Inter- and Intracrystalline Isotopic Disequilibria: Techniques and Applications

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INTRODUCTION

In the last ~20 years, we have seen a significant expansion of techniques related to geochemical and isotopic microsampling of materials in the earth sciences. From constraining pre-eruptive histories of flood basalt magmas to identifying the natal rivers of origin of anadromous fishes, these techniques have had significant impacts in a wide variety of scientific fields. Nowhere has the impact been greater than in identifying the sources, processes, and timing of processes involved in igneous magmatic systems. Both technique refinements and the development of new technologies have aided in advancing microsampling applications, thus allowing for a better understanding of the sources and mechanisms responsible for changing geochemical and isotopic signatures in natural systems. In this chapter, we focus on the techniques and technologies associated with radiogenic isotope microsampling and review applications of these techniques as utilized in scientific investigations.

Isotope microsampling is a logical extension of earlier studies that evaluated individual components of magmas and magma systems, including melts and minerals. From the use of petrographic microscopes and the later introduction of the electron microprobe, the focus on internal chemical variations in melts and minerals is critical to assessing the petrogenetic histories of igneous rocks. Even today, these technologies are used to ensure that further trace element and isotopic analyses are undertaken in a textural and major element context. For trace elements and isotopes, early studies (e.g., Cortini and van Calsteren 1985) confirmed variations in the melt and mineral components of many igneous rocks but focused on mineral or glass separates. Potential information associated with isotopic variations retained by individual crystals or internal variations within individual crystals was lost. Later studies such as Geist et al. (1988) focused on isotope variations within single megacrysts to constrain mixing scenarios between basaltic, andesitic, and rhyolitic magmas, and Davidson et al. (1990) used microdrilling to document isotopic variations across an enclave-host magma interface and to identify xenocrystic crystals from within enclaves. These represent early studies that truly focused on “internal” isotopic variations of magmatic components from igneous systems and foreshadowed the potential of future studies utilizing isotopes at the microscale to identify magmatic processes and constrain their impacts on magmatic systems.
Isotope microsampling can be separated into two broad categories: 1) microspatial analyses and 2) microanalyte analyses. For microspatial analyses, samples commonly originate from micromilling, laser ablation sampling, or secondary ionization mass spectrometry (SIMS). For microanalyte analyses, samples are commonly obtained from single crystals or micromilling. As implied by the name, microspatial analyses target a limited area/volume of material such as a limited number of rings of a fish otolith or a single growth layer of a magmatic phenocryst, with the ultimate intent of constraining isotopic variability in the growth history of the target material. Constraining magmatic growth histories of phenocrysts exemplifies the utility of microspatial analyses. Phenocrysts grow from core to rim by the addition of sequential layers of material. Plagioclase, for example, typically contains high concentrations of Sr that allow for small portions of mineral to be successfully analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. By analyzing sequential layers, changes in the isotopic character of the magma in which the crystal grew, imposed by open-system processes, can be constrained (Tepley et al. 2000; Ramos et al. 2005). Thus, microspatial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analyses are well-suited to identify and track the effects of open-system processes occurring during mineral growth.

With microanalyte techniques, spatial resolution may be sacrificed to obtain the minimum required amount of analyte needed for a successful analysis. An example is that of Sr or Pb in quartz. The mineral structure and composition of quartz (SiO$_2$) does not readily allow for Sr and Pb elemental substitution, two elements commonly used as radiogenic tracers. As a result, Sr and Pb concentrations in quartz are low and typically result from melt or mineral inclusions captured during growth of individual crystals. Low Sr and Pb concentrations and the small size of quartz-hosted inclusions usually preclude them from being individually analyzed by microspatial techniques. However, these crystals can be approached from a microanalyte perspective using single grain analyses where all analyte is assumed to result from inclusions rather than the quartz host. Such single crystals must however be large enough to contain enough inclusions to yield the minimum required amount of analyte for successful analyses. Thus, microspatial and microanalyte techniques overlap to some degree but they also diverge so as to become very different in nature and, thus, scientific interpretation.

To comprehensively address isotope microanalysis techniques, we introduce the types of isotope analyses undertaken, the technologies involved in these isotope analyses, the critical aspects of these isotope analyses, and review a range of applications which have been undertaken. Our intent is to offer a broad review of successful applications, not an exhaustive review of all studies.

**MICROSPATIAL ISOTOPE ANALYSIS**

Early petrographic studies focusing on mineral phenocrysts from volcanic rocks documented textural evidence for highly variable magmatic histories recorded during mineral growth. Assessments of these varied histories were initially evaluated by measuring *in situ* major element variations (e.g., core to rims transects) using the electron microprobe targeted toward individual mineral phenocrysts. Such measurements were critical in assessing major element chemical changes of magmas occurring during mineral crystallization. These changes could result from a myriad of magmatic processes including, but not limited to, crystal fractionation, magma mixing, magma recharge, and/or processes associated with assimilation/fractional crystallization (AFC). Major element variations, however, could only account for broad assessments supporting major element modification of magmas in which crystals grew. Major elements alone could not, for example, confirm the presence of external inputs into magmatic systems such as required by AFC processes. Thus, identifying endmembers responsible for such external changes was more problematic.
In contrast to major elements, radiogenic isotopes offer an intriguing alternative in assessing the influence of either internal (closed-system) or external (open-system) inputs into magmatic systems and constraining the isotopic composition of the endmembers involved. Combining major element and isotopes has vast potential in understanding igneous petrogenesis in addition to other scientific fields. Initially, microdrilling (referred to as micromilling in this chapter) using diamond-embedded bits designed for the dental and engineering industries was used to obtain small samples in a microspatial context. Early attempts obtained samples on scales of 300 µm diameter by 300 µm depth and typically targeted Sr isotopes (e.g., Tepley et al. 1999). Fortunately, for most systems, even this level of microspatial sampling documented large isotopic variations in magmatic phenocrysts resulting from open-system processes affecting phenocryst-related host magmas. Early targets included minerals such as plagioclase and calcite, minerals generally characterized by high Sr contents (≥500 ppm). After milling, samples were dissolved and purified using chromatographic techniques and analyzed using thermal ionization mass spectrometry (TIMS). Analyte amounts were large (≥100 ng Sr) and required purification to removed interfering elements (e.g., Rb) prior to analysis. Partly as a result, micromilling became accepted as a tool for better understanding processes associated with magmagenesis and the popularity of the technique increased to the point that commercial micromills were built.

Since the mid- to late-1990s, micromilling has been a relatively common technique for acquiring samples, especially for materials requiring purification using column chromatography (e.g., Rb-rich potassium feldspar, Knesel et al. 1999). In addition, bits are now either diamond-embedded or made from highly pure tungsten carbide. Both are commonly used for silicate and carbonate applications that target a range of problems in igneous petrology. In addition, applications associated with biology and ecology have used isotopes to trace mammal movements (e.g., Hoppe et al. 1999) and identify the natal rivers of origin of marine caught salmon (e.g., Barnett-Johnson et al. 2005). Even mineral formation rates in meteorites have been examined using micromilling (Bizzarro et al. 2004; Thrane et al. 2006).

In addition to micromilling, two in situ techniques are commonly utilized for microspatial isotope analyses. The first uses secondary ionization mass spectrometry (SIMS) to analyze material that is removed from the surface of samples bombarded by oxygen ions, cesium ions, or electrons. Such analyses are typically used to measure radiogenic Pb isotope ratios that do not require high measurement precisions in minerals such as zircon (Davis et al. 2003; Ireland and Williams 2003). More recently, common Pb isotope ratios have been measured to variable precisions in U- and Th-poor materials such as melt inclusions. These measurements are generally limited to ratios involving the more abundant 206Pb, 207Pb, and 208Pb isotopes and have been useful in identifying mantle endmember components involved in ocean island basalt (OIB) volcanism (e.g., Saal et al. 1998). In addition to Pb isotopes, recent work by Weber et al. (2005) measured Sr isotopes in aragonite otoliths to evaluate natal river sources of salmon (Bacon et al. 2004). As such, expansion of SIMS-related techniques have also allowed for a broader spectrum of microspatial studies.

