriched than enclave interiors. These observations indicate that the rinds were not generated by isochemical quenching, binary mixing between enclave and host monzogranite, or in-situ magmatic differentiation. Instead, rinds appear to have been formed by chemical reaction between the solidified enclave and a hydrous K-rich residual melt or fluid formed after progressive crystallization and cooling of the host magma body, transforming amphibole in the enclave into biotite-rich rinds. Field observations show snapshots of biotite-rich rinds being eroded away and new rinds simultaneously forming on freshly eroded surfaces of enclaves, consistent with rinds being formed by chemical reaction instead of as quenching products. Deformation of enclaves is accommodated primarily by ductile attenuation of the thin rind while the enclave as a whole tends to rotate as a rigid body with minimal internal deformation other than localized brittle failure. A comparison of the aspect ratios and cross-sectional areas of mafic bodies in the pluton shows that those with high aspect ratios (indicating greater accumulated strain) are systematically more biotite-rich and have smaller cross-sectional areas than those with lower aspect ratios, which are amphibole-rich. These relationships not only confirm that biotite-rich lithologies are more deformable but also indicate that the high aspect ratio biotite-rich bodies (also known as schlieren) derive from small parent bodies, consistent with a derivation from eroding enclave rinds rather than from the enclave itself. Finally, geochemical and thermodynamic modeling indicates that the biotite-rich rinds formed when the host felsic magma had cooled to a low melt fraction state (F = 0.15–0.3; 700–760 °C), suggesting that such reactions occur late in the lifespan of a magma body. Thus, mafic–felsic mixing may not be an efficient process for making intermediate magmas unless the magma body can reside at this low temperature range long enough to permit rind formation and subsequent deformation.

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1. Introduction

Mafic enclaves are ubiquitous in felsic plutons, and their presence has been interpreted as evidence of mixing between mafic and felsic magmas (Pabst, 1928; Walker and Skelhorn, 1966; Reid et al., 1983; Vernon, 1984; Furman and Spéra, 1985; Didier, 1987; Frost and Mahood, 1987; Vernon, 1990; Wiebe et al., 1997; Ratjeski et al., 2001; Barbarin, 2005). The abundance of enclave-bearing plutons has motivated the hypothesis that mixing may be an important mechanism by which intermediate magmas, like andesites, form (Eichelberger, 1975; Reid et al., 1983; Frost and Mahood, 1987; Ratjeski et al., 2001). Although many studies have demonstrated that geochemical mixing trends exist between enclave and granitoid end-members, the exact processes by which mixing occurs remain unclear (Frost and Mahood, 1987; Zorpi et al., 1989; Sisson et al., 1996; Reubi and Blundy, 2009). A common feature of enclaves is that they are finer-grained than their host pluton and often have dark, fine-grained margins. This has led to the interpretation that enclaves are chilled upon contact with felsic magma and that these
fine-grained margins represent quench rinds (Wager and Bailey, 1953; Chapman, 1962; Blake et al., 1965; Walker and Skelhorn, 1966; Furman and Spera, 1985; Vernon, 1990; Wiebe et al., 1997; Barbarin, 2005). Such a scenario is expected given that mafic magmas have higher liquidus and solidus temperatures than silici-
cmic magmas and therefore should freeze if intruded into a silicic magma host. However, freezing of mafic magmas would result in a high viscosity contrast between the solidified enclaves and the pa-
tially molten host magma, thereby inhibiting deformation of en-
claves and mechanical mixing (Frost and Mahood, 1987; Paterson et al., 2004). Mixing might only be efficient in basalt-dominated systems as the basaltic host would provide sufficient heat to com-
pletely melt felsic material, but the reverse, that is, mixing of ma-
fic enclaves incorporated into felsic-dominated systems, is more difficult. How do we reconcile the rheological difficulties of mafic–felsic mixing with the apparent evidence for mixing based on the presence of mafic enclaves and associated schlieren?

Here we examine enclaves from the Cretaceous Bernasconi Hills Pluton in the northern Peninsular Ranges of southern California. At this locality, rinds on mafic enclaves are chemically distinct from both the host rock and enclave core and therefore cannot represent isochemical quench rinds. We demonstrate that these rinds are K and biotite-rich and exhibit highly enriched REE pat-
terns compared to enclave interiors and host rock. This implies that the rinds may instead represent reaction products between the enclave and interstitial liquids within the host magma body. We propose that these biotite-rich rinds form by reaction between hydrous residual liquids or fluids and the solidifying mafic enclave during the late stages of pluton crystallization. We further show that these rinds are rheologically weak and hence become preferentially deformed relative to their parent enclave, resulting in their delamination or erosion from the enclave and the forma-
tion of biotite-rich schlieren. We propose that enclave deformation and the formation of schlieren is thus limited by the generation of biotite-rich reaction rinds. Therefore, magma mixing, in at least some felsic systems, may be limited by chemical reaction between enclaves and interstitial melt.

