Microsampling and Isotopic Analysis of Igneous Rocks: Implications for the Study of Magmatic Systems

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Abstract
Isotopic fingerprinting has long been used to trace magmatic processes and the components that contribute to magmas. Recent technological improvements have provided an opportunity to analyze isotopic compositions on the scale of individual crystals, and consequently to integrate isotopic and geochemical tracing with textural and petrographic observations. It has now become clear that mineral phases are commonly not in isotopic equilibrium with their host glass/groundmass. Isotopic ratios recorded from core to rim of a mineral grain reflect the progressive changes in the magma composition from which the mineral crystallized. The sense of these changes and the relationship between isotopic composition and petrographic features, such as dissolution surfaces, can be used to constrain magma evolution pathways involving open system processes such as magma mixing, contamination and recharge.
INTRODUCTION: ISOTOPE RATIOS AS TRACERS

Radiogenic isotope ratios\(^1\) are commonly used in geochemistry as petrogenetic tracers, yielding information on time-integrated elemental fractionation through processes of melting, crystallization, metamorphism, metasomatism, and contamination. Because of the time-dependent ingrowth of daughter isotopes, the isotope ratios of elements such as Sr, Nd, Hf, and Pb can be considered monitors of parent-daughter element partitioning due to past events (Dickin 2005, Faure 1986). On this basis, the spectrum of isotopic ratios can be subdivided into ranges that characterize different sources potentially involved in producing magmas. At one extreme lies depleted mantle, which has, over geological time, attained high \(^{143}\text{Nd}/^{144}\text{Nd}\) (from high \(^{147}\text{Sm}/^{144}\text{Nd}\)), high \(^{176}\text{Hf}/^{177}\text{Hf}\) (from high \(^{176}\text{Lu}/^{177}\text{Hf}\)), and low \(^{87}\text{Sr}/^{86}\text{Sr}\) (from low \(^{87}\text{Rb}/^{86}\text{Sr}\)). At the other extreme is ancient continental crust with corresponding low \(^{143}\text{Nd}/^{144}\text{Nd}\), low \(^{176}\text{Hf}/^{177}\text{Hf}\), and high \(^{87}\text{Sr}/^{86}\text{Sr}\), reflecting long-term incompatible element enrichment. Between these two extremes lie a range of mantle isotope compositions, representing end-members with different enrichments at different times, attesting to long-term plate tectonic processes, such as melt extraction and lithospheric recycling, and an even greater range of isotope ratios within the highly heterogeneous continental lithosphere.

The commonly analyzed radiogenic isotopic ratios of Sr, Nd, Pb, and Hf are not fractionated by processes of melting and crystallization\(^2\) (Dickin 2005, Faure 1986) and have thus become a commonly used tool for fingerprinting source contributions in magma suites. A large body of isotopic data has been collected over the past 30 years from magmatic rocks, in progressively increasing quantity and investigative detail as both techniques and understanding have improved. For much of this time, analyses were largely restricted to powdered whole rocks, based on considerations of required sample mass and the level of detail of the investigation. Further, because whole-rock geochemical analyses for major and trace elements were carried out routinely, an isotopic estimate for the same bulk powder was an obvious consideration.

Studies employing radiogenic isotope ratios as tracers have been based largely on the assumption that fresh, young, magmatic rocks are isotopically homogeneous at the scale of minerals (and their inclusions). Indeed, homogeneity between crystal separates and groundmass has been used in the past as a test of sample integrity with respect to alteration or weathering (Halliday et al. 1984), and therefore as a validation of in situ analytical methods (Christensen et al. 1995). Technical advances in the past decade have enabled us to analyze smaller samples, with no loss of precision (Charlier et al. 2006; Davidson et al. 1998, 2001, 2007; Harlou et al. 2005; Ramos et al. 2004). As a result, studies of magmatic samples have led to the realization that primary isotopic heterogeneity at the grain scale (Cioni et al. 1995, Geist et al. 1988, Simonetti & Bell 1993, Tilling & Arth 1994) and the subgrain scale (Charlier et al. 2006; Davidson et al. 2001, 2007; Harlou et al. 2005; Ramos et al. 2005) is commonplace. This contribution

\(^1\)Throughout the paper, isotope ratios refers to radiogenic isotope ratios.

\(^2\)Strictly speaking, there may be very small mass fractionations, but these are effectively normalized by fractionation corrections during analysis.
reviews the theory and methods of isotopic microanalysis in igneous samples and the interpretations permitted by the data.

**MINERAL-SCALE ISOTOPE DATA: WHAT DO THEY MEAN?**

The basic utility of mineral-scale isotopic data as a petrogenetic tool (Figure 1) relies on the following assumptions:

1. When a crystal begins to grow from magma, the isotopic composition of the crystal is identical to that of the host magma from which it grows.
2. Changes in the isotopic composition of the magma will be reflected in the isotopic composition of the crystal layers that subsequently grow.

Thus, variations in isotopic composition from core to rim of a crystal are a record of the change in isotopic composition that the magma underwent during crystal growth. These principles are referred to as crystal isotope stratigraphy (CIS) (Davidson et al. 1998) and indeed follow many of the laws of simple stratigraphy, albeit at a much smaller scale. Progressive layers or growth zones from core to rim in a crystal represent a time sequence from older to younger in the evolution of the magma from which the mineral crystallized. Dissolution surfaces and significant compositional breaks represent unconformities where crystals were partly dissolved and experienced a time of no growth prior to the resumption of crystallization.

An example of how variations in magmatic composition would affect a crystal growing at a constant rate is given in Figure 2. In (a) crystal A growing from time $t_0$ to time $t$ will have a core with an isotopic composition $R_0$, and a rim with isotope ratio $R$, and at time $t$ will have a bulk crystal isotope ratio of $R_A$. Crystal B, which starts growing later at time $t_1$, will share the same rim isotope composition ($R$) but will have a different core isotope ratio ($R_1$) when compared with A. If the crystals were separated whole from the rock, they would have bulk compositions that are different ($R_A$ and $R_B$, respectively), reflecting the integrated isotope ratio over the different time intervals over which they grew. The whole rock, in the most simplistic case being a mixture of A and B crystals and liquid (glass), has an isotopic ratio $R_{WR}$ somewhere between that of the final liquid ($R$) and that of the lowest isotope ratio bulk crystals ($R_A$). The exact value of $R_{WR}$ depends on the relative amounts of A, B, and glass, and of the concentrations of the element of which isotope ratio $R$ is composed, in these three components. A population of crystals nucleating and growing progressively through time from $t_0$ to $t$ in the magma would define a linear distribution in $R$ versus crystal size (see inset). The larger crystals have grown for longer at the same growth rate, and will have lower whole-crystal isotope ratios, because they started growing earlier when the magma was at its lowest isotope ratio.