Micromspatial analyses have also benefited from the attainment of increased accuracies and greater measurement precisions using laser ablation sampling. Advances in laser sampling systems and multi-collector inductively coupled mass spectrometry have combined to greatly expand potential targets for Sr and Pb isotope analyses to include highly elementally complex materials such as clinopyroxene and volcanic rock groundmass. In the last 5-7 years, great strides have been made in obtaining highly accurate Sr and Pb isotope measurements with variable but consistently greater measurement precisions which on occasion rival those typical of TIMS (e.g., Ramos et al. 2004; Kent 2008). Below, we review micromspatial techniques and applications.
Micromilling

**Technique.** Historically, the concept of removing growth zones or intracrystalline sub-samples from larger samples for chemical analyses was governed by the scientific benefit of such analyses. All sub-disciplines in geology have gained some advantage from applying such techniques from evaluating sulfur isotopes in sulfur-bearing phases in breccias (Lambert et al. 1982), to obtaining X-ray diffraction data from micromilled minerals in calc-silicate granulites (Maaskant et al. 1980), to identifying fish provenance by micromilling otoliths for Sr isotopic analyses (Kennedy et al. 2002). Applying micromilling in igneous petrology for the purposes of evaluating isotopes in magma-related materials was first accomplished by Davidson et al. (1990) in which the cores of plagioclase feldspar crystals, and a small droplet of chilled mafic melt in the same hand sample, were milled using small bits and a basic drill press. Since then, micromilling has been and continues to be used successfully in a range of igneous-related applications.

Applications to igneous petrogenesis, however, are limited by the capability to physically sample intended target materials and to efficiently capture micromilled materials for chemical processing. As early as 1945, an experimental motorized microdrill was developed for extracting hard minerals from polished surfaces of large samples (Wagner 1945). In 1977, a device using a series of levers and joints that allowed for fine movements of a probe or hypodermic needle called a micromanipulator was used for extracting small crystals, 10-20 µm in diameter, from thin sections for further chemical analysis (Rickwood 1977). It was also common to use either hand-held drills (e.g., Dremel™) or mounted drill presses (e.g., Sherline™ vertical mill) assisted with either binocular or petrographic microscopes to mill material from a variety of target materials as long as spatial resolution was not critical. Advances in micrometer stages, optical systems, and finally, computer-assisted or -driven milling devices allowed for sampling on fine spatial scales that are used today (e.g., NewWave™ MicroMill™ or New Hermes™ Vanguard VMC).

Davidson et al. (1990), and many subsequent microdrilling studies, successfully analyzed Sr isotopes in plagioclase. Plagioclase, by far the most common mineral in arc-related volcanic rocks, has great potential to record temporal chemical and isotopic changes associated with magma chamber dynamics (Anderson 1983; Stamatelopoulou-Seymour et al. 1990; Blundy and Shimizu 1991; Singer et al. 1995). It is usually one of the first minerals on the liquidus and commonly crystallizes during magmatic differentiation of basalts and andesites. Compositional zoning in plagioclase typically reflects primary growth owing to slow CaAl-NaSi diffusive exchange within the crystal structure (Grove et al. 1984), and textural features preserved in phenocrysts help identify changing physical and chemical parameters in the host magma from which it crystallizes (e.g., Ginibre et al. 2002, 2004). Combined chemical and textural zoning may be used to reconstruct the conditions in which plagioclase grew, and by proxy, the chemical and physical evolution of the magma itself. Lastly, plagioclase usually contains high concentrations of Sr and relatively low concentrations of Rb which make it ideally suited for Sr isotope evaluations targeting initial Sr isotope ratios (i.e., \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios that have not been measurably influenced by radiogenic ingrowth). In addition to plagioclase, phases such as potassium feldspar, pyroxene, hornblende, apatite, glass, etc., may also be analyzed for Sr isotopes or integrated with additional constraints such as Pb or Nd isotopes from these same phases.

Ultimately an optimal mineral phase and isotope system must be chosen that will yield the most productive results for addressing the specific scientific problem of interest. To accomplish this goal, a balance between elemental concentrations, the precision of the milling technique, the ability to remove milled material from the crystal surface, and the ability of the analytical technique (TIMS or solution MC-ICPMS) to analyze the chemically processed sample accurately and precisely (as the precision required may be a function of the specific scientific application) must be pursued. As noted by Davidson et al. (2007), there is a trade-off
between the concentration of the target element and the required minimum amount of material milled and processed such that ample analyte must be acquired to provide for precise and accurate results. As Figure 1 illustrates, higher concentrations of the target element require less overall amounts of material to be sampled, which offers the potential for finer spatial resolution. Alternatively, lower concentrations require greater amounts of milled sample, and thus, coarser spatial resolution.

For example, Sr readily substitutes for Ca in plagioclase feldspars, thus concentrations typically range from a few hundred to a few thousand ppm. Approximately 1-3 ng of Sr are needed for a highly precise TIMS analysis (Charlier et al. 2006), although processing such small samples requires exceptional care. Therefore, a plagioclase with a relatively low Sr concentration of 100 ppm would require ~0.01 mg of sample to yield 1 ng Sr. Alternatively, for a plagioclase with 1000 ppm Sr, only 0.001 mg of sample is required. Clearly the limiting step may be the ability to recover, handle, and process such small amounts of material for analysis. To do so requires having a consistent blank and good knowledge of the blank concentration and isotopic composition (at such low analyte levels, blank corrections become increasingly important). The ideal circumstance is to have a well-characterized sample-blank relationship where blank corrections are minimal.

Micromilling techniques vary between 1) milling individual holes in crystal growth zones to 2) milling shallow troughs along growth zones, in each case generating enough material to undertake appropriate isotopic analyses. Early milling efforts used individual holes in which several small (<300 µm diameter x <300 µm depth) holes were drilled into a phenocryst with overlapping holes used to obtain finer spatial resolution (e.g., Siebel et al. 2005; Tepley et al. 1999, 2000). One disadvantage associated with this method is the lack of lateral or depth-related spatial resolution. Knesel et al. (1999) used a variant of this technique by utilizing a single, large-diameter hole (~600 µm) drilled into sanidine phenocrysts with material removed

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**Figure 1.** Diagram of concentration versus mass associated with different mineral phases and the masses of material needed to produce 1 ng, 10 ng and 100 ng of target analyte for analysis. Also shown are ranges of Sr concentrations in selected minerals found in typical volcanic rocks. [Used by permission of Annual Reviews, from Davidson et al. (2007), *Annual Review of Earth and Planetary Sciences*, Vol. 35, Supplemental Material, Fig. 1, p. 1].
at various controlled depths. So, although surficial lateral resolution was lost, depth resolution was maintained by carefully controlling milling depths. The shallow-trough method of milling, described in Charlier et al. (2006), uses a computer-controlled milling machine equipped with a binocular microscope, an adjustable speed motor, and a computer controlled X-Y stage reproducible to ±1 micron. The computer-controlled milling machine allows for sampling multiple holes within growth zones and for designating the milling depth of each hole, such that sufficient material is removed from the sample using multiple holes rather than a single deep hole. The advantage is that lateral- and depth-related spatial resolution is increased in comparison to milling single holes.