2. Geologic background

The Peninsular Ranges Batholith (PRB) intruded during the mid to late Cretaceous and is the southernmost intrusion in the chain of North American Mesozoic batholiths spanning from Alaska to Baja California. The PRB has been divided into western and eastern zones based upon regional variations in lithology, geochemistry and age of individual plutons as well as metamorphic grade of sur-
rounding wallrock (Gastil, 1975; Gromet and Silver, 1987; Gastil et al., 1988; Todd et al., 1988; Kistler et al., 2003; Wetmore et al., 2003; Lee et al., 2007). This boundary between western and eastern zones is inferred to represent a tec tonic suture between accreted island arc terranes and the Paleozoic North American continental margin, respectively (Gastil, 1975; Todd et al., 1988; Kistler et al., 2003; Wetmore et al., 2003; Lee et al., 2007). In the northern PRB the boundary runs roughly north–south until the Agua Blanca Fault in Baja California, where it trends southeast until the middle of the quarried section of the pluton. The diorite weathers dark gray and superficially resembles mafic enclaves, but is distin-
guished by its coarse-grained texture and more heavily weathered appearance.

4.2. Enclaves

Mafic enclaves occur as gray to blackish blobs throughout the Bernasconi Hills Pluton and range in size from a few centimeters to a meter in longest dimension. Enclaves show varying degrees of attenuation as shown in Fig. 1. Enclave size and shape vary on the scale of a few centimeters in some parts of the pluton and these variations are most pronounced where there is a large enclave density such as in enclave swarms. The range of enclave shapes indicate that multiple stages in the strain history of a typical en-
clave are preserved within the pluton, giving a continuous view of how physical interaction between enclaves and the host magma progresses with respect to the enclave.

Almost all enclaves are mantled by thin (~0.2–2 cm thick) rinds, which differ from the amphibole-rich enclave interiors by being darker in coloration, finer-grained, and biotite-rich. In many cases, the biotite-rich rinds appear to delaminate, erode or shear off from

3. Analytical methods

Mafic enclaves and the adjacent host granitoid were collected from the quarried section of the Bernasconi Hills Pluton. En-
claves were selected on the basis of being relatively unweth-
ered and having a sufficiently thick rind for geochemical analysis. Each enclave was separated into host rock, rind and enclave in-
terior subsamples with a saw. Whole rock geochemistry samples were crushed to a fine powder in a tungsten carbide mill and fused with a lithium tetraborate–lithium metaborate mix. Ma-
Jor oxide compositions were determined by X-ray fluorescence spectrometry (XRF) at California State University, Fresno (see Busby et al., 2008). Trace element concentrations were deter-
mined at Rice University by laser ablation-ICP-MS (LA-ICP-MS) with a ThermoFinnigan Element 2 equipped with a New Wave 213 nm laser ablation system for the same fused glass disks used in XRF analyses. External standards used for LA-ICP-MS analy-


sions within the interior of the pluton.
Fig. 1. Relationship of biotite-rich rinds to mafic enclaves and host monzogranite. (A) An undeformed enclave with a well-developed rind. (B) Slightly elongated enclaves with delaminating rinds. As rinds delaminate, rinds continue to form on the newly exposed enclave surface. (C) Elongated enclaves with eroded rinds and associated schlieren. The rinds and schlieren are biotite-rich and appear to be rheologically weak, resulting in higher rates of strain accumulation than the enclave as a whole.

the parent enclave (Fig. 1B), suggesting that strain accumulates preferentially in the rind or at the rind–enclave interior interface while the enclave interior remains largely undeformed except for occasional evidence of brittle fracture. Rinds appear to form on enclave surfaces at all stages of enclave development, with new biotite-rich rinds re-forming after earlier ones are mechanically eroded away (Fig. 1B).

4.3. Schlieren

Schlieren are dark, fine-grained, biotite-rich segregations within the host granitoid. They vary in length (several cm to >3 m) and thickness (<1 cm to 10 cm) and are characterized by a foliation fabric defined by preferentially aligned biotite crystals. Schlieren are most common near the margins of enclave swarms and appear texturally identical to the biotite-rich rinds associated with enclaves. In many cases they are observed in close proximity to rinds and in some cases appear to derive directly from them (Fig. 1B–C).

4.4. Aspect ratio of mafic enclaves and selvages

The quarried face of the pluton is primarily perpendicular to the large scale foliation defined by the attenuated mafic enclaves. We measured the long (a) and short (b) axes of enclaves and associated biotite and amphibole-rich selvages in order to compare their aspect ratios (a/b) and cross-sectional areas (A = πab) perpendicular to the foliation plane. Selvages look superficially similar to rinds and are distinguished from enclaves by being darker and finer-grained. They generally have higher aspect ratios (a/b) and lower cross-sectional areas compared to enclaves (Fig. 2), indicating that the selvages accumulate more strain than the enclaves and are therefore more deformable. Low aspect ratios determined for enclaves indicate that enclaves do not attenuate appreciably and instead rotate.