In Figure 2b evolution of the liquid is punctuated by a recharge event at $t_E$, which instantaneously lowers its isotope ratio. Again, crystals A and B nucleate at times $t_0$ and $t_1$, respectively, whereas crystal C nucleates at $t_0$ but undergoes partial dissolution at $t_E$ before resuming growth. In this case, the bulk crystal isotope ratio versus time curves mimics those of the magma with a downward spike at $t_E$. The crystal that began growth at $t_0$ would decrease its bulk isotope ratio after recharge, but the effect would be buffered compared with the dramatic change in $R$ of the liquid because
Figure 1

Schematic illustration of the principles of crystal isotope stratigraphy (CIS)—magma system schematic illustration courtesy of Gary Hincks. (a) A mantle-derived isotopic signature is transferred into a system of transport and storage in the lithosphere. Isotopic signatures are modified by processes such as contamination, magma mixing, and recharge—as represented by the arrow on the graph of initial isotopic ratio (R_i) versus time. The rock resulting at time of eruption/emplacement (e) will have a different isotopic ratio from that of the magma first introduced. But the crystals that grow during magma evolution (and the entrapped melt inclusions) provide a record of isotopic evolution with time. The completeness of this record depends on the time at which the crystals started (and finished) growing in the system. Early-formed crystals and crystal cores may record the earliest stages—including the original input composition, whereas late-formed crystals or crystal rims record conditions closer to those pertaining at eruption/emplacement. (b) Magmas, which may have different compositions, are homogenized before crystals begin to grow. In this case, CIS can provide no useful additional information. The key to the approach is integrating petrographic observations and data with in situ isotopic analysis. Note that the principles summarized here are equally valid if the isotopic variability is entirely introduced from the mantle rather than as a result of crustal processes. It should nevertheless be appreciated that the isotopic variability, however introduced, must exist at the site of crystallization. This site of crystallization is typically in the crust, as can be verified by mineral stability and mineral and melt inclusion barometry.
there is already a large volume of crystal with lower isotope ratio. In contrast, crystal B, which began to grow at \( t_1 \), is much smaller and therefore the bulk crystal is more sensitive to the change in isotope composition of the host liquid. It is possible also for a crystal such as A to undergo dissolution in response to the event at \( t_E \). In this case, the bulk crystal R versus time curve would show a discontinuity at \( t_E \) with R dropping to a value representing the residual bulk crystal after the outer zones had been resorbed (R_D). Note how the bulk crystal isotope ratios of the late-nucleating crystal (R_b) and the crystal that undergoes dissolution (R_C) rise more steeply after \( t_E \) because the volume of crystals B and C at \( t_E \) is smaller than that of crystal A, so the subsequent overgrowths from the magma have a relatively greater effect. A population of crystals nucleating and growing progressively through time in this magma (undergoing a recharge/mixing event at time \( t_E \)) would define an R versus size curve with a minimum corresponding to the size of crystals that had nucleated around \( t_E \) (see Figure 2b inset).

From the above schematic illustration, we can consider three separate scales smaller than that of the whole rock: bulk mineral separates, single whole grains, and the subgrain (growth zone and/or inclusion) scale. In many cases, a full appreciation of the isotopic heterogeneity in a sample requires a combination of data enveloping these scales (Figure 3).
Figure 3
Schematic comparison of information provided from analysis of bulk mineral separates (left panel), individual whole grains (middle panel), and intragrain isotopic profiling (right panel), respectively. The upper illustration shows four crystals (A–D) from the same rock, each with different isotopic zoning patterns. Bulk separates average isotopic compositions and lead to limited variation compared with whole rock. Single-crystal analyses integrate the isotopic composition over the entire crystal (compare with Figure 2). Only with subgrain (CIS) analysis does it become clear that the color-coded zones represent discrete events, which are shared to different extents by the four crystals.

DETERMINING IN SITU ISOTOPE RATIOS: METHODOLOGY
The application of in situ isotopic profiling of natural materials extends well beyond the magma systems that are the focus of this contribution. $^{87}$Sr/$^{86}$Sr profiling of shells and fish earbones (otoliths), for instance, can provide information on the growth of organisms under changing environmental conditions (Kennedy et al. 2002). Metamorphic processes (fluid flow and mineral reactions) can also be tracked through isotopic profiling of metamorphic mineral grains (e.g., Christensen et al. 1989).
As seen in Figures 1–3, interrogating the crystal isotopic record to recover a faithful history of magma system evolution relies on the coincidence of several criteria. The crystal species should ideally cover a crystallization range spanning as much as possible of the temperature gap between liquidus and solidus to record as much of the magmatic history as possible. Given the complex behavior of many magma systems, it helps if the crystals are not easily dissolved in response to sudden changes in composition in magmatic composition or water content, as might be expected during episodes of recharge or magma mixing (Walker et al. 1979, Grove et al. 1982). On the other hand, some response to processes (sudden changes in composition of solid solution minerals and/or partial dissolution surfaces, e.g., Ginibre et al. 2002, 2004) serve as useful petrographic guides (Wallace & Bergantz 2005). Matters are helped if crystals are sufficiently large and abundant that they can be texturally characterized or subdivided into populations. Entrapment of primary melt inclusions in the crystals is an advantage. Finally, of course, the crystals need to contain the elements of interest for isotopic analysis in sufficient abundance to make analysis feasible.

In this regard, zircons have been long-used as isotopic tracers, as they are very resilient in magma systems, contain high abundances of many isotopically relevant elements (U, Th, Pb, Hf, Sm, Nd), and can be characterized by methods such as back-scattered electron (BSE) imaging, cathodoluminescence (Pagel et al. 2000), or textural studies (Bindeman 2003) and thereby can be distinguished as distinct populations. Indeed, owing to their importance in U-Pb dating studies, zircons are effectively the subject of a distinct subbranch of studies in igneous petrogenesis and therefore are not covered in this review. The interested reader is referred to Hanchar & Hoskin (2003).

There are a number of analytical approaches in use to determine isotope ratios of Sr, Pb, Nd, and Hf in situ from minerals and glasses. The principal approaches are ion probe (secondary ionization mass spectrometry; SIMS), laser ablation inductively coupled plasma (ICP) multi-collector mass spectrometry (LA-MC-ICPMS), and micromilling followed by wet chemistry and thermal ionization mass spectrometry (micromilling-TIMS). For the most part, these are complementary, so there is not a given method of choice. Nevertheless, it is important to choose a method commensurate with the specific problem of interest. Issues that need to be considered are

1. Analytical precision needs to be sufficient to resolve among individual sample sites within the overall range of the isotopic data. The larger the isotopic range of the system, the less stringent the need for precision. Thus, a precision of 200 ppm (e.g., 0.704 ± 0.00014) may be entirely adequate for a system with a total range in 87Sr/86Sr of 0.01 (say 0.704 to 0.714), but of no use where the total range is 0.0001 (say 0.7040 to 0.7041).
2. Spatial resolution needs to be adequate for sampling at the scale of the mineral growth zones or melt inclusions (typically 10–100 μm).
3. Interferences (the presence of isotopes of different elements with similar mass—such as 87Rb on 87Sr) and isotopic mass-fractionation effects (changes in isotope ratio that occur during analysis, due to, for instance, kinetic effects
evaporation from a filament or ablation from a substrate) need to be characterized and corrected for accurately (e.g. Thirlwall 1997).

4. The method needs to be sufficiently efficient (time, resources) to allow enough analyses to be collected to characterize the system adequately.

Given these constraints, it is immediately clear that for a given approach there is a trade-off between spatial resolution, element concentration, and precision. Precision is strongly related to the flux of ions of a specific isotope arriving at the mass spectrometer detector. Thus, for a given precision, the higher the concentration of the element in the sample, the less sample is needed (see Supplemental Figure 1, follow the Supplemental Material link from the Annual Reviews home page at http://www.annualreviews.org)—modern TIMS instrumentation can achieve excellent precision and reproducibility for Sr samples ≪ 10 ng (Charlier et al. 2006). Minerals with high concentrations of the element of interest can be analyzed at smaller spatial resolution than those with low abundances. Thus, Pb isotope ratios in alkali feldspars can be analyzed at small spot sizes but Pb isotope ratios in plagioclase feldspars are difficult, although not impossible, to measure (Mathez & Waight 2003), requiring much greater sample volumes to account for the lower Pb concentrations in the latter.