Depending on the milling device, the user will have to determine the desired milling location. Hand-operated milling machines are best used with a micrometer stage so as to maximize lateral spatial resolution. Previous workers used a detachable micrometer stage (Fig. 2) that was secured to both the vertical mill and a petrographic microscope (e.g., Tepley et al. 1999, 2000). The advantage with this technique is the ability to precisely determine locations of drill sites under the microscope, record locations, re-fit the stage to a vertical mill, and then precisely return to pre-determined drilling sites. Vertical spatial resolution, however, suffers using this method because of the imprecision of determining when the bit is at the sample surface. Computer-controlled milling machines are more precise for both lateral and vertical spatial resolutions, and software accompanying milling machines helps to determine drill tip location, sample surface location, and milling depth (Charlier et al. 2006). Options such as milling depth, location, holes versus troughs, and rate of milling are controlled using accompanying software.

Following milling, recovering material from the sample surface can be accomplished either by the dry method, collecting material with a small plastic scoop, or the wet method, collecting material using water. In the wet method, a drop of ultra-pure (18.2 MΩ) water is used as both a cooling agent for the bit and sample collection medium. As material is milled from the sample surface, milled particulates collect in the water creating a slurry. Charlier et al. (2006) describe the added technique of placing a warmed square of Parafilm™ with a small ~4 mm hole cut into it on the sample surface. The hole in the Parafilm™ is placed over the desired milling site and aids in slurry collection by confining the water to the drilling area and preventing it from draining into possible surface cracks of the polished thick section. Both methods use a micro-pipette with 0.5-10 µL tip to suction/collection the slurry. Suctioning additional water drops from the sample surface may be needed to ensure greater recovery of milled material.

If determining the isotopic compositions of samples is the primary goal, samples can be placed directly into digestion beakers and be dissolved. However, if isotope dilution is required, samples must be dried, weighed, and spiked. In this case, a sample weighing method must be devised. Early studies (Tepley et al. 1999, 2000) use a small square piece of clean aluminum foil, shaped around a circular mold, to make a flat-bottomed, aluminum collection vessel into which the sample is pipetted and dried. Once dry, the aluminum vessel containing the sample is weighed and the weight recorded. Sample is then carefully scraped into a digestion beaker. The aluminum vessel, less sample, is then re-weighed; the difference between the two is the sample weight. In general, this method results in relatively poor sample recoveries as a result of remaining sample adhering to the aluminum vessel or loss resulting from static electricity. Errors in sample weight affect element concentrations determined by isotope dilution but will not compromise the isotopic composition of the sample.

Charlier et al. (2006) developed a more precise method of weighing micromilled samples. These authors used a small receptacle made of gold foil that was weighed, loaded with sample, dried, re-weighed, and placed into the Teflon digestion beaker along with digestion acids. The gold foil was impervious to digestion acids and was removed and re-weighed after digestion where the difference in weight was the sample weight. Similarly, Ramos et al. (2005) used pre-
(a) Sherline microdrill.

Petrographic microscope with micrometer stage attached.

Microdrill with micrometer stage attached.

Microdrill with manual Z-direction control and plate for micrometer attachment.

(b) New Wave Instruments Micromill.

Moveable binocular zoom microscope head

Microscope optical axis

X-Y offset

Video camera

Figure 2. Illustrations of different milling devices. a) Sherline™ vertical mill shown with removable micrometer stage attached to petrographic microscope and to the mill. The sample is secured in a removable upper portion of the micrometer stage. This allows the operator to maintain a centered stage while being able to remove the sample for washing between milling events. The upper portion can then be re-attached to the stage in the same orientation and settings. b) Images illustrating various components of the NewWave™ MicroMill™ including the moveable stage, binocular microscope and video camera, tungsten carbide mill bit in sample collection water slurry, and illustrations of how the sample is pipetted into a beaker for chemical analysis. [Used by permission of Elsevier B. V., from Charlier et al. (2006), Chemical Geology, Vol. 232, Fig. 1, p. 117].
weighed, pre-cleaned Teflon disks on which samples were dried and re-weighed. The samples plus Teflon disks were placed into digestion beakers. The advantage of these methods was that the user could theoretically recover the entire dried sample for a fairly accurate sample weight.

Samples sizes vary according to bit diameters and milling depths and, most importantly, are controlled by how much material is needed for high precision analysis. Because samples are generally small, additional precautions must be taken to ensure cleanliness of beakers and reagents used in the dissolution process. Using multiply-distilled reagents and freshly distilled acids during dissolution is recommended. The amount of reagents used in the digestion process is limited by 1) the minimal amount of reagent used to maintain low blanks, and 2) the minimum amount of reagents required to prevent samples from drying during the digestion process. If too small a volume of reagent is used, heating will vaporize the reagent and require an extra cooling stage for re-condensing the sample or require re-digestion. Approximately 0.3-0.5 ml of reagent is minimally required to meet these conditions. Typical beakers used in this process are Savillex™ 3 ml Teflon screw-top beakers which are cleaned in a thorough fashion. Further sample processing and column chromatography is described in the Single Crystal Analyses section below.

Standard dissolution techniques for most rock digestions can also be used for micromilled samples: HF and concentrated HNO₃ for the first stage, 7N HNO₃ for the second stage, and 6N HCl for the third stage (Ramos 1992). Samples can then be re-dissolved in the acid required for chromatography. Samples are generally spiked prior to digestion unless sample splitting is required. In general, splitting while samples are dissolved in 6N HCl is best. Mixed spikes (e.g., Rb/Sr, Sm/Nd) are typically used to ensure that critical element ratios are preserved even if weighing errors have occurred. Required spike amounts can be calculated using a spreadsheet and estimated concentrations of elements of interest in the sample.

**Applications to volcanic rocks.** Whole-rock isotopic measurements are important in understanding broad petrogenetic histories of volcanic systems. However, whole-rock sampling produces average chemical and isotopic characteristics that either obscure or completely eliminate potential variations in mineral and melt components of rocks both isotopically and geochemically. Micromilling techniques were developed to extract isotopic and geochemical traits that whole-rock processing and whole-crystal analyses cannot obtain, thus allowing researchers to more thoroughly constrain the petrogenetic histories of volcanic and plutonic systems. Here, we review micromilling studies that have aided and, in some cases, complicated our understanding of crustal-level volcanic processes.

Micromilling, sample processing, and undertaking TIMS analyses are time consuming, therefore a thorough sampling methodology is required prior to initiating studies. Micromilling can be combined with a range of additional techniques including Nomarski Differential Interference Contrast (NDIC), a reflected light technique (Anderson 1983; Pearce and Clark 1989) used to enhance compositionally dependent textural features, and electron microprobe analysis to elucidate potential compositional variations in target phenocrysts. The combined use of Nomarski interferometry, electron microprobe analysis, and Sr-isotopic microanalysis to provide textural, chemical and isotopic information is termed Crystal Isotope Stratigraphy (CIS; Davidson and Tepley 1998). These techniques help define a more thorough sampling strategy and, once accomplished, provide information that would have otherwise been lost as a result of the averaging effects of whole-rock techniques.

One of the first studies to employ these techniques was that of Tepley et al. (2000) who investigated the 1982 eruption of El Chichón Volcano in Mexico. Tilling and Arth (1994) had previously found that mineral separates (plagioclase, clinopyroxene, hornblende, anhydrite, apatite and groundmass) from the same hand sample of the 1982 eruption were isotopically heterogeneous. Tepley et al. (2000) found texturally complex plagioclase phenocrysts
characterized by multiple dissolution zones, large variations in An contents associated with dissolution surfaces, and monotonic decreases in $^{87}\text{Sr}/^{86}\text{Sr}$ from core to rim (Fig. 3). They interpreted these data as reflecting crystal growth in an increasingly contaminated magma reservoir that was recharged with similar trachyandesitic magma with lower $^{87}\text{Sr}/^{86}\text{Sr}$. The lower $^{87}\text{Sr}/^{86}\text{Sr}$ recharge magma presumably fluxed the reservoir with hotter and more volatile-saturated melt causing textural discontinuities in the plagioclase, with consequent large magnitude changes in An contents, and eventual eruption. Decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in plagioclase resulted from crystal growth following re-equilibration in newly mixed magma. Thus, utilizing crystal isotope stratigraphy, Tepley et al. (2000) were able to elucidate a more detailed picture of the petrogenetic evolution of El Chichón Volcano that otherwise would have been overlooked as a result of whole-rock chemical and isotope averaging.