5. Petrography

5.1. Granitoid rocks

Plagioclase (~30%) and quartz (~50%) occur as subhedral and anhedral crystals and comprise the bulk of the host pluton. Alkaline feldspar (~15%) is also present as subhedral grains, some of which are zoned. Biotite (~1%) is scarce, but when present, it occurs in clots as coarse subhedral and anhedral crystals (Fig. 3). Hornblende (~5%) is generally more abundant in the host rock than biotite and occurs mostly in clots of stubby dark green crystals. Apatite, ilmenite, magnetite, sphene and zircon are observed as accessory phases.

5.2. Enclaves

Mafic enclaves are mineralogically zoned between an outer fine-grained, biotite-rich rind and an inner biotite-poor region (Fig. 3). Enclave interiors are composed of quartz (~35%), plagioclase (~20%) and hornblende (~32%). Quartz is generally equigranular, suggesting recrystallization, and is most abundant near the center of the enclave. Plagioclase occurs as lathes and subhedral grains and is present in roughly equal proportions throughout the enclave interior. Biotite (~13%) forms subhedral to anhedral brown
to yellow–brown crystals. It is not abundant in enclave interiors, but when present it is typically associated with hornblende. Hornblende commonly forms clots of subhedral to anhedral dark green crystals, although it also occurs as an interstitial phase between quartz and plagioclase in the central parts of the enclave interior. Hornblende is most abundant in the outer region of the enclave interior, adjacent to the biotite-rich rind. Apatite and magnetite are present as accessory minerals within enclaves.

Rinds are finer-grained than the enclave interior and have a higher density of mafic minerals. They are biotite-rich (30%), and contain hornblende (∼25%), plagioclase (∼10%) and quartz (∼35%). Biotite occurs as euhedral to subhedral yellow–brown crystals and is most abundant along the outer portions of rinds and steadily decreases in abundance towards the rind–enclave boundary (Fig. 3). Additionally, biotite crystals within rinds are aligned parallel to the enclave–host magma interface, which contrasts with the lack of orientation within the enclave interior. Hornblende generally forms stubby, anhedral crystals and is roughly aligned with biotite. Quartz and plagioclase are both equigranular. Plagioclase is aligned parallel to biotite. Rinds do not contain any accessory minerals other than apatite, which is typically observed as fine-grained needles within plagioclase and quartz.

6. Geochemistry

6.1. Major elements

The host monzogranite is characterized by ∼72 wt% SiO$_2$, ∼0.8 wt% MgO, ∼3 wt% CaO, ∼3 wt% Fe$_2$O$_3$, ∼13–14 wt% Al$_2$O$_3$, and ∼5 wt% alkalis (Table 1).

Enclave interiors are intermediate (basaltic trachy–andesite to trachy–andesite; 56–59 wt% SiO$_2$) in composition. Interestingly, enclave interiors are more alkalic (Na$_2$O + K$_2$O ∼6 wt%) than the surrounding host rock despite having lower SiO$_2$ and higher MgO (∼3 wt%) content (Fig. 4A). Na$_2$O is slightly greater in enclave interiors than in either the enclave rind or host rock due to the abundance of hornblende within the enclaves. Enclave rinds are less felsic (SiO$_2$ ∼52–55 wt%), more potassic (∼1.6–2.6 wt%), and have higher MgO and Fe$_2$O$_3$ content (∼3.4 wt% and ∼12–13 wt%, respectively) than enclave interiors and host tonalite (Fig. 4A–B). Rinds are significantly more potassic than the host monzogranite despite being more mafic. One rind is more felsic (SiO$_2$ ∼57.6 wt%) and has less MgO (3 wt%), and Fe$_2$O$_3$ (10 wt%) than other measured rinds, but is still more potassic (K$_2$O ∼1.9 wt%) than measured enclave interiors and host monzogranite.

6.2. Trace elements

Trace element concentrations for host monzogranite, enclave interior, and enclave rinds have been normalized to the bulk continental crust (BCC; Rudnick and Fountain, 1995) (Fig. 4C) and show systematic differences between each lithology. Normalized heavy rare earth element (HREE) concentrations for all samples are subparallel to BCC and are enriched by 2 to 12 times with respect to BCC.

The host monzogranite is less enriched in the REEs (Fig. 4C) compared to enclave interior and rind samples. The LREE contents of enclave interiors are similar to that of the rinds but the HREEs are lower in the enclaves than in the rinds. Rinds show varying degrees of REE enrichment compared to enclave cores and host monzogranite.
Table 1
Whole rock major oxide and trace element compositions.