The second factor influencing precision and accuracy for a given ion flux at the detector is the capacity to correct confidently for interferences. SIMS and LA-MC-ICPMS approaches are more vulnerable in this regard than micromilling followed by TIMS because the latter involves a chemical separation and purification procedure. Indeed, SIMS analysis for Sr isotope ratios is currently unable to return sufficient precision for most isotopic tracing studies because isobaric interferences of $^{87}$Rb on $^{87}$Sr cannot be adequately accounted for.

Many workers have opted to focus on feldspars for CIS studies. Plagioclase is a common mineral in many mafic to intermediate magma systems, crystallizing over a wide P-T range. As a solid-solution mineral with a composition sensitive to magma $P_{H_2O}$, plagioclase responds to changes in melt composition and $P_{H_2O}$ (Sisson & Grove 1993), exhibiting abrupt changes in anorthite (An) content and trace element content (Barbey et al. 2005, Costa et al. 2003, Zellmer et al. 1999) commonly accompanied by distinct and easily-observed dissolution surfaces (Ginibre et al. 2002, 2004). Most importantly, plagioclase contains high abundances of Sr, making microsampling for Sr isotope studies viable. LA-MC-ICPMS determinations of $^{87}$Sr/$^{86}$Sr in plagioclase can now be carried out with reasonable levels of precision and accuracy (Ramos et al. 2004). Nevertheless, interferences, backgrounds, fractionation effects, and the limited flux of ions per unit time for a material of given Sr concentration mean that micromilling, chemical separation, and TIMS analysis currently provide superior accuracy, precision, and spatial resolution (Charlier et al. 2006). The limitations on the latter method are the need to maintain low blanks (typically <10 pg Sr, representing <1% of a 1 ng sample) and the unavoidably time-consuming nature of the analysis. The choice between the methods should normally be dependent on the capacity to achieve adequate precision to distinguish variations in $^{87}$Sr/$^{86}$Sr within the range presented by a given magma system.
Alkali feldspar has received attention for similar reasons as plagioclase (e.g., Gagnevin et al. 2005a,b; Zellmer & Clavero 2006). It is a common mineral in evolved magmas such as granites and, like plagioclase, typically contains abundant Sr. However, the high Rb contents of alkali feldspar can be an analytical challenge to in situ approaches, which need to account for mass interferences of $^{87}\text{Rb}$ on $^{87}\text{Sr}$. For non-zero-age rocks (which includes all plutons), the Rb/Sr ratio must be measured simultaneously to account for radiogenic ingrowth. Thus, for alkali feldspar, spiked wet-chemical methods are currently technically easier than laser-ablation measurements for the acquisition of precise and accurate Rb-Sr data.

Alkali feldspar has the added advantage of typically containing much higher Pb concentrations than plagioclase—making Pb isotope studies also tractable through LA-MC-ICPMS or microsampling and TIMS. Pb isotope ratios in K-feldspar (50–100 ppm Pb) can be analyzed with ~100 micron laser spot sizes (Gagnevin et al. 2005b). The Pb isotopic compositions of K-feldspars as determined by LA-MC-ICPMS have consequently been used successfully in terrane correlations (Connelly & Thrane 2005) and in provenance studies (Tyrell et al. 2006).

Melt inclusions have been the subject of Pb isotopic investigations by SIMS (e.g., Saal et al. 1998, 2005; Shimizu et al. 2005) and LA-MC-ICPMS (Jochum et al. 2004), although sensitivity to common Pb is insufficient and only inter-isotope ratios of $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$ are reported. LA-MC-ICPMS has also been used by Jackson & Hart (2006) to determine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on melt inclusions, although their technique is strongly limited to larger, high-Sr inclusions, typical of enriched OIB and the required interference corrections (for species of different elements or molecules but with the same mass, see Thirlwall, 1997) are extremely convoluted. Sr isotope ratio measurements on individual melt inclusions with Sr concentrations more typical of tholeiitic basalts have recently been made by Harlou et al. (2005) using micromilling-TIMS. This offline approach employs dissolution and ion exchange column chemistry enabling Rb to be separated, thus interferences are obviated and precise Sr isotope ratios can be acquired at sub-nanogram levels. A ~10% aliquot of the micromilled sample can also be analyzed via ICPMS for trace element concentrations.

Much has been written in the technical literature about the various methodologies and advantages of each method (compare with summary of approaches in the mid-1990s; Neal et al. 1995), but the short summary of the relative advantages and disadvantages given in Table 1 might be helpful to allow researchers to pick the appropriate tools to tackle specific problems. This review focuses on the relatively new approach of micromilling-TIMS. Notwithstanding the disadvantages listed in Table 1, it delivers high spatial resolution and the highest possible precision for a given sample size.

**Interpreting Results 1: Accounting for Postcrystallization Modification of Isotopic Ratios**

A simple generic template for the interpretation of isotopic profiles across crystals under ideal circumstances is given in Figure 4. Interpretations of isotopic data as
Table 1: Comparison of isotopic microsampling methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Spot size</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
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<tbody>
<tr>
<td>SIMS</td>
<td>30–50 μm</td>
<td>Very good spatial resolution</td>
<td>Fractionation and interference effects require rigorous standardization</td>
<td>Ireland 1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Small beam sizes produce low number of ions per unit time and limit precision</td>
<td></td>
</tr>
<tr>
<td>LA-ICPMS (multicollector)</td>
<td>Typically 50–200 μm</td>
<td>Rapid large numbers of samples can be analyzed in short times</td>
<td>Fractionation and interference effects are still not well characterized and may need more rigorous matrix-matched standard comparisons</td>
<td>Waight et al. 2002, Ramos et al. 2004, Davidson et al. 2001</td>
</tr>
<tr>
<td>Micromill-TIMS</td>
<td>&gt;30 μm</td>
<td>Chemical separation and TIMS leads to excellent precision and obviates interference corrections</td>
<td>Offline mechanical milling and chemistry is very time consuming Blanks have to be carefully controlled and monitored, maintained at &lt;1% Impractical to characterize very large numbers of samples</td>
<td>Charlier et al. 2006</td>
</tr>
</tbody>
</table>

1 Area of beam/mill hole. LA-ICPMS methods may raster over a larger area to improve precision. Depth of SIMS analyses is a few micrometers, whereas LA-ICPMS spot is deeper (but depth is typically less than hole width to prevent significant signal decay and more severe fractionation effects). Micromill-TIMS hole depths are also less than width—in the most recent approaches described by Charlier et al. (2006) drills are tapered and therefore volume is dominated by the shallow part of the hole.

Phenocryst: mineral that has crystallized directly from the magma (rock) in which it is hosted.
General representation of possible interpretations of CIS data based on (a) comparison of isotope ratios among cores and rims of crystals and (b) nature of the isotope profile zoning. In (a), the schematic models have no explicit association with particular depths in the crust [other than magmas tend to ascend so in cases of polybaric crystallization cores will crystallize earlier (deeper) and rims later (shallower)]. In (b), R represents schematic isotope ratio profile across the section line in the crystal where color shading represents isotope ratio.
DIFFUSION AND TIMESCALES

Diffusion distances inside the crystal are proportional to $\sqrt{Dt}$, whereas growth distances are proportional to $Gt$ ($D =$ diffusivity, $G =$ growth rate, and $t =$ time). At short timescales, diffusion is dominant, but as $t$ grows, $Gt$ overtakes $\sqrt{Dt}$ in importance. For example, in a mineral of intracystal diffusivity, $D = 1 \times 10^{-20} \text{ m}^2\text{s}^{-1}$, growing at a rate of $G = 1 \times 10^{-13} \text{ ms}^{-1}$, growth effects are more significant than diffusion effects at timescales of over $1 \times 10^6 \text{ s}$, or roughly 12 days, corresponding to a layer of crystal 100 nm thick. Thus, effects of shorter duration than 12 days occurring during crystal growth will suffer from some amount of diffusional interaction with the surrounding magma during the period of growth. If growth is slower or intracrystalline diffusion faster, this critical timescale increases. If in the above case the growth rate was ten times slower, the critical timescale is 100 times greater at $1 \times 10^8 \text{ s}$ (about three years) and the band disrupted by diffusion during growth is wider, at one micrometer. These length scales are, for plagioclase at least, generally much smaller than the smallest analyzable zone size, and so the assumption that the crystal was in isotopic equilibrium with melt at the time and point of crystallization can be regarded as valid.