Numerous other studies have used crystal isotope stratigraphy to evaluate the petrogenetic histories of a range of different volcanic rocks. Tepley et al. (1999) investigated mixing...
relationships and mafic inclusion disaggregation at Chaos Crags, a series of rhyodacite and dacite domes containing variably quenched basaltic andesite inclusions on the flank of Lassen Peak in Lassen Volcanic National Park, California (USA). The principal findings from this study were that three styles of mixing occurred in the system: 1) limited mixing at the interface between rhyodacite magma and a ponded basalt layer to form a basaltic andesite, 2) mechanical dispersal of blobs of this material into the rhyodacite magma, and 3) disaggregation of the inclusions through shear forces in the resident magma. In the initial mixing episode, rhyodacitic magma containing large plagioclase phenocysts mixed into the basalt. These plagioclase phenocrysts reacted in the hotter and more mafic liquid and formed reaction textures and upon cooling, grew rims in equilibrium with the predominant magma composition. These rims had higher An contents and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than cores. Disaggregation of the basaltic andesite inclusions dispersed the contents of the inclusions into the more felsic magma in a later mixing event. In this study, the complex pathways of mixing were easily discerned through combined textural analyses, crystal chemistry variations, and isotopic analyses using micromilling. It was suggested that these types of mixing processes were more common than previously thought and that they may be responsible for the creation of intermediate lavas in arc environments.

Hora (2003) and Davidson et al. (2007) also documented the complex mixing of magmas and movement of crystals within a volcanic system through use of single crystal isotope analyses and intra-crystalline micromilling and isotopic analyses at Ngauruhoe Volcano (New Zealand). Micromilled plagioclase crystals in basaltic andesite lavas showed increases in $^{87}\text{Sr}/^{86}\text{Sr}$ from cores to rims which were consistent with crystals growing in magmas that became progressively more contaminated with higher $^{87}\text{Sr}/^{86}\text{Sr}$ melts. Accompanying clinopyroxene phenocrysts with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggested that they crystallized in a low $^{87}\text{Sr}/^{86}\text{Sr}$ melt prior to plagioclase crystallization. Subsequent remobilization, prior to eruption, combined the two minerals in later-erupted volcanic rocks. Just as in Tepley et al. (1999), micromilling allowed researchers to document changes in isotopic values within crystals and, when integrated with textural and compositional information and single crystal isotopic analyses, to trace the pathways of interaction of magmas in evolving volcanic systems.

Similar magma/crystal dynamics were illustrated by Perini et al. (2003). These authors showed that potassium feldspar megacrysts hosted in mafic alkaline potassic, ultrapotassic, and differentiated rocks retained both initial Sr isotopic homogeneity and heterogeneity and could be seen in eruptive products at nearby volcanoes in central Italy. At Monte Cimino, isotopic results from micromilling potassium feldspar megacryst cores and rims suggested that they nucleated and grew in a trachytic magma but were subsequently mixed into latite and olivine latite melts. At Vico volcano, micromilling and isotopic analyses of potassium feldspar megacrysts and isotopic analyses of whole-rock hosts showed a complex relationship. Three scenarios were observed; 1) a megacryst was isotopically homogenous from core to rim and in isotopic equilibrium with its host trachyte; 2) a megacryst was isotopically heterogeneous from core to rim and not in isotopic equilibrium with its host tephri-phonolite; and 3) a megacryst was isotopically homogenous from core to rim but not in isotopic equilibrium with its host olivine latite. As a result, Perini et al. (2003) created a complex model in which some crystals were derived from an older trachytic melt similar in composition to the host trachytic melt, some crystals were co-genetic with their current host, and some crystals were xenocrysts.

As these studies have illustrated, crystals commonly record complex textural, compositional, and isotopic characteristics that result from volcanic systems that recycled previously crystallized phenocrysts, commonly referred to as antecrysts, from crystal-rich mush piles genetically related to the system but not actively crystallizing from the prevalent magma (e.g., Jerram and Davidson 2007). An excellent example that illustrated these complex interactions was Armienti et al. (2007). This study compared whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with those of rims and cores of clinopyroxene “phenocrysts” and a hornblende megacryst from an historic eruption of Mount Etna (Italy). Results showed that pyroxenes and hornblende were in isotopic disequilibrium
with their hosts, except for a very thin rim on a single clinopyroxene crystal that was in $^{87}\text{Sr}/^{86}\text{Sr}$ equilibrium with the host rock. To further justify an antecryst origin, these authors evaluated crystal size distributions (CSDs) (see Armienti 2008 in this volume) of the mineral phases hosted in lavas erupted in 2001. Clinopyroxenes with disequilibrium isotopic ratios were part of a group of larger crystals that defined a separate trend on the CSD diagram which supported a different growth history in comparison to smaller phenocrystic minerals in the lavas. Together, evidence suggested that crystals in isotopic disequilibrium with their host rocks grew in a different, but related, magma compared to the prevalent magma feeding the current eruption. The authors suggested that these “disequilibrium” crystals originated from a cumulate mush that existed at depth, and that some were entrained in recently erupted magma.

Chadwick et al. (2007) also applied crystal isotope stratigraphy to plagioclase-bearing basaltic andesite lavas from Merapi volcano. They documented significant Sr isotope variations in cognate plagioclase phenocrysts. Chadwick et al. (2007) attributed the isotopic variability in phenocrysts to extensive magma-crust interaction in two forms: 1) direct incorporation of high-An content, high-$^{87}\text{Sr}/^{86}\text{Sr}$ plagioclase xenocrysts originally from a sedimentary protolith which were present as crystal cores that were subsequently overgrown by plagioclase in equilibrium with resident magma, and 2) plagioclase crystal growth in resident magma that was progressively contaminated by calcareous and volcaniclastic xenoliths and carbonate crust with concurrent crystal fractionation. Constraining the exchange of mass between various reservoirs in this magmatic system through micromilling allowed Chadwick et al. (2007) to speculate that incorporation of the proposed crustal material (limestone) may have major effects on the volatile budget of the volcano. They suggested that this interaction, which is more significant than previously thought, may have significant consequences on the eruptive behavior at Merapi Volcano and other volcanoes built on carbonate platforms.

Lastly, Morgan et al. (2007) combined textural analysis in the form of crystal size distributions (CSD) and microsampling techniques to understand magma supply and mixing processes at Stromboli Volcano (Italy). Plagioclase phenocrysts from a 26,000 year-old sample were targeted in which time and growth rate data were determined through CSD, and changing isotopic information of the supply magma was determined through micromilling and TIMS. The authors constructed a model in which isotopic micromilling results and respective sampling positions were overlaid and then stretched and shifted to generate an isotopic timeline. The end result was an isotopic evolution line that represented, by proxy, magma evolution of the evolving Stromboli magmatic system. Combining the information, Morgan et al. (2007) were able to determine the timescales of mixing, crystallization and contamination prior to eruption of Stromboli. In this study, as with Waight et al. (2000a), it was shown that micromilling was a powerful tool for determining magma chamber processes. However, when combined with other process-related techniques or contrasting in situ isotopic analyses, the technique became even more useful.

Applications to plutonic rocks. Unlike volcanic rocks, plutonic rocks cool slowly and are thus affected by diffusive re-equilibration associated with long-term high-temperature environments, or by variable isotopic exchange associated with hydrothermal fluids. Additionally, plutonic age determinations and high parent/daughter ratios in potential target isotopic systems can yield sources of error that must be evaluated. Discussions of these problems, some of which are outlined here, can be found in Davidson et al. (in press) and Davidson et al. (2005). Given these caveats, we discuss notable studies that apply micromilling to plutonic rocks and host minerals that show a range of alteration from little or no diffusive re-equilibration to full isotopic resetting.