<table>
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<tr>
<th>Lithology</th>
<th>Sample name</th>
<th>BH01T1FH Granitic host</th>
<th>BH01T2FH Granitic host</th>
<th>BH01T1R1 Enclave rind</th>
<th>BH01T1R2 Enclave rind</th>
<th>BH01T2R1 Enclave rind</th>
<th>BH01T2R2 Enclave interior</th>
<th>BH01T1E1 Enclave interior</th>
<th>BH01T2E1 Enclave interior</th>
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<tr>
<td>SiO₂ (wt%)</td>
<td>72.4</td>
<td>72.6</td>
<td>54.8</td>
<td>52.0</td>
<td>57.6</td>
<td>53.9</td>
<td>56.2</td>
<td>59.1</td>
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<td>TiO₂</td>
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<td>0.4</td>
<td>1.11</td>
<td>1.33</td>
<td>0.94</td>
<td>1.06</td>
<td>0.98</td>
<td>0.85</td>
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<tr>
<td>Al₂O₃</td>
<td>13.1</td>
<td>13.5</td>
<td>16.6</td>
<td>17.4</td>
<td>16.0</td>
<td>16.2</td>
<td>16.0</td>
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<tr>
<td>Fe₂O₃</td>
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<td>11.8</td>
<td>12.8</td>
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<td>0.07</td>
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<td>0.22</td>
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<td>MgO</td>
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<td>0.76</td>
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<td>3.4</td>
<td>2.99</td>
<td>3.42</td>
<td>3.17</td>
<td>2.95</td>
<td></td>
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<tr>
<td>CaO</td>
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<td>3.16</td>
<td>5.44</td>
<td>5.6</td>
<td>5.39</td>
<td>6.67</td>
<td>5.62</td>
<td>5.5</td>
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<tr>
<td>Na₂O</td>
<td>4.15</td>
<td>4.28</td>
<td>4.18</td>
<td>4.34</td>
<td>4.27</td>
<td>4.25</td>
<td>4.41</td>
<td>4.39</td>
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<tr>
<td>K₂O</td>
<td>0.86</td>
<td>0.98</td>
<td>2.31</td>
<td>2.6</td>
<td>1.85</td>
<td>1.64</td>
<td>1.75</td>
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<td>P₂O₅</td>
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<td>0.129</td>
<td>0.173</td>
<td>0.111</td>
<td>0.117</td>
<td>0.105</td>
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<tr>
<td>Total</td>
<td>98.34</td>
<td>98.87</td>
<td>99.99</td>
<td>99.86</td>
<td>99.41</td>
<td>99.50</td>
<td>98.24</td>
<td>98.71</td>
<td></td>
</tr>
</tbody>
</table>

| Cs (ppm)  | 1.65        | 0.11                    | 2.20                    | 0.11                   | 6.61                   | 0.57                   | 7.46                        | 0.38                        | 4.12                        |
| Pb        | 0.71        | 0.61                    | 0.71                    | 0.45                   | 6.09                   | 0.67                   | 7.32                        | 0.04                        | 5.65                        |
| Th        | 2.5         | 0.3                     | 2.5                     | 0.2                    | 3.2                    | 0.2                    | 1.2                         | 0.1                         | 1.7                         |
| U         | 1.29        | 0.15                    | 1.29                    | 0.23                   | 1.41                   | 0.12                   | 1.37                        | 0.04                        | 0.76                        |
| Ba        | 5.99        | 15                      | 699                     | 1                      | 1074                   | 47                     | 1236                        | 3                           | 712                         |
| Nb        | 12.1        | 12.1                    | 12.1                    | 12.1                   | 12.1                   | 12.1                   | 12.1                        | 12.1                        | 12.1                        |
| La        | 23.1        | 0.5                     | 18.5                    | 11.1                   | 35.1                   | 2.1                    | 370                         | 0.9                         | 218                         |
| Ce        | 5.34        | 4.9                     | 40.9                    | 3.8                    | 11.1                   | 14                     | 122                         | 4                           | 663                         |
| Sr        | 79.1        | 57.0                    | 60.0                    | 57.0                   | 18.1                   | 19                     | 219                         | 0.3                         | 116                         |
| Nd        | 36.9        | 25.0                    | 28.0                    | 25.0                   | 84.7                   | 7.9                    | 114.2                       | 0.9                         | 56.8                        |
| Zr        | 379.2       | 20.0                    | 305.4                   | 20.0                   | 135.8                  | 8.1                    | 141.3                       | 3                           | 136                         |
| Sm        | 9.9         | 4.9                     | 7.9                     | 4.9                    | 20.9                   | 2.3                    | 35.4                        | 1.3                         | 14.8                        |
| Eu        | 2.25        | 0.43                    | 1.88                    | 0.43                   | 2.88                   | 0.34                   | 3.14                        | 0.43                        | 2.12                        |
| Tb        | 1.74        | 0.09                    | 1.33                    | 0.12                   | 3.44                   | 0.35                   | 6.63                        | 0.51                        | 2.50                        |
| Dy        | 10.4        | 0.3                     | 7.8                     | 0.5                    | 21.9                   | 1.0                    | 41.1                        | 1.0                         | 15.6                        |
| Y         | 33.3        | 2.6                     | 41.6                    | 2.1                    | 95.0                   | 1.7                    | 146.9                       | 2.1                         | 75.4                        |
| Ho        | 2.15        | 0.15                    | 1.56                    | 0.16                   | 4.18                   | 0.08                   | 7.86                        | 0.14                        | 3.15                        |
| Er        | 6.18        | 0.12                    | 4.64                    | 0.59                   | 12.5                   | 0.82                   | 22.6                        | 0.58                        | 9.36                        |
| Yb        | 5.4         | 0.8                     | 4.6                     | 0.7                    | 11.1                   | 0.6                    | 18.2                        | 0.2                         | 8.9                         |
| Lu        | 0.97        | 0.22                    | 0.76                    | 0.13                   | 1.85                   | 0.21                   | 2.86                        | 0.22                        | 1.14                        |