(Costa et al. 2003, Morgan et al. 2004, Zellmer et al. 1999), and tracer diffusion is effectively faster at attaining near-equilibrium than the required volume diffusion for isotopic resetting (see sidebar Diffusion and Timescales).

We can therefore be confident that mineral scale (at least $\geq 50 \mu \text{m}$) isotopic variations in volcanic rocks effectively record a snapshot of the magma system prior to the time of eruption. Perhaps surprisingly, the few studies that exist of mineral-scale isotopic studies in plutonic rocks, which have cooled more slowly, demonstrate that minerals in plutonic rocks are also not isotopically equilibrated (Gagnevin et al. 2005a,b; Tepley & Davidson 2003; Waight et al. 2000, 2001) (see Supplemental Figure 3 for the relationships among temperature and composition that control diffusivity in minerals and equilibration timescale). In the case of plagioclase, the higher emplacement temperatures of more mafic intrusions are offset by lower diffusivities of Sr in the more anorthite-rich plagioclase, compared with those of albite-rich plagioclase, which characterizes lower temperature granites (Cherniak & Watson 1994, Giletti & Casserly 1994).

Interpreting Results 2: Integrating Isotope Data with Major and Trace Element Data

The true potential of isotopic microanalysis as an investigative tool is only fully realized when it is combined with trace-elemental, major-elemental, or textural data (e.g., Müller 2003) informative of other processes and factors (Table 2). Work based
Table 2  Petrographic and geochemical approaches that may be integrated to fully appreciate magma system evolution

<table>
<thead>
<tr>
<th>Technique</th>
<th>Information</th>
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| Microisotopic studies            | • Isotopic evolution of magma system  
• Not affected by short-term fluctuations in intensive parameters such as P, T, H2O, therefore, gives a relatively simple view of a single, changing parameter |
| CSD                              | • Population growth history—gives time aspect on population development  
• Significant changes in crystallization behavior or mixed populations can be seen in kinked CSDs |
| BSE imaging                      | • Compositional information [e.g., feldspar crystals (Ginibre et al. 2002)]  
• Textural features such as dissolution surfaces representing changes in T, P, H2O |
| 3-D reconstruction (e.g., X-ray CT, serial section) | • Direct information on size, shape, and distribution of crystals (e.g. Mock & Jerram 2005, Gualda 2006)  
• Identification of mixed populations  
• Provides ideal sampling strategy for micro analysis |
| EPMA and SIMS analysis           | • Measurement of major, minor, and trace elemental abundances at the microscale, indicative of the chemical changes associated with textural changes. Allows processes to be associated with the variations seen in BSE imaging  
• Due to the small scale of the analyses, diffusion profiles are often observable that can yield timescale information (Morgan & Blake 2006) |
| LA-ICPMS                         | • Trace elemental variations, albeit at a larger scale than via SIMS or EPMA. An advantage is speed of analysis, but the technique is destructive and leaves less material for isotopic sampling. Diffusion profiles are not readily measurable via LA-ICPMS owing to the large size of analysis points |
| Cathodoluminescence              | • Good for understanding internal crystal structure. Also, different colors may be associated with different processes or paragenesis and so may aid the subdivision of samples with reference to chemical data (e.g. Ginibre et al. 2004) |

on major-element contents of feldspar crystals has attempted to address similar problems, considering crystals in terms of their relationship to a “phylogeny” (Wallace & Bergantz 2005). In this conceptual case, crystals all share the same recent history—potentially represented by the rim compositions grown immediately before eruption—but diverge in common characteristics as their histories are traced back through time from rim to core. Isotopic work can simplify this process in terms of removing the high-frequency fluctuations from the signal, and for the relatively straightforward system of Stromboli Volcano this was achieved for a single lava sample (Morgan et al. 2005)—see case study below, yielding information on crystallization versus contamination and cumulate incorporation processes. Comparing the stratigraphies of several crystals in a given sample may therefore give a better overall record of the evolution of the magma, which the rock represents, but remains highly time-consuming work. The principles and utility of isotopic microanalysis in volcanology can be summarized in a few illustrative case studies, presented below.
SINGLE-CRYSTAL VERSUS CORE-TO-RIM DATA (CASE STUDIES FROM EL CHICHÓN, NAGARUHOE, AND TAYLOR CREEK)

To illustrate the theoretical cases discussed above, we present case studies from contrasting magma systems. At Ngauruhoe Volcano (New Zealand) and El Chichón (Mexico), isotope heterogeneity in recently erupted basaltic andesite and trachyandesite lavas, respectively, argue for open system processes occurring during differentiation (Hora 2003, Tepley et al. 2000). At Ngauruhoe, $^{87}\text{Sr}/^{86}\text{Sr}$ data from single plagioclase crystals, albeit limited, reveal crystal cores with lower $^{87}\text{Sr}/^{86}\text{Sr}$ and crystal rims with higher $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 5a). This observation is consistent with growth of crystals from a progressively more contaminated magma. In a simple model (Figure 2a) we would expect larger plagioclase crystals to have a lower (integrated) single-grain $^{87}\text{Sr}/^{86}\text{Sr}$ than the smaller ones, and this is indeed observed for eruptions in 1870, 1949, and 1954. We would also expect the groundmass (representing the liquid) to have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ than the minerals. Generally, this is the case. Where analyzed, clinopyroxene has relatively low $^{87}\text{Sr}/^{86}\text{Sr}$, suggesting that it crystallized mainly during the earlier stages of evolution when the magma had relatively low $^{87}\text{Sr}/^{86}\text{Sr}$. There are, however, difficulties in such a simple explanation. In the 1974–75 eruption, for instance, the small plagioclase crystals have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$. This can be explained by sequestering of early-formed phases into cumulates with later remobilization just before eruption, or simply by mixing of crystal populations that have undergone separate differentiation events in different parts of a magma system. The observations implicate open system differentiation, but underscore the need to (a) obtain isotopic data for a large population of crystals in any given rock and (b) combine these data with textural and other geochemical observations, which will help constrain the process or processes that dictated magma evolution pathways (Table 2).

At El Chichón Volcano (Mexico), a similarly diverse suite of isotope data from mineral separates of the 1982 eruption (Tilling & Arth 1994) has been investigated at the single-crystal scale (Figure 5b). The El Chichón plagioclase population is more conducive to in situ isotopic study than that at Ngauruhoe because plagioclase crystals are considerably larger (up to 5 mm compared with typically <1 mm), and Sr concentrations are very high (1500–2000 ppm compared with 200–700 ppm). Tepley et al. (2000) report consistent core-to-rim variations for El Chichón feldspars, with rim $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than those of the core. Thus, the magma from which plagioclase rims grew was apparently less contaminated than that from which the cores originated. Furthermore, changes in isotopic composition from core to rim appear to correlate with textural features (dissolution surfaces), which suggests that changes in isotopic composition of the magma reflect discrete events such as magma recharge, that produces an environment in disequilibrium with the growing crystal (Davidson et al. 2001, Davidson & Tepley 1997, Tepley et al. 2000).