One of the first to utilize intracrystalline isotopic micromilling on plutonic rock components was Waight et al. (2000a) who determined initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\varepsilon\text{Nd}_\text{i}$ on cm-scale feldspars in a 395 Ma S-type granite from the Wilson’s Promontory Batholith of the
Lachlan Fold Belt (SE Australia). This research tested whether isotope variations could be preserved in plutonic rocks with obvious magma mixing/mingling textures that remained at moderate temperatures for millions of years. Additionally, this study was an excellent plutonic analogue to volcanic equivalents in which the interactions between different magmas and crystals were explored (e.g., Tepley et al. 1999). Evidence for magma mingling included numerous mafic microgranular enclaves hosted in a monzogranite, and feldspar megacrysts in both the host and enclaves. Micromilling of megacrysts revealed significant decreases in initial $^{87}\text{Sr}/^{86}\text{Sr}$ and complementary increases in $\varepsilon\text{Nd}(i)$ from cores to rims in both alkali and plagioclase feldspars (Fig. 4). High-temperature diffusive or hydrothermal re-equilibration would effectively produce homogeneous isotope signatures rather than a complementary divergent trend, therefore such processes could be ruled out. Thus, this research verified not only that micromilling techniques could be applied to slow-cooling, old plutonic systems when evaluated for the possibility of hydrothermal alteration, but also that application of these techniques to petrogenetic problems could trace the movement of crystals between plutonic systems with different isotope characteristics.

Not all plutonic systems are immune to alteration processes however. Waight et al. (2000b) documented both initial Sr and Nd isotopic heterogeneity and homogeneity in plagioclase megacrysts in comparison with their respective host magmas residing in enclaves in two I-type plutons from the Lachlan Fold Belt (SE Australia). In the Swifts Creek pluton, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios of plagioclase megacrysts were distinct from their host enclaves which confirmed results from earlier studies that concluded an admixed nature to the enclaves (Eberz and Nicholls 1988; Eberz et al. 1990). In this case, Waight et al. (2000b) modeled feldspars as having crystallized in a primitive granitoid which were then transferred to their current host. In the Bridle Track pluton, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of feldspars, the enclaves in which they resided, and the granitic host of the enclaves were indistinguishable. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the same crystals and hosts were slightly different which suggested a mingled magma origin, as did field evidence, petrology and whole-rock data. Waight et al. (2000b) concluded that a

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**Figure 4.** Sr and Nd isotope traverses from a potassium feldspar megacryst hosted in a mafic enclave from Wilson’s Promontory Batholith (Australia). Unfilled squares represent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and filled squares represent initial $\varepsilon\text{Nd}$ values for the same micromilled holes. Filled boxes represent initial isotope range of host granite and unfilled boxes represent initial isotope ratio of enclave for $^{87}\text{Sr}/^{86}\text{Sr}$ (left) and $\varepsilon\text{Nd}$ (right), respectively. [Used by permission of Springer-Verlag, from Waight et al. (2000a), *Contributions to Mineralogy and Petrology*, Vol. 139, Fig. 4, p. 235].
significant Sr isotope equilibration process occurred to homogenize Sr isotopes of megacrysts, enclaves, and granitoid host, but was unable to homogenize Nd isotopes completely. In these cases, the use of multiple isotope systems constrained the altered nature of the samples and allowed for appropriate interpretation.

Siebel et al. (2005) determined that sub-solidus thermo-metamorphic or hydrothermal alteration affected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in potassium feldspars residing in various Late Paleozoic plutonic rocks of the Bavarian Forest. In some cases, potassium feldspars were homogenized along with bulk groundmass via a post-crystallization fluid phase. In other cases, interaction of post-magmatic hydrothermal fluids produced isotopic heterogeneities. In all cases, the propagation of errors associated with assumed crystallization ages, parent/daughter ratio measurements, and isotopic ratio measurements were evaluated to ensure accurate initial age calculations.

In many of these studies, the use of micromilling allowed workers to follow the paths of crystal migration and growth in various magmas. Halama et al. (2002) focused on plagioclase megacrysts from gabbroic dikes in the Gardar Province (South Greenland) to trace the path of plagioclase-rich mushes, postulated to migrate from the crust-mantle interface, through the crust eventually ponding within the crust and forming massive anorthosites. Halama et al. (2002) used major element zoning patterns, in situ trace element variations, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations in the plagioclase megacrysts to formulate a model for anorthosite formation.

Another plutonic micromilling study that elucidated processes similar to magma interaction processes in volcanic environments was Perlroth (2000), documented in Davidson et al. (in press; 2005). This study explored Sr isotope contrasts in potassium feldspar megacrysts in the ~400 Ma Shap Granite (NW England). The Shap Granite has abundant potassium feldspar megacrysts and mafic inclusions, many of which contain potassium feldspar megacrysts rimmed by plagioclase. A leading hypothesis was that potassium feldspar megacrysts grew in the Shap Granite and were then transferred into a boundary layer mixture along an interface between the two magmas which eventually produced mafic enclaves of a mixed nature. Thermal and chemical equilibration of the potassium feldspar with the inclusion mafic magma allowed the plagioclase rims to grow. There is some debate (Pidgeon and Aftalion 1978; Rundle 1992) about the age of the Shap Granite, and this led to equivocation regarding age-corrected initial Sr isotope ratios of samples micromilled from a potassium feldspar megacystal. However, if a younger age were accepted for the Shap Granite, then the isotopic data became consistent with megacryst growth in the granite followed by crystal transfer and rim re-equilibration within mafic enclaves, thus mimicking processes involved in volcanic systems.

The significance of these plutonic studies is threefold: 1) original isotopic disparities in minerals of old plutonic rocks can persist for extended time periods, and can be measured using micromilling, however this is not always the case, 2) multiple isotopic systems (Sr, Nd, Pb) can be used in a complementary fashion in some cases to rule out the effects of both slow cooling, high-temperature alteration and/or hydrothermal isotopic resetting, and 3) interpretations based on micromilling techniques require precise and accurate measurements of the age of the plutonic body, the parent/daughter ratio and isotopic ratio of the sample in question, and appropriate error propagation of all measurements.

In long-lived volcanic and plutonic systems, sub-solidus isotopic diffusive re-equilibration is a process that warrants careful evaluation. For example, Gagnevin et al. (2005) not only documented Sr isotopic zoning in potassium feldspar megacrysts in the 7 Ma Monte Capanne monzogranite (Elba, Italy), but also evaluated whether diffusive re-equilibration may have affected the system. Micromilling transects from core to rim of several potassium feldspar megacrysts revealed high to low initial $^{87}\text{Sr}/^{86}\text{Sr}$ values. These observations suggested crystal growth in a crustally contaminated magma with high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios followed by growth in magma recharged with mafic melt with lower initial $^{87}\text{Sr}/^{86}\text{Sr}$. However, to test whether
changes in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were due to isotope re-equilibration, Gagnevin et al. (2005a) modeled the isotopic data to determine timescales required for diffusive exchange. Results showed that at least 20 m.y. were needed to produce the isotopic profiles of the megacrysts. Thus, they considered this amount of time unrealistic given other published results for similar granite crystallization histories.