| 1 SD      | 0.11             | 0.11             | 0.07             | 0.07             | 0.11             | 0.07             | 0.11             | 0.07             | 0.11             | 0.07             |
| 1 SD      | 0.07             | 0.07             | 0.04             | 0.04             | 0.04             | 0.04             | 0.04             | 0.04             | 0.04             | 0.04             |
| 1 SD      | 0.04             | 0.04             | 0.03             | 0.03             | 0.03             | 0.03             | 0.03             | 0.03             | 0.03             | 0.03             |
| 1 SD      | 0.03             | 0.03             | 0.02             | 0.02             | 0.02             | 0.02             | 0.02             | 0.02             | 0.02             | 0.02             |
| 1 SD      | 0.02             | 0.02             | 0.01             | 0.01             | 0.01             | 0.01             | 0.01             | 0.01             | 0.01             | 0.01             |
rinds compositions. Mixing between mafic enclave and felsic host alone cannot explain not collinear with the felsic and mafic end-members, mechanical activated REE concentrations (Fig. 4). Because rind compositions are than both the enclaves and the host monzogranite and have ele-
claves. However, our geochemical data demonstrate that the rinds are compositionally distinct from the enclave and the host lava. The quenching hypothesis also predicts that rinds would form only during the initial injection of hot mafic magmas into the cold felsic host, but our field observations indicate that biotite-rich rinds form continuously, with new rinds forming even after earlier rinds are eroded off (Fig. 1B).

The mixing scenario predicts that rind compositions should fall along linear mixing arrays between the felsic host and mafic enclave end-members. Rinds, however, are more mafic and potassic than both the enclaves and the host monzogranite and have elevated REE concentrations (Fig. 4). Because rind compositions are not collinear with the felsic and mafic end-members, mechanical mixing between mafic enclave and felsic host alone cannot explain the rind compositions.

Generation of biotite-rich rinds via in situ crystallization of the mafic enclave also may not be supported by our study. Eberz and Nicholls (1990) proposed that geochemical zonation observed in enclaves in the Swifts Creek Pluton of southeastern Australia is the product of early crystallization that occurs when liquid mafic en-
claves come in contact with felsic host magma thereby cooling and crystallizing inwards from the inner margin of the enclave. They suggest that enrichment in K and incompatible trace elements in rinds is caused by diffusion from the host magma into the enclave interior. However, if biotite-rich rinds form exclusively when enclave magmas first come in contact with felsic host magmas, rinds should not form afterwards because the enclave would have already solidified due to rapid thermal equilibration on the small length-scales under consideration. Instead, we observe that rinds form continuously as can be seen by the presence of rinds during different stages in the strain history of an enclave (Fig. 1), precluding an origin by in-situ differentiation of the enclave itself.

The fourth scenario, gas-filter pressing, was proposed as a means of generating compositional zonation within mafic inclusions in volcanic rocks (Anderson et al., 1984; Bacon, 1986; Sisson and Bacon, 1999). In this process, residual melt is driven out of a crystallizing inclusion by excess pressure imposed by exsolved vapor, resulting in rhyolitic glass within a rind near the margins of the inclusion. Bacon (1986) suggested gas-filter pressing may occur in plutonic settings as a possible way of generating felsic haloes and veins adjacent to enclaves. Because residual liquids would be more evolved than the initial enclave magma, it is plausible that they would provide the enrichments in K and REEs observed in rinds. This is consistent with our geochemical observations and may provide an explanation for the origin of biotite-rich rinds on enclaves. However, like quenching, gas-filter pressing predicts that rinds form at only one instant, that is, during expulsion of residual liquids from the enclave as it is crystallizing. This is inconsistent with the continual generation of rinds observed in this study (Fig. 1B).

All of the above scenarios may operate at some level in magmatic systems, but none these scenarios alone adequately explains the origin of biotite-rich rinds. Instead, our field and geochemical observations are most easily explained if the rinds are products of continuous reaction between solid mafic enclaves and hydrous residual liquids or fluids in the host magma (Fig. 5). We suggest that rinds are preferentially deformed and eroded from the parent

**Fig. 4.** Whole-rock major (A and B) and trace element geochemistry (C) of host monzogranite, mafic enclave interiors, and rinds. Rinds are both more mafic and potassic than their parent enclave and the host rock. They are also substantially enriched in heavy rare earth elements, but show extreme depletions in Eu, Zr and Sr. Oxides are in wt%.