Finally, in a rhyolite dome of the Taylor Creek Complex (New Mexico, USA), core-to-rim isotopic traverses in single sanidine crystals can be compared with single-crystal data across the spectrum of sizes (Figure 5c; Knesel et al. 1999). In this example, the single crystal data exhibit a pattern of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ with size...
up to a maximum value, after which $^{87}\text{Sr}/^{86}\text{Sr}$ decreases. Single-crystal data for three individual sanidines of different size show the same overall pattern, with $^{87}\text{Sr}/^{86}\text{Sr}$ low in the core, increasing rimward to a maximum value, then decreasing toward the rim. The single-crystal data set and the core-to-rim traverses are consistent with growth of the crystals in a progressively contaminated rhyolite magma, followed by growth in a magma with decreasing $^{87}\text{Sr}/^{86}\text{Sr}$. The cause of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ was suggested by Knesel et al. (1999) to be recharge and mixing with less contaminated rhyolite (cf Hervig & Dunbar 1992). In contrast with the El Chichón case, growth appears to take place during mixing, suggesting that mixing might be more protracted owing to the high viscosities of the rhyolite liquids. At El Chichón, mixing led to dissolution and subsequent crystal growth from a hybridized liquid with a lower but relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$.

In all three cases, mixing of melts of different isotopic composition appears to be an important process (Figure 5d). At Ngauruhoe and El Chichón, the mixing is reflected in disequilibrium textures between growth zones. At Ngauruhoe, the magma mixed is more differentiated and has higher $^{87}\text{Sr}/^{86}\text{Sr}$, whereas at El Chichón (repeated) magma mixing appears to reflect recharge by a more primitive melt. At Taylor Creek, the mixed magma was evidently similar in composition (rhyolitic) and did not produce disequilibrium features, but was isotopically distinct, being lower in $^{87}\text{Sr}/^{86}\text{Sr}$.

**PHENOCRYSTS, XENOCRYSTS, AND ANTECRYSTS**

The case studies summarized above demonstrate that a rich and detailed record of magma evolution can, in principle, be extracted by applying isotope studies at the mineral-grain scale. However, in all three examples, a single, simple pathway of magma evolution cannot account for all of the observed data. Models such as those in Figure 2 predict that all crystals should have the same isotopic compositions at their rims (identical to the host groundmass), and that smaller crystals should typically have higher bulk $^{87}\text{Sr}/^{86}\text{Sr}$ than larger ones. We propose that the crystals found in many magmatic rocks may not have shared common histories and crystallized from the liquid (glass/groundmass) in which they are now hosted, but rather represent a liquid (glass/groundmass) laced with a crystal cargo that has been inherited from liquids that existed at different places and times in the magma system. The crystals are then not true phenocrysts. Neither are they strictly xenocrysts, as they are grown and recycled from closely related progenitor magmas rather than accidentally incorporated from older unrelated wallrocks. W.E. Hildreth (personal communication) has suggested the term “antecryst” to denote phases that originate in the magma system but are not true phenocrysts (cf Charlier et al. 2005). On this basis, we propose that magmatic rocks can be represented by mixtures of liquid (solidified to glass/groundmass), recycled antecrysts, and true phenocrysts (Figure 6). Most microlites, grown during the last stages of eruption, are of similar composition to true phenocryst material (Tépley et al. 1999). Large crystals, which have traditionally been referred to as phenocrysts, can be shown in many cases to be antecrysts, albeit commonly rimmed by equilibrium phenocryst material. In the representation of Figure 6, closed systems
Figure 5
Case studies of whole crystal versus single crystal isotope variations. (a) Ngauruhoe (after Hora 2003), (b) El Chichón (Teply et al. 2000), (c) Taylor Creek (Knesel et al. 1999), (d) Summarizes schematically the simple magma evolution pathways inferred for the three systems from combining C/S with textural observations and major element (electron microprobe) data.
Figure 5
(Continued)
lie only along the line P-L and would be expected to be isotopically homogeneous at the mineral scale. All other magmas are amenable to investigation by CIS provided there is measurable isotopic diversity within the system. To apply CIS however, crystal types ideally need to be distinguishable on the basis of petrographic criteria. True xenocrysts—material accidentally picked up from older preexisting wallrocks—can usually be identified petrographically and are easily identified using the in situ microanalytical isotopic approaches discussed above (Chadwick et al. 2005, Perini et al. 2003, Waight et al. 2001).

This realization is not necessarily new—researchers studying andesites have for many years recognized the disequilibrium textural features and mineral compositions of phases in orogenic magmas, and have used this observation to underscore the importance of magmatic mingling and mixing (e.g. Bacon 1986, Clynne 1999,
WHAT SIGNIFICANCE HAS THE ISOTOPIC COMPOSITIONS OF CRYSTAL RIMS?

In our simple conceptual model (Figure 2), the outermost rims of the crystal are in equilibrium with the isotopic composition of the host magma—represented in the magmatic rock as glass or groundmass. As we have seen from the case studies summarized above, crystal rims do not always share the isotopic composition of the groundmass. Of course this may be due in part to the resolution at which we can sample the crystal rims; if less than approximately 50 μm, the analytical method used (micromill or laser) will likely be sampling a mixture of rim material and internal zone(s). Nevertheless, the use of textural features to constrain sampling strategies means that we can be aware of this limitation, and, in general, we can be confident
that we are sampling a texturally consistent rim inferred to be in equilibrium with the groundmass of the host. Thus, isotopic differences between rim and host magma imply that either (a) the host magma changes its isotopic composition more quickly than crystal growth on the scale that we can sample (∼50 μm) can reflect such changes, or (b) crystals have been recently brought into contact with the liquid in which they are now hosted and, at the time of eruption, are either undergoing dissolution or have had insufficient time to reequilibrate to the new conditions and resume growth.

In either case, if crystal growth rates are as reported in the literature (e.g., $10^{-11}$ to $10^{-14}$ ms$^{-1}$ for plagioclase) then events such as contamination, cumulate recycling, and magma mixing must take place over timescales much less than 150 years (the maximum time it would take for plagioclase to grow ∼50 μm). Although it is possible that a crystal edge, like an unconformity, is actually dissolved/eroded over longer timescales, this is unlikely because dissolution is typically a faster process than crystal growth (Tsuchiyama 1985). In fact, these magmatic processes may well be the progenitors to magmatic eruptions, which occur over weeks to years and are recorded in geophysical and geochemical precursors such as seismicity and gas fluxes. The prospect exists that magmatic events preceding eruptions and dictating the nature, style, and size of eruptions may be recorded in the crystals disgorged on eruption (Morgan et al. 2004, 2006; Morgan & Blake 2006).
Core-to-rim $^{87}\text{Sr}/^{86}\text{Sr}$ profiles of two feldspar crystals from the Oruanui Ignimbrite, New Zealand (a) and two from the Fish Canyon Tuff, Colorado, USA (b). Note sampling pits in 3 of the four feldspars analyzed (the other is photographed prior to sampling). Note also in the case of the (upper) Oruanui feldspar the need for careful petrography integrated with CIS—for this crystal the core is clearly not in the “middle” of the crystal, which has been broken during explosive eruption. Panel (c) shows crystal growth rates, which typically become slower as magmas are more evolved (cooler, more SiO$_2$-rich and more viscous; e.g., Cashman 1990). If growth rate is known (or estimated) then features on crystals (width of rims, distance between dissolution surfaces) can be related to time.