Isotopic variations in plutonic minerals also allowed researchers to constrain cooling times based on the lack of diffusive equilibration in minerals with intracrystalline isotope contrasts. An example was the Rum Intrusion (NW Scotland) where Tepley and Davidson (2003) demonstrated that select plagioclases crystallized in liquids contaminated by isotopically diverse wallrocks whereas other plagioclases crystallized in homogeneous uncontaminated magmas. Both types of crystals were then transported to the floor of the magma reservoir where they cooled together. Preservation of isotopic heterogeneity within some of these crystals allowed Tepley and Davidson (2003) to calculate a maximum amount of time that the Rum magma chamber was held at high temperature based on the diffusivity of Sr in plagioclase feldspar. Figure 5 illustrates how cooling rate (linear or exponential) affects the isotopic equilibration of crystals of various lengths. Given that isotopic disequilibrium (regardless of the magnitude) in the Rum plagioclases existed on length scales of 1-2 mm, only cooling rates below the 2

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Diffusive re-equilibration models used to determine the effective scale of Sr exchange owing to cooling from an initial temperature $T_0$. Both linear and exponential models are considered. In the linear cooling models, $k$ represents linear cooling rates of 0.01 to 1°C yr$^{-1}$ and is represented in the diagram by solid lines. In the exponential cooling models, represented in the diagram by dashed lines, $\alpha$ is the effective temperature decay constant and $\tau_{1/2}$ is the time taken for the temperature to drop from $T_0$ to $T_0/2$ (see Reddy et al. 1996 for mathematic formulations of these equations). Diffusive exchange is dependent on plagioclase composition. In this case, the diagram illustrates labradorite ($\text{An}_{50-70}$) at 1200°C. Since all plagioclase crystals evaluated are $\leq$2 mm, only the modeled cooling rates within the shaded box are acceptable solutions. Note that diffusive exchange effectively ceases when temperature cools to below 1000 °C. This is indicated by the solid dot on each cooling curve. [Used by permission of Springer-Verlag, from Tepley and Davidson (2003), *Contributions to Mineralogy and Petrology*, Vol. 145, Fig. 11, p. 639].
mm equilibration length line (shaded area) were acceptable solutions to the cooling rate determination. Ultimately, the modeling indicated that the cooling rate for the Rum Intrusion was \(-0.1\, ^\circ\text{C yr}^{-1}\) or faster and Sr isotope equilibration essentially ceased at \(T = 1000\, ^\circ\text{C}\) (circle on cooling path line) after which there could be no further appreciable diffusion or addition to the equilibration length.

The issue of \textit{in situ} crystallization versus crystal transport was revisited by Davidson et al. (in press) who documented isotopically distinct initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in plagioclase and pyroxene phenocrysts in the Dias Intrusion (Dry Valleys, Antarctica). This work evaluated whether minerals crystallized \textit{in situ} (in which case the assumption is that different crystals share the same isotopic composition owing to growth in the same magma) or in magmas with different isotopic compositions and were transported to their current hosts. Scatter in age-corrected isotopic results suggested that plagioclase and pyroxene crystallized in different environments and were transported to their current position in the Dias Intrusion.

As these studies demonstrate, the possibility of extracting petrogenetic information in plutonic rock mineral phases through micromilling is possible, however, several issues must be evaluated. As Davidson et al. (in press) point out, one issue is whether the system under study can support mineral-scale isotopic heterogeneity. Small, upper crustal intrusions tend to cool more quickly than large, high-temperature, slow-cooling magmas. The added time associated with slow-cooling magmas tends to force isotopic equilibration. Another issue is confidence in age corrections of the magmatic body. Measurement errors associated with the age of the body and parent/daughter ratios (e.g., \(\text{Rb}/\text{Sr}, \text{Sm}/\text{Nd}\)) magnify resulting errors associated with determining whether initial, mineral-scale isotopic heterogeneity existed. Lastly, effects owing to post-emplacement alteration need to be evaluated. As Waight et al. (2000a,b) have shown, using multiple isotopic systems may alleviate the uncertainty associated with data obtained through singular isotopic system analyses.

**Secondary ionization mass spectrometry (SIMS)**

\textit{Technique}. Microspatial measurements of Pb and Sr isotopes have been undertaken using secondary ionization mass spectrometry (SIMS). SIMS based analyses can be targeted to micron-length sample sites although analyses can vary widely in measurement precisions as a result of relatively low ion beam intensities (e.g., compared to TIMS). For Pb isotope measurements using SIMS, analyses typically focus on the more abundant \(^{206}\text{Pb}, {^{207}\text{Pb}},\) and \(^{208}\text{Pb}\) masses and are only minimally affected by potential interfering elements/molecules (e.g., \(\text{HfSi}^+\)) as a result of the use of variable mass resolutions (e.g., 1800-2000 for feldspars and 3000 for glasses; Layne and Shimizu 1997) which still allow for high ion beam transmissions. For melt inclusions, a \(^{16}\text{O}^-\) ion beam and high resolution (~3500) is used to ensure minimal influence of potential interfering elements at the Pb isotope masses (Saal et al. 1998, 2005). In addition, typical spot sizes are \(-20-30\) microns. And although precisions are generally poor (0.2 to 1.2%), Pb isotope ratios have proven to vary widely in target materials, such that SIMS analyses have successfully identified large Pb isotope variations in, for example, melt inclusions.

\textit{Applications}. Saal et al. (1998) first used SIMS to measure Pb isotope ratios in olivine-hosted melt inclusions to identify an isotopically diverse suite of magmas involved in ocean island volcanic plumbing systems that could not be resolved by conventional whole-rock analyses. These authors found that melt inclusions retained a range of EMII and HIMU mantle endmember components that spanned 50% of the worldwide Pb isotope variation observed in ocean island basalts in only a few sampled basalts. This study also demonstrated that large ranges of Pb isotope signatures were retained by olivine-hosted melt inclusions in individual basalt flows. These signatures were only retained in melt inclusions because melt aggregation had homogenized variable melt fractions prior to eruption. Saal et al. (2005) expanded this investigation to include three endmember mantle compositions (HIMU, EMI, and EMII) and presented a model in which melts of an ocean lithospheric component (i.e., Pacific MORB)
were thought to mix with wallrock components originating from either HIMU, EMI, and EMII magmas as reflected by linear Pb isotope trends.

Kobayashi et al. (2004) also analyzed melt inclusions for Pb isotopes in conjunction with lithium and boron isotopes at Hawaii and concluded that recycled materials from ancient subducted crust were incorporated into the mantle sources generating Hawaiian basaltic volcanism. Results again confirmed that melt inclusions retained greater isotopic diversity, as compared to whole rocks, and demonstrated the utility of combining SIMS-measured Pb isotope ratios with additional isotopic constraints to identify and constrain the chemical nature of the sources contributing to ocean island volcanism. And although these studies focused on melt inclusions, Layne and Shimizu (1997) demonstrated that Pb isotopes could also be successfully measured in plagioclase, potassium feldspar, pyrite, and chalcopyrite using SIMS.

In addition to Pb isotopes, Weber et al. (2005) developed a procedure to measure Sr isotopes in fish otoliths using the Sensitive High Resolution Ion Microprobe (SHRIMP). Compared to laser ablation and TIMS, SHRIMP generated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios had relatively poor precisions ($^{87}\text{Sr}/^{86}\text{Sr} \pm 0.001$ to 0.0001) but even at these levels Bacon et al. (2004) effectively identified the natal rivers of salmon originating from North American cratonic regions and western North American Paleozoic accreted terrains. SIMS Sr isotope measurements usually had greater amounts of interfering elements and molecules, however, and beam intensities were generally lower than TIMS due the limited volume sampled.