Trace elements have been normalized to model bulk continental crust (Rudnick and Fountain, 1995).
This equation indicates that increases in K$_2$O and Al$_2$O$_3$ activity or felsic melts or fluids, suggesting the following simplified reaction:

\[
\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 0.5\text{K}_2\text{O}(m) + 0.5\text{Al}_2\text{O}_3(m) = \text{K}\text{Mg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 2\text{CaO}(m) + 2\text{MgO}(m) + 5\text{SiO}_2(m)
\]

(1)

where oxides represent components within the melt or fluid. For simplicity, we assume end-member chemical formulas for amphibole and biotite, so Eq. (1) is meant solely for conceptual purposes. This equation indicates that increases in K$_2$O and Al$_2$O$_3$ activity or decreases in CaO, MgO, or SiO$_2$ activity in the magma drive the conversion of amphibole to biotite. At equilibrium, Eq. (1) requires the following relationship at a given temperature and pressure to yield the schematic activity diagram in Fig. 7A:

\[
\frac{-\Delta G_r}{RT} = 2\ln a_{\text{CaO}}(m) + 2\ln a_{\text{MgO}}(m) + 5\ln a_{\text{SiO}_2}(m) - 0.5\ln a_{\text{K}_2\text{O}}(m) - 0.5\ln a_{\text{Al}_2\text{O}_3}(m)
\]

(2a)

The quantity on the left hand side is a constant, representing the \(P-T\) specific Gibbs free energy of pure substances at a standard state for reaction (1) divided by the gas constant and temperature. The right hand side expresses the natural logarithm of the activities of each component in the melt or fluid. Eq. (2a) can be simplified if we assume that the system contains quartz and plagioclase so that the SiO$_2$ activity is buffered and the Al$_2$O$_3$ activity is roughly buffered, yielding:

\[
\ln a_{\text{MgO}} = 0.5\ln a_{\text{CaO}}/a_{\text{K}_2\text{O}} + C
\]

(2b)

where C is a constant that includes the Gibbs free energy of reaction and the activities of SiO$_2$ and Al$_2$O$_3$. Eq. (2b) is expressed in the schematic activity diagram in Fig. 7B. It can be seen that increases in the K$_2$O activity in the melt or fluid must be the primary driver of converting amphibole to biotite. This is at odds with the fact that the K$_2$O concentration in the host magma is actually lower than that in the enclave interior as shown previously (Fig. 4B). This suggests that the bulk host magma may not have been the reactant. Instead, it is the K$_2$O activity in the residual liquid/fluid that is of interest. As we will show below, the K$_2$O content or K$_2$O/CaO ratio of interstitial liquids/fluids increases substantially during crystallization, thus we hypothesize that it is these interstitial liquids that are involved in the reaction rather than the bulk magma (crystals + liquid) itself.

We can evaluate this hypothesis by modeling the major element evolution of the residual liquid during crystallization of the host magma using the thermodynamic MELTS application (G. Ch往来o and C. Sack, 1985; A. Asimow and G. Ch往来o, 1998). This was done for variable bulk H$_2$O contents (0–4 wt%) over a range of pressures (2–3 kbar) applicable to emplacement of the Bernasconi Hills Pluton as inferred from the crystallization pressure map by Ague and Brimhall (1988) for plutons in southern California. We assumed closed system equilibrium conditions because crystal–liquid segregation of felsic magmas is relatively inefficient. All of our MELTS calculations reproduce the main constituent mineral phases observed in natural samples (Qtz, Plag, Amp, Kfs) except biotite, which was not stabilized. This may be due to the lack of comprehensive thermodynamic models for biotite in MELTS. In any case, biotite mode is low in the felsic host and, based on texture, appears late in the crystallization sequence. Because our model is focused on the composition of residual liquids in the felsic host, the effect of biotite on liquid compositions is small for most of the crystallization history.