In this regard, it is important to note that rim-host disequilibrium has been observed in many crystals from large-volume ignimbrites (Figure 7). Of the two microsampled crystals shown from the Oruanui Ignimbrite (New Zealand), one has a rim in isotopic equilibrium with the groundmass glass (as approximated by the crystal-poor bulk rock) and the other has a rim that is quite distinct. Both feldspars shown from the Fish Canyon Tuff (USA) have rims far from equilibrium with the host liquid (glass). The sampling scale of the crystal rims can be appreciated from examination of the distribution of the micromill pits (which are $\sim 50\,\mu\text{m}$ diameter). A simple consideration of growth rates summarized in Figure 7c suggests that these crystals with isotopically distinct rims were unlikely to have been in contact with the melt represented by the immediately adjacent glass for more than $\sim 10,000\,\text{years}$. This observation is
Crystal size distribution (CSD): a means of quantifying the 3-D crystal population in terms of the population density at different size intervals.

at odds with models advocating protracted (>100,000 years) closed-system evolution to incubate large volumes of silicic magma (e.g., Christensen & DePaolo 1993, Christensen & Halliday 1996, Halliday et al. 1989), but does corroborate suggestions that some large-volume silicic systems [such as Fish Canyon (Bachman et al. 2002) and Taupo (Charlier et al. 2005)] represent remobilized plutons.

Figure 7 gives a useful indication of the potential applicability of CIS to unraveling the timescales of magmatic processes. Crystals in basaltic and andesitic systems can grow to sizes of the order ∼1 mm in months to years. Dissolution surfaces in crystals are typically spaced at a few hundred micrometers or less, again the time taken to grow each zone between dissolution surfaces is of the order of months to years, although the time represented by the dissolution surface itself, like unconformities in the sedimentary record, may be much longer. The application of diffusional analysis techniques to elemental variations across dissolution horizons brings an opportunity to determine residence times of crystals in magmas. The diffusion profile (elemental or isotopic) can be assessed in light of an independently determined magmatic temperature and using appropriate published diffusivities. In this regard, elemental techniques provide better time resolution (e.g., Costa & Dungan 2005, Morgan et al. 2004, Morgan & Blake 2006, Zellmer et al. 1999) than equivalent modeling for isotopic ratios (Davidson et al. 2001, Morgan et al. 2005, Ramos et al. 2005) because the analytical resolution for trace elemental analysis is spatially finer (<50 μm), shows a greater contrast (tens of percent for trace elements versus fractions of a per mil for isotope ratios), and the diffusing species studied are not limited to those of isotopic significance, meaning that a range of timescales can be investigated owing to differing diffusivities of elements with a range of partitioning behaviors.

INTEGRATING CIS WITH ROCK AND MINERAL TEXTURES (CASE STUDY FROM STROMBOLI)

It is implicit that petrographic observations are fundamental to providing a context for interpretation of in situ isotopic determinations to constrain magma evolution (Table 2). The evolution of the mineral assemblage and its petrographic textures goes hand in hand with the isotope stratigraphy. Quantitative approaches to measuring mineral distributions and textures developed in recent years have been instrumental in constraining the evolution of magmas. Crystal size distributions (CSDs) (Higgins 2000, Marsh 1988) can be used to determine growth rates (from the slopes) and to identify mixing of crystal populations (from segments with different slopes, e.g. Jerram et al. 2003). It seems opportune, therefore, to combine the information provided by CIS with that gleaned from textural analysis.

To illustrate the integration of different techniques with isotopic microanalysis, we present some results from Stromboli Volcano, Italy (Figure 8). Thick sections were prepared and crystals analyzed with electron microprobe and BSE imaging. Textures were quantified by CSD measurements prior to micromilling-TIMS of selected crystals. Three crystals were selected for analysis, one of which is shown in Figure 8c,d. The BSE image as shown was calibrated against the microprobe data (Ginibre et al. 2002) and a high-resolution anorthite profile was extracted from the
Integration of CIS profiles with crystal size distribution (Morgan et al. 2005). (a) The CSD is for a 26 kyr lava from Stromboli Volcano and shows two segments of different slope (emphasized by dashed lines). The overlain CIS profiles for three different crystals (distinguished as different color shading) show a change from constant $^{87}\text{Sr} / ^{86}\text{Sr}$ at $\sim 0.70645$ in the cores to gradually decreasing $^{87}\text{Sr} / ^{86}\text{Sr}$ towards the rim. Vertical thickness of CIS boxes represent precision on the isotopic ratio. Horizontal width represents sampling thickness (corrected for three-dimensional effects and shifted to correspond with the other crystals). The most detailed traverse is shown for crystal STR46-3 as zones A–L. (b) An electron microprobe profile of An content, (c) a sketch of definable growth zones as sampled by micromilling, and (d) a backscattered image of that crystal (STR46-3) are also shown.

Note that the three crystals do not share the same isotopic compositions at their rims. Portions of the crystal population are interpreted to represent a crystal cargo that has been mechanically incorporated into the liquid in which they are now frozen.
and with which they only share a portion of their mutual evolutionary history. One crystal has a rim composition in equilibrium with the host groundmass, the others have higher $^{87}\text{Sr}/^{86}\text{Sr}$ rims, suggesting that they have been isolated from the magma earlier (and therefore did not experience the most recent growth episode). This observation allows us to shift the isotope profiles (and stretch them) so that they overlie each other and represent a common time line from right (core) to left (rim). The timeline of Figure 8a shows a marked increase in isotopic ratio of the crystal core between crystal lengths of 1 mm and 2.5 mm. The onset of the change in ratio (vertical gray band) correlates with the presence of a pronounced kink in the CSD (emphasized by the dashed line segments in Figure 8a) between 2 mm and 2.5 mm crystal size. Plateau ratios could therefore be due to (a) an inherited population of crystal cores and (b) a population of crystals of size less than 2.5 mm, along with rims on inherited cores. This interpretation is consistent with both CSD and isotopic data sets.

WHAT CAN ISOTOPIC STUDIES OF MELT INCLUSIONS ADD TO OUR UNDERSTANDING OF MAGMA SYSTEMS?

Melt inclusions have long been held as key tools for unlocking magma sources (Lowenstern 2003) because they represent instantaneous samples of magma trapped in growing crystals (Figure 9). As such, just as with growth zones in crystals, they may present a stratigraphic (core-to-rim) record of magma composition evolution through time. In principle, magma elemental compositions can be recovered directly from analysis of homogeneous melt inclusions, in contrast to crystal growth zones, which have partitioned elements from the magma (and therefore require knowledge of partitioning behavior). In practice, crystallization of daughter crystals, or crystallization of the outer margin of the melt inclusion, can modify compositions significantly and needs to be accounted for (Danyushevsky et al. 2002).

By virtue of their small sizes (typically 10–100 μm), isotopic information has proved far more difficult to recover from melt inclusions than elemental information. Nevertheless, isotope compositions have the specific advantage that they are not compromised by crystallization, and there is no need for careful rehomogenization. With the advent of analytical techniques capable of recovering isotopic data from melt inclusions, a number of important studies have documented considerable isotopic diversity among melt inclusion populations.