### Laser ablation sampling

**Sr isotope technique.** Christensen et al. (1995) first demonstrated the utility of measuring Sr isotopes in carbonate and plagioclase using laser ablation (LA) sampling in conjunction with multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The advantages of laser sampling were clear: samples were easily prepared and analyses could be obtained rapidly, bypassing time-intensive digestion and purification procedures. Although true for some minerals such as carbonate, accurate analyses of other materials still offer significant challenges. Since the Christensen et al. (1995) evaluation, refinements in the utility and longevity of commercial laser ablation systems and advances in multi-collector inductively coupled mass spectrometers have combined to greatly expand the use of laser sampling associated with microspatial isotope analyses. Further studies by Davidson et al. (2001) evaluated plagioclase glasses with variable Rb/Sr ratios, while Waight et al. (2002), Bizzarro et al. (2003), and Schmidberger et al. (2003) expanded the range of analyzed materials to include apatite, clinopyroxene, and sphene. Ramos et al. (2004) also demonstrated that highly accurate Sr isotope measurements could be obtained on less Sr enriched carbonates ($\leq 1000\ ppm$ Sr), plagioclases ($\leq 750\ ppm$ Sr), and clinopyroxenes ($\leq 50\ ppm$ Sr), in addition to elementally complex materials such as basaltic and basaltic andesite fine-grain groundmass (Figures 6, 7, and 8). Additionally, accurate assessments of Sr isotopes using laser ablation sampling of aragonite otoliths have greatly benefited ecological studies of fishes (e.g., Thorrold and Shuttleworth 2000; Woodhead et al. 2005; Barnett-Johnson et al. 2005).

Two requirements are generally necessary for successful laser ablation isotope measurements: 1) analyte abundances must be relatively high, although precisions associated with materials characterized by low analyte abundances may still be sufficient to address investigations involving large dynamic isotope ranges, and 2) potential interfering elements and molecules must be minimal or their respective impact on measured ratios must be accurately removed. If high analytical precisions are not required (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$ of $\geq 0.00004$), laser sampling can be a very efficient means of acquiring data from a time perspective, and thus, is highly advantageous as compared to undertaking micromilling and purification using column chromatography.

Since laser ablation analyses involve direct sampling of unpurified materials, measurement accuracies may be highly dependent on the presence of interfering elements, thus target materials with low interfering element abundances are generally preferred. Such effects are
best exemplified in Sr isotope measurements. Sr isotope ratios can be influenced by a variety of interfering elements including $^{87}$Rb, $^{84}$Kr, $^{86}$Er$^{2+}$ (mass/charge = 84), $^{168}$Yb$^{2+}$, $^{172}$Yb$^{2+}$, and $^{170}$Yb$^{2+}$ (Davidson et al. 2001; Ramos et al. 2004). Many potential molecular species such as Ca dimers (e.g., $^{44}$Ca$^{43}$Ca, Waight et al. 2002), Ca argides (e.g., $^{44}$Ca$^{40}$Ar, Woodhead et al. 2005), and Fe oxides (e.g., $^{56}$Fe$^{16}$O$_2^+$, Schmidberger et al. 2003) may also influence Sr isotope ratios (Fig. 9). In addition, isotopes such as $^{85}$Rb, which is monitored for $^{87}$Rb corrections, may also be influenced by interfering elements such as $^{170}$Yb$^{2+}$ and $^{170}$Er$^{2+}$. Thus, even isotopes that are measured for interference corrections may be affected, potentially compromising accurate interference corrections. For the VG Element Axiom™ and Nu Plasma™ mass spectrometers, Ca-dimers and Ca-argides pose significant challenges to obtaining accurate Sr isotope measurements in Ca-rich minerals such as carbonate and plagioclase. Careful interference correction procedures, however, have been successfully used to obtain accurate Sr isotope measurements (e.g., Woodhead et al. 2005). In contrast, Sr isotope measurements on Ca-doped NBS 987 standard solutions and Ca-rich minerals, including carbonate and plagioclase, are only minimally affected (Hart et al. 2005) or not affected (Ramos et al. 2004) by Ca dimers and Ca argides when using the ThermoFinnigan Neptune™. Although it is unclear why Ca-dimers and Ca-argides are either present or absent, differences in the design of plasma interfaces or the standard running parameters used (per
machine/manufacturer) may result in variations in ionization potentials and in the interfering molecules and ions present. And although not directly evaluated, similarities between Sr isotope ratios obtained on plagioclase using laser sampling in conjunction with the GV IsoProbe™ compared to those obtained using micromilling and TIMS (Davidson et al. 2001), also allow for only a minimal influence of Ca dimers and Ca argides during analyses. Tables 1a and 1b show two different collector configurations for Sr isotope measurements and relevant first order interferences for the ThermoFinnigan Neptune™ and Nu Plasma™, respectively. Select interfering elements may be present during all analyses, Rb and Kr for instance, but the presence of others may depend on the specific mass spectrometer being used. Great care must be taken to identify and constrain all potential interferences. Ultimately, correcting for interfering elements affecting Sr isotope masses, and relevant corrections, is both the most challenging and most critical aspect of obtaining accurate Sr isotope ratios using laser ablation. Thus, it is beneficial to confirm the accuracy of results using alternative, proven methods such as micromilling/TIMS.

Figure 7. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of two single clinopyroxene crystals from a primitive Grand Canyon basalt (MgO wt% of ~10%) from the western United States determined using laser ablation sampling. Filled squares with $2\sigma$ error bars represent multiple laser ablation trough analyses and gray squares with $2\sigma$ error bars represent micromilled samples from the same crystals. Stippled fields reflect $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured from four separate single crystals using column chromatography and TIMS. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured using 160x500 µm laser ablation troughs in grain 6 overlap those of single crystals (lower diagram) confirming accuracy of measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Results for grain 7, however, reflect variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that lie outside the field of single crystals illustrating the capability of laser ablation sampling to identify within-crystal variations that are not detectable using single crystal analyses [Used by permission of Elsevier, from Ramos et al. (2004), Chemical Geology, Vol. 211, Fig. 9, p. 151].
To offer a general starting point in which to undertake Sr isotope analyses using laser ablation, Tables 2a and 2b are presented to illustrate machine and laser settings. These parameters are used in conjunction with the ThermoFinnigan Neptune™/UP213 New Wave™ laser and the Nu Plasma™/Lambda Physik Compex 110ARF™ excimer laser, respectively, and will change depending on the specific mass spectrometer and laser being used. Many of the previously mentioned studies utilize different mass spectrometers and lasers and will include basic information for machine and laser settings. Additionally, the Faraday collector configurations and major interfering elements described above can be used initially and refined as necessary. Further evaluations should be undertaken to ensure that additional interferences are not present. This can be accomplished in many ways, but Ramos et al. (2004) had success in using NBS987 standard solutions doped with potential interferences such that specific elements or molecules could be individually evaluated as potential interferences.

Once interferences are identified, a correction procedure must be designed and applied to remove their impact from the desired ratios of interest. This may be complex. For the ThermoFinnigan Neptune™, all Faraday collectors are used to measure the isotopes of Sr and interfering elements and molecules. If more isotopes were needed to be measured, a peak-hopping routine would be required. It is critical that ion intensities from at least one isotope per interfering species is measured, independent of the effects of additional interfering elements.

Figure 8. $^{87}$Sr/$^{86}$Sr and $^{84}$Sr/$^{86}$Sr variations of fine-grained Pisgah Crater (USA) basaltic groundmass. Filled squares with 2σ error bars result from laser ablation sampling using 160×500 µm troughs and 80 µm diameter pits. Gray squares and stippled field represent results from four separate micromilled holes of fine-grained groundmass. $^{87}$Sr/$^{86}$Sr results reflect variable errors but results overlap those from micromilled samples and attest to the accuracy of $^{87}$Sr/$^{86}$Sr obtained using laser ablation sampling. $^{84}$Sr/$^{86}$Sr variations deviate from micromilled samples analyzed using TIMS and partly reflect variations presumably resulting from pit-induced fractionation effects. [Used by permission of Elsevier, from Ramos et al. (2004), Chemical Geology, Vol. 211, Fig. 8, p. 149].