Our modeling results indicate that K$_2$O/CaO begins to rise significantly in the residual liquid at melt fractions of 0.55 to 0.6 (Fig. 8A). This melt range suggests that biotite-rich rinds form when residual liquid fractions decrease to values below 0.5. The increase in K$_2$O/CaO in our modeled residual liquid is due to segregation of Ca into feldspar rather than to a dramatic rise in the K$_2$O content of the magma. As shown in Fig. 8A the increase in K$_2$O/CaO becomes more pronounced with increasing H$_2$O content in the melt.
We can use trace element systematics as additional constraints. Qualitatively, the REE signatures of the rinds require reaction with a highly evolved residual liquid: REE abundances overall are enriched by at least a factor of 2 compared to the host magma and Eu is highly depleted. The only process that could generate this signature is segregation of a plagioclase-bearing assemblage, such that the Eu behaves compatibly and is sequestered into plagioclase while the remaining REEs behave incompatibly and remain with the residual liquid, resulting in a large Eu depletion relative to other REEs. The extent to which REEs can be fractionated and enriched by crystallization can be quantified by modeling the REE evolution of residual liquids formed by equilibrium crystallization of the host magma (given the small length-scales considered here we assume equilibrium crystallization). Our starting composition was assumed to be the average measured REE content of the host monzogranite. Crystallizing phases are assumed to be in equilibrium with the residual melt. The average REE composition of rinds is used in conjunction with modeled REE patterns to estimate the melt fraction range of rind formation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Modeling residual liquids with REEs and major oxides. Melt fraction is indicated by color as shown in A. (A) Evolution of residual liquids as constrained by K$_2$O/CaO ratios using the MELTS thermodynamic program (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) for magmas with 0, 1, and 4 wt% initial H$_2$O. Calculated magma temperatures vary based upon initial H$_2$O content; 1113 °C to 960 °C (anhydrous), 1045–706 °C (1 wt% H$_2$O), 865–706 °C (4 wt% H$_2$O). Residual liquids and rinds have higher K$_2$O/CaO than the bulk melt and indicate that residual liquids, rather than the bulk host monzogranite, react with enclaves. (B–C) Modeling conditions of rind formation with REE patterns. The starting composition (F = 1) is average host monzogranite and the relative proportion of crystallizing phases is taken from petrographic mode estimates of the host monzogranite. Crystallizing phases are assumed to be in equilibrium with the residual melt. The average REE composition of rinds is used in conjunction with zircon-free models. The range of melt fractions between 0.15 and 0.3 (Fig. 8B). The range of melt fractions predicted by this model corresponds to a temperature range of ~700–760 °C at 2 kbar and up to 770 °C at 3 kbar as estimated by our MELTS calculations for a melt with 1 wt% H$_2$O. Given the uncertainties in partition coefficients and phase proportions, the modeled absolute abundances and REE enrichment/depletion may not match exactly what we see in the rinds, but this is not a major concern because it is the overall shape of the REE abundances (i.e., anti-correlated behavior of Eu relative to HREEs) that are of interest. These low melt fractions imply that the formation of the rinds must have taken place during the later stages of the Bernasconi magma chamber. Such extreme fractionation also explains the relative depletions in Sr seen in the rinds (Figs. 4C) as Sr would be sequestered into plagioclase during earlier stages of the magma chamber.

Zircon saturation temperature estimates (Watson and Harrison, 1983; Miller et al., 2003) for the host rock provide a means of determining whether biotite-rich selvages and schlieren could have formed by direct crystallization of the host magma as opposed to
enclave-magma reactions. We calculate zircon saturation temperatures of \( \sim 850^\circ C \), which represent minimum bounds on temperature. These temperatures are above the thermal stability of biotite for the pressures considered here (Spear, 1995; Patiño Douce and Harris, 1998; Miller et al., 2003). This suggests that the host magma had not stabilized biotite at the time of zircon saturation. The fact that large concentrations of biotite within the host rock, such as enclave rinds and schlieren, are only observed in association with enclaves and that, elsewhere, biotite is only a scarce intergranular phase suggests that most of the biotite is produced by enclave–residual melt reactions late in the crystallization history of the magma.

7.3. Reaction-limited mixing and the origin of schlieren

Enclave–rind relations observed in the field demonstrate that new rinds form by continuous influx of residual liquids/fluids into the enclave as older rinds are eroded from the parent enclave (Fig. 1B). Thus, mechanical mixing and rind formation appear to be coupled. Our measurements of enclaves and biotite-rich selvages indicate that biotite-rich rinds can preferentially deform because they are rheologically weak compared to the solid enclave interior, but rather rotate within the magma. Rinds on the other hand can be mechanically mixed and more easily homogenized into the host magma, potentially enabling mafic–felsic mixing of otherwise solid mafic enclaves. Similarities in the mineralogy and texture of rinds, selvages and schlieren strongly support the hypothesis that rinds erode from enclaves, become selvages and develop into schlieren with increasing strain as illustrated in Fig. 6. In some cases attenuation is so extreme that schlieren are almost texturally indistinguishable from the host monzogranite.

Deformable, biotite-rich rinds can only form when the following conditions are met: (1) \( K_2O \) and \( H_2O \) activities in the residual liquids are high enough to stabilize biotite, (2) transport rates of \( K \) or residual liquids into the rind are fast enough to facilitate continuous reaction, and (3) enclaves and host magma must be within the thermal limit of biotite stability. The first condition implies that the formation of biotite-rich rinds does not occur in dry felsic systems, so mixing basalts into dry rhyolites would be predicted to be inefficient. Water may therefore play a fundamental role in the formation of rinds. Our thermodynamic calculations indicate that once a free fluid phase is formed, that is, once the residual melt is water-saturated, the system exhibits eutectoid behavior and temperature is buffered over a large range of melt fractions (Vielzeuf and Holloway, 1988; Patiño Douce and Johnston, 1991) as seen by the increasing nonlinearity of \( F \) versus \( T \) with increasing water contents (Fig. 9). This is because the release of latent heat of crystallization is delayed to low temperatures rather than uniformly released throughout the entire crystallization interval (Fig. 9). Additionally, if the melt is saturated in \( H_2O \) it can remain mobile for a longer period of time, allowing more time for rind-forming reactions to take place as well as erosion and deformation of eroded rinds. The presence of a free-fluid phase may also increase the rate of rind formation because chemical diffusivities are faster in water than in silicate melts, thus satisfying the second condition above. Enclaves and the host magma are likely at thermal equilibrium during the later stages of a magma chamber (i.e. when rinds are predicted to form), and our thermodynamic calculations suggest that both are within the thermal stability of biotite by that time, thus satisfying the third condition above. Reactive formation of rheologically weak rinds may be the rate-limiting step for efficient homogenization of mafic materials in felsic-dominated systems. We suggest that schlieren deformation fabrics and orientations reflect late-stage magma chamber processes involving flow of a crystal-rich mush.