Isotopic studies of melt inclusions in olivines and pyroxenes (individual inclusions or whole grain aggregates) have commonly shown ranges in isotope ratios, which far exceed those of the host bulk rocks (e.g. Saal et al. 1998, 2005; Yurimoto et al. 2004 for SW Pacific OIB; and Jochum et al. 2004, Kobayashi et al. 2004 for Hawaiian basalts; Figure 10). The diversity in melt inclusions is often accompanied by a trend to isotopic compositions, which are more contaminated than those of the host (although contamination trends in Pb isotope space are less straightforward than those involving Sr isotopes). This observation is not consistent with the notion that melt inclusions trapped in early-formed phases represent primitive aliquots of melt. It is consistent with the earliest stages of crystallization (where magmatic temperatures are high and the system may not have insulated itself with its own cumulate such that
Figure 9
Schematic illustration of alternative interpretations of melt inclusion isotope data. (a) Melt inclusions are trapped from successive aliquots of magma (i, ii, and iii) derived from different mantle (sub Moho) sources. (b) The melt composition from which the crystal grows changes within the storage and delivery system owing to processes such as contamination and recharge from other parts of the system (cartoon adapted from Wolff et al. 1999). Note that in reality, relative to the system, either the crystal can stay in one place with the magma composition changing around it or the magma compositions can be fixed, with the crystal being transferred among different magma volumes in the system.
Compilation of data from minerals—either profiled for CIS, dissolved whole single crystals, or in some cases (e.g., Bryce & DePaolo 2004) aggregated and dissolved and melt inclusions. Comparison is based on an x-axis scale that simply converts the isotopic ratios to ranges relative to the minimum value for each system, set as zero. (a) Pb isotopes and (b) Sr isotopes.

Figure 10

Data sources as listed on figure. Abbreviations: WR = whole rock, MI = melt inclusion, cpx = clinopyroxene, plag = plagioclase, mt = magnetite, apt = apatite, anh = anhydrite, ol = olivine

magma-wallrock contact is at its most extensive) involving significant contamination. Saal et al. (2005), for instance, suggest that the diversity of melt inclusions in olivines from Polynesia (Figure 10a) reflect interaction with and contamination by the oceanic lithosphere through which the magmas pass.

Olivine-hosted melt inclusions from a single NW Iceland ankaramite lava (Figure 10b) span 65% of the total $^{87}\text{Sr}/^{86}\text{Sr}$ range shown by OIB (contrasted with the whole-rock hosts, which cover only 5% of the global OIB range in $^{87}\text{Sr}/^{86}\text{Sr}$). Even larger Sr isotopic variations have been documented within olivine hosted MIs from the Baffin Island picrites (Harlou et al. 2006). The Sr isotopic range of these melt inclusions are three times that of the North Atlantic MORBs. Hence, these
detailed Sr isotopic studies of individual melt inclusions evidently illustrate that they record chemical details that are not detectable in the host lavas.

Large isotopic variations among melt inclusion compositions are generated when a magma sequesters olivine phenocrysts that have crystallized in different parts of the system. Olivine entrapping melt inclusions in the central parts of a magma chamber or conduit (distal to the wall rock) may have an isotopic signature inherited from the source region, with little contamination. In contrast, melt inclusions trapped in crystals growing in boundary layers at the periphery of the magma storage and channeling system (where rising melts interact with the wall rock) may record large isotopic heterogeneities reflecting contributions from the wall rock lithologies encountered en route (Harlou et al. 2006).

Wolff et al. (1999) analyzed single inclusion-bearing quartz grains from the Bandelier Tuff (New Mexico, USA) for $^{87}\text{Sr}/^{86}\text{Sr}$. The melt inclusions have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ than the host, which was interpreted to reflect crystal growth in an environment more contaminated than the main body of magma. Such an environment
might be adjacent to the chamber margin or dike/sill walls, where wallrock melts are mixed into an interaction zone. Such contact zones are the most likely place for crystallization to occur because they represent the location where the magma experiences the greatest relative undercooling, and they offer surfaces to promote nucleation and epitaxial growth and are preferential sites for melt inclusion entrapment (Wolff et al. 1999).

**CIS VERSUS WHOLE-ROCK DATA AND THE ISSUE OF SCALE**

A compilation of presently available mineral and melt inclusion CIS data is given in Figure 10. The figure compares whole rock data with the associated mineral and melt inclusion data. For ease of comparison, the x-axis is a relative scale, and a number of panels are used to illustrate adequately the dynamic range present; which is extraordinarily large relative to analytical precision. The compilation focuses on Pb (206Pb, 207Pb, and 208Pb) and Sr isotopes (few CIS data are available for Nd, see Waight et al. (2000) for an example) and on common magmatic minerals (rather than accessories such as zircon). A wide spectrum of rock types are represented from basalts to rhyolites, and tectonic settings from intraplate to convergent margin. Rocks from both oceans and continents are represented.

Care must be taken in drawing conclusions from this comparison, which comprises a number of separate studies, using different techniques, and altogether amounting to a fairly limited volume of data. We must, for instance, bear in mind that most of the Pb isotope studies are on melt inclusions (by SIMS), only a few from single sanidine crystals, whereas the Sr isotope studies are dominated by single minerals (or mineral profiles by micromilling-TIMS) with fewer melt inclusion studies. Nevertheless we tentatively note the following:

1. There is no obvious link between composition and isotopic heterogeneity at the mineral scale. Basalts seem to show comparable diversity to rhyolites.
2. Similarly, there is no convincing sense that continental samples are more isotopically diverse at the mineral scale than oceanic samples.

What is convincing is that the intrarock isotopic diversity typically greatly exceeds that of the whole-rock suite from which the crystals and their melt inclusions have been derived. Thus, the isotopic diversity increases as the scale on which it is observed decreases. This observation was made for whole rocks by Zindler & Hart (1986) as a consequence of which they suggested that mantle heterogeneity existing at small length scales—as exemplified, for instance, in peridotite massifs such as Ronda—was averaged out during the melting process. The extension of their observation to isotopic diversity within single minerals can be explained by either of the following:

1. Isotopically diverse melts from the mantle are transferred to the lithosphere where they are mixed efficiently to average their compositions and result in a narrower range of isotopic compositions from the erupted rocks than from the input melts (cf Figure 1). In this case, crystals must grow before the melts are homogenized and the isotopic diversity of the inclusion suite is a better
representative of the diversity of mantle sources than whole-rock compositions (e.g., Bryce & DePaolo 2004, Saal et al. 1998, Yurimoto et al. 2004; Figure 10a).

2. Isotopically (relatively) homogeneous melts from the mantle are transferred to the lithosphere where they interact with isotopically heterogeneous lithologies. In this case the mineral CIP profiles or inclusion suites do not reflect the diversity of primary melts, but rather are a secondary feature developed largely during differentiation (e.g., Ramos & Reid 2005; Figure 10b). Nevertheless, it may be possible to access the primary magma composition(s) through this approach by extrapolating toward the end-member compositions (Figure 1).

Distinguishing between the above alternatives is critical (although we should note that they need not be mutually exclusive). If it turns out that isotopic diversity is inherited from open-system processes during differentiation and ascent through the lithosphere, then we may be erroneously attributing compositional characteristics to mantle sources.