Firstly, Kr contributions are removed by measuring on-peak baselines during normal gas flow through the ablation cell without firing the laser. Background Kr signals, present as a result of Kr impurities in the He and Ar gas supplies, are directly measured as elevated ion counts per second at masses of interest. Figure 9, A) Mass scans at resolving power of 3000 illustrating the presence and magnitude of a range of interfering elements on the VG Axiom MC-ICPMS at or near Sr and Rb masses of interest. B) Mass scan at normal resolving power illustrating the presence and magnitude of a range of half-mass and whole-mass interfering elements. [Used by permission of Elsevier, from Waight et al. (2002), International Journal of Mass Spectrometry, Vol. 221, Fig. 4, p. 234].
### Table 1a. Collector block configuration of the ThermoFinnigan Neptune™ MC-ICPMS (modified after Ramos et al. 2004) with potential interferences illustrated.

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<td>$^{86}\text{Sr}_{9.86%}$</td>
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<td>$^{168}\text{Yb}^{\text{2+}}$</td>
<td>$^{170}\text{Yb}^{\text{2+}}$</td>
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<td>$^{174}\text{Yb}^{\text{2+}}$</td>
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### Table 1b. Collector block configuration of the Nu Plasma™ MC-ICPMS (modified after Woodhead et al. 2005) with potential interferences illustrated.

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**Table 2a.** Operating parameters of the ThermoFinnigan Neptune™ MC-ICPMS and Nu Plasma™ MC-ICPMS (modified from Ramos et al. 2004 and Woodhead et al. 2005).

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<td>RF power</td>
<td>1200 W</td>
<td>1350 W</td>
</tr>
<tr>
<td>Argon cooling gas flow rate</td>
<td>15 L/min</td>
<td>13 L/min</td>
</tr>
<tr>
<td>Auxiliary gas flow rate</td>
<td>0.8 L/min</td>
<td>0.9 L/min</td>
</tr>
<tr>
<td>Interface cones</td>
<td>Nickel</td>
<td>Nickel</td>
</tr>
<tr>
<td>Acceleration voltage</td>
<td>10 kV</td>
<td>4 kV</td>
</tr>
<tr>
<td>Mass resolution</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Mass analyzer pressure</td>
<td>5-8×10⁻⁹ mbar</td>
<td>4×10⁻⁹ mbar</td>
</tr>
<tr>
<td>Detection system</td>
<td>Nine Faraday collectors</td>
<td>Eight Faraday collectors</td>
</tr>
<tr>
<td>Sampling mode</td>
<td>Three or ten blocks of 10 × 8 s integrations for laser and solution analysis, respectively</td>
<td></td>
</tr>
<tr>
<td>Background/baseline</td>
<td>3 min on peak in 2.0% HNO₃</td>
<td>on peak</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Glass cyclonic spray chamber fitted with a Micromist PFA nebulizer</td>
<td>?</td>
</tr>
<tr>
<td>Uptake mode</td>
<td>Free aspiration</td>
<td>Free aspiration</td>
</tr>
<tr>
<td>Sample uptake rate</td>
<td>50 µL/min</td>
<td>?</td>
</tr>
<tr>
<td>Typical sensitivity on $^{88}$Sr</td>
<td>55-60 V/ppm (10-11 ohm resistors)</td>
<td></td>
</tr>
<tr>
<td>Ar sample gas flow rate</td>
<td>0.60-1.05 L/min, optimized to maximize $^{88}$Sr signal</td>
<td>0.85 L/min, optimized to maximize $^{88}$Sr signal</td>
</tr>
<tr>
<td>Beam dispersion</td>
<td>(Dispersion Quad)</td>
<td>−25</td>
</tr>
</tbody>
</table>

**Table 2b.** Operating parameters of UP213 New Wave™ and Helex/ Lambda Physik Compex™ 110ArF excimer laser (modified from Ramos et al. 2004 and Woodhead et al. 2005).

<table>
<thead>
<tr>
<th>Laser</th>
<th>UP213 New Wave™ Laser</th>
<th>Helex Lambda Physik Compex 110ArF excimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>213 nm</td>
<td>193 nm</td>
</tr>
<tr>
<td>Spot dimensions</td>
<td>160 µm × 500 µm trough or 80 µm × 500 µm trough or 80 µm diameter spot</td>
<td>105 µm diameter spot</td>
</tr>
<tr>
<td>Energy density</td>
<td>~7-10 J</td>
<td></td>
</tr>
<tr>
<td>Pulse rate</td>
<td>10 Hz</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
<td>Helium</td>
</tr>
<tr>
<td>He auxiliary gas flow rate (for analysis of Sr isotopes in plagioclase)</td>
<td>0.85 to 0.95 L/min, optimized every run session</td>
<td>0.2 L/min, optimized every run session</td>
</tr>
</tbody>
</table>
signals (compared to electronic baselines) at the 83, 84, and 86 mass positions and removed during baseline correction. Typical signals were always less than 3 mV of 83Kr. Although this methodology worked for Ramos et al. (2004), Hart et al. (2005) questioned whether on-peak baselines accurately account for Kr contributions and instead used the 84Kr intensity corrected for 84Sr contributions to calculate 86Kr contributions. Thus, as is typical for laser ablation analyses, the user will have to evaluate which procedure works more effectively in this regard.

After Kr, REE$^{2+}$ corrections are undertaken. The 167Er$^{2+}$ and 171Yb$^{2+}$ ion intensities can be measured in the low 3 and center Faraday collectors, respectively, which are set at half-mass positions (Tables 1a and 1b). From the 167Er$^{2+}$ ion intensity, interfering 166Er$^{2+}$, 168Er$^{2+}$ and 170Er$^{2+}$ intensities can be calculated using the 166Er$^{2+}$/167Er$^{2+}$, 168Er$^{2+}$/167Er$^{2+}$, and 170Er$^{2+}$/167Er$^{2+}$ ratios measured from reference solutions. These contributions can then be mathematically removed from the mass 83, 84, and 85 ion intensities prior to correcting for the next interfering element/molecule. Yb interference corrections can then be pursued in the same fashion.

After REE$^{2+}$, 87Rb corrections can then be undertaken. Ramos et al. (2004) applied a procedure that used the interference corrected 85Rb intensity and the mass bias factor determined from the interference corrected 86Sr/88Sr ratio to determine the 87Rb contribution to the ion intensity at mass 87. In contrast, Hart et al. (2005), which intended to measure glasses with significantly higher Rb/Sr ratios, determined that 87Rb contributions could not be accurately assessed to the degree needed for samples with high Rb/Sr by using 86Sr/88Sr determined mass bias corrections. As a result, these authors applied Rb corrections that incorporated 85Rb/87Rb ratios determined on an external set of glasses in which respective 87Sr/86Sr ratios had previously been measured.

Although a complete set of correction procedures are reviewed here, selected materials may not require correction for all potential interferences, thus appropriate correction procedures will need to be determined for each type of material analyzed. In addition, if analyses are undertaken at poor vacuum conditions, peak-tailing corrections may also need to be applied.

After correcting for Rb, standard normalization of Sr isotopes to 86Sr/88Sr = 0.1194 can be undertaken to correct for mass spectrometer mass bias/mass fractionation. Note that this normalization is ~10 times larger than that for TIMS, thus inaccurate normalization can have a much greater impact on resulting normalized Sr isotope ratios. Ultimately, this correction procedure proved effective in generating accurate 87Sr/86Sr isotope ratios but only variably accurate 84Sr/86Sr ratios in a broad array of target materials (Ramos et al. 2004). For analyses using the Nu PlasmaTM, it is unclear how separation between Ca dimers, Ca argides, and REE$^{2+}$ would be accomplished, and as of yet, successful Sr isotope analyses of REE-rich minerals such as clinopyroxene are absent. For the GV IsoprobeTM, no detailed evaluation of interferences has been undertaken probably because most are removed by use of a collision cell. It has been demonstrated, however, that relatively accurate Sr isotope ratios can be obtained on REE-rich minerals such as clinopyroxene (Schmidberger et al. 2003), so it is assumed that REE interfering effects are generally minor. Vroon et al. (2008) offers a review of correction and reduction procedures from a range of studies using laser ablation for further reference.