7.4. Reactive processes and implications for the formation of intermediate rocks

Reaction between mafic and felsic phases has been alluded to by others as a potentially important process in the generation of intermediate magmas. Chapman (1962) proposed the concept of a pseudo-chill margin on diabase dikes at Mount Desert Island, Maine. Although these dikes have a greater abundance of primary mafic minerals (pyroxenes, olivine) compared to the enclaves described here, the pseudo-chill margins share some petrographic characteristics with biotite-rich rinds. For example, both are fine-grained and more biotite-rich than associated mafic rocks. Chapman suggested that these margins formed by recrystallization at the dike-granitoid contact and do not necessarily represent true chill margins. This view was largely dismissed (Blake et al., 1965; Walker and Skelhorn, 1966), but our results support the suggestion by Chapman that these rinds are not isochemical chill margins.
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More recently, Beard et al. (2005) showed that silicic magmas can be generated by reaction between basalts and crustal xenoliths. Interestingly, they also observe that amphibole and biotite are both products of reactive processes.

In addition to work by Chapman (1962) and Beard et al. (2005), other previous studies have noted fine-grained biotite-rich rinds along enclaves and mafic intrusions (Pabst, 1928; Bishop, 1963; Blake et al., 1965; Furman and Spera, 1985; Frost and Mahood, 1987; Wiebe, 1994; Sisson et al., 1996; Wiebe et al., 1997). The fact that biotite-rich rinds have been observed in a variety of felsic plutons suggests that reactive processes may play a role in generating intermediate compositions and implies that the reactive processes recognized in the Bernasconi Hills Pluton occur elsewhere as well. However it remains to be seen whether mixing, even with the help of reactive processes, is the dominant mechanism by which intermediate magmas are formed. A recent study on the Zr and P systematics of arc magmas suggests that crystalliquid segregation, rather than mafic–felsic mixing, is the dominant process of generating intermediate magmas (Lee and Bachmann, in press).

8. Conclusions

We have shown that fine-grained, biotite-rich rinds on mafic enclaves are generated by reaction between solid mafic enclaves and a residual melt or fluid and that these rinds erode from enclaves to mix with the host magma. This is in contrast to previously proposed hypotheses of isochemical quenching, binary mixing, and in-situ differentiation and is supported by the following evidence: (1) rinds are more potassic (~1.8–2.6 wt%), more mafic (~3.4 wt% MgO and ~12–13 wt% Fe2O3, respectively), and more enriched in REEs than both enclaves and host monzogranite; (2) enclaves are mineralogically zoned with biotite-rich rinds mantling hornblende and quartz-richer interiors; (3) hornblende is often most abundant within the enclave interior, adjacent to rinds and is suggestive of textural re-equilibration; (4) rinds are observed eroding from enclaves into the host magma followed by the formation of new rinds on freshly eroded surfaces throughout the strain history of an enclave; (5) differences in aspect ratios of enclaves and biotite-rich selvages (petrographically equivalent to rinds) indicate that rinds are preferentially deformed and may be mechanically mixed into the host magma.

Petrographic observations and phase relations show that rind formation can only occur when the following conditions are met: (1) K2O and H2O activities in the residual liquid are high enough to stabilize biotite, (2) enclaves and magma are within the thermal stability limit of biotite, and (3) transport rates of K into the enclave are fast enough to facilitate reaction before the host magma becomes rheologically locked. Rare earth element enrichments in rinds suggest that rinds form at low melt fractions (F = 0.15–0.3) and thermodynamic calculations indicate that reactions take place over a temperature range of 700–770 °C and thus late in the life of the magma body when much of the bulk magma is crystallized. However, the eutectic-like behavior of H2O-saturated melts (Fig. 9) suggests that the host melt may remain rheologically active over a range of F within this temperature interval.

Our model of reaction–limited mixing indicates that schlieren in the Bernasconi Hills Pluton represent the mechanical mixing of eroded rinds into the host magma and suggests that structures associated with schlieren are representative of late-stage magmatic processes rather than conditions of emplacement. Because mafic–felsic mixing is limited by these late-stage chemical reactions, it seems likely that mixing of mafic magmas into felsic host magma is not efficient unless the life of a magma chamber can be prolonged just above its solidus.