CUMULATE RECYCLING AND EVOLUTION OF MAGMAS TRANSITING THE CRUST

Danyushevsky et al. (2002) point out that melt inclusion populations in olivine commonly demand that crystals are aggregated following separate evolutionary histories. Indeed, it can be shown that crystal populations are invariably made up of chains and clusters of crystals to a certain degree, implying a recycling of crystal frameworks such as those developed in crystal mushes (Jerram et al. 2003). This conclusion is consistent with petrographic and geochemical observations such as those of Dungan & Davidson (2004) for Ttara-San Pedro Volcano (South Chile), Heath et al. (1998) for Soufriere Volcano (Lesser Antilles), and Price et al. (2005) for Ruapehu/Tongariro (New Zealand), showing that crystals are largely recycled from cannibalized cumulate, and with models of multiply staged crystallization and remobilization, such as the mush column model of Marsh (1998, 2004) and its precursors (Cox 1980, Thompson et al. 1972). Such mixing between “young” melts and older crystal cores can also satisfy chronological constraints raised by U-series disequilibria. Specifically, young $^{226}Ra$-$^{232}Th$ ages reflect melts generated $\ll 8000$ years ago, which contributed to groundmass and crystal rims, whereas older $^{230}U$-$^{238}U$ ages on the same rocks are dominated by contributions from recycled older (>10 kyr) cumulate crystal cores (Turner et al. 2003).

Currently, popular models suggest that much magma processing occurs deep in the crust driven by the thermal engine of magma emplaced near the Moho (Annen et al. 2006, Dufek & Bergantz 2006, Petford & Gallagher 2001, Price et al. 2005). Magma systems may inherit significant isotopic diversity from this stage of evolution as thermal considerations predict that it is where the magma is most capable of assimilating crust. However, predicted ascent paths for volatile-bearing magmas recross the liquidus, resulting in dissolution of the crystal cargo entrained from depth (Annen et al. 2006). There exists, then, an apparent paradox between the observation of core-to-rim isotope variation in crystals that requires the host magma to change its isotopic composition during crystal growth, and the expectation that significant
crystallization may take place largely in response to decompression during eruption (Blundy & Cashman 2005) rather than owing to cooling deeper in the system in an environment conducive to development of isotopic heterogeneity. These observations can, however, be reconciled in the following ways:

1. Isotopic diversity is transferred from the deep crust to shallow levels where it is stored in cumulates. On average, <20% of the magma flux from the mantle erupts at the surface (Crisp 1984); wholly crystallized material in the shallow-to-mid crust is common.

2. Subsequent magmas intercept the precursor cumulates, remobilizing the crystals as antecrysts (Figure 6).

3. Partial dissolution of these crystals can change the isotopic composition of the host magma from which subsequent crystallization may occur.

4. On ascent to the surface, significant crystallization occurs both as microlites and epitaxially as rims to the antecrysts. This can represent volumetrically a major fraction of the total crystals (a 100 μm rim on a 2-mm-diameter crystal represents some 30% of its volume), and so can have significant leverage on melt elemental composition.

The key to establishing the evolution pathways of magmas confidently lies in integrating CIS approaches with textural quantification (as described above) and with careful P-T-XH2O determinations of the crystal cargo and melt inclusion populations.

MICROSAMPLING AND FUTURE DIRECTIONS

The advent of multicollector mass spectrometry and gradual improvement of chemical techniques has given us the capacity to determine the isotopic composition of mineral materials at the subgrain scale, within the limitations summarized earlier. We argue that isotopic microsampling has opened up new avenues for understanding magmatic sources and processes, with a new level of detail and confidence that is obscured by traditional bulk rock approaches. The limitations on our capacity to analyze small samples are imposed largely by technical considerations, which may still see advances. In standard TIMS analysis, only a small fraction of the sample (~<1%) is ionized and transmitted to the detector—>99% of the sample is effectively lost. Any increase in the ion flux at the detector over present capabilities would allow us to analyze smaller samples. Better signal-to-noise ratios would similarly lead to improved precision at smaller sample sizes and detectors that can operate in the cross-over area where signals are too intense for ion counting but not quite enough for good Faraday cup measurements. At the same time, direct in situ techniques such as LA-MC-ICPMS could be improved by better filtering of interfering species (the purpose for which collision cells are being developed). Advances in the 3-D reconstruction of crystal populations through sectioning and imaging techniques (e.g., Mock & Jerram 2005, Gualda 2006) provide the exciting prospect of fully targeted microsampling where the true 3-D location of analysis is quantified, and specific aspects of the crystal population can be identified for analysis, further improving the spatial resolution of the data.
SUMMARY POINTS

1. Isotopic variations in magmatic minerals and their melt inclusions reflect isotopic variations in the magmas from which they crystallized. Thus, core-to-rim isotope profiles represent an evolutionary record of the magma from crystal nucleation to eruption/emplacement.

2. Crystals commonly do not spend their entire crystallization history in the magma in which they are finally hosted. They have typically grown in different places and at different times in the magma system (and can be referred to as antecrysts).

3. Recycling of earlier-formed cumulate phases appears to be an important process in aggregating antecrysts into magmas.

4. Integration of isotopic microsampling techniques with petrographic and geochemical approaches is important in fully constraining magma evolution—allowing us to correlate isotopic changes with events such as recharge and mixing (manifest in dissolution horizons and inclusion zones) and allowing us to evaluate the timescales of these processes (by diffusional modeling of element profiles across crystal growth zones).

5. The isotopic diversity observed through microsampling attests to the importance of open-system processes during magmatic differentiation.

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LITERATURE CITED


Tsuchiyama A. 1985. Dissolution kinetics of plagioclase in the melt of the system
diopside-albite-anorthite, and the origin of dusty plagioclase in andesites. *Con-

of plagioclase growth and residence times in island arc lavas from Tonga and
the Lesser Antilles, and a model to reconcile discordant age information. *Earth

Tyrell S, Haughton PDW, Daly JS, Kokfelt TF, Gagnevin D. 2006. The use of
common Pb isotopic composition of detrital K-feldspar grains as a provenance
tool and its application to Upper Carboniferous palaeodrainages in Northern

Waight TE, Baker J, Peate D. 2002. Sr isotope ratio measurements by double-
focusing MC-ICPMS: techniques, observations and pitfalls. *Int. J. Mass Spectr.*
221:229–44

Waight TE, Maas R, Nicholls IA. 2000. Fingerprinting feldspar phenocrysts using
crystal isotopic composition stratigraphy: implications for crystal transfer and

Waight TE, Wiebe RA, Krogstad EJ, Walker RJ. 2001. Isotopic responses to basaltic
injections into silicic magma chambers: a whole rock and microsampling study
of macrorhythmic units in the Pleasant Bay layered gabbro-diorite complex,

Walker D, Shibata T, Delong SE. 1979. Abyssal tholeiites from the Oceanographer
25

Wallace GS, Bergantz GW. 2005. Reconciling heterogeneity in crystal zoning data:
an application of shared characteristic diagrams at Chaos Crags, Lassen Volcanic

evidence for a long-lived silicic magma chamber. *Geology* 31:533–36

Wolff JA, Ramos FC, Davidson JP. 1999. Sr isotope disequilibrium during differen-
tiation of the Bandelier Tuff, New Mexico: constraints on the crystallization of
a large rhyolitic magma chamber. *Geology* 27:495–98

isotopic compositions in olivine-hosted melt inclusions from HIMU basalts and
possible link to sulfide components. *Phys. Earth Planet. Int.* 146:231–42

Zellmer GF, Blake S, Vance D, Hawkesworth C, Turner S. 1999. Plagioclase resi-
dence times at two island arc volcanoes (Kameni Islands, Santorini, and Soufriere,
136:345–57

Zellmer GF, Clavero JE. 2006. Using trace element correlation patterns to decipher
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RELATED RESOURCES

Bill White’s online geochemistry text: http://www.geo.cornell.edu/geology/classes/geo455/Chapters.HTML

TiMAG (textural and isotopic microanalysis group) at the University of Durham:
http://www.dur.ac.uk/earth.sciences/research/research_groups/timag/
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**Errata**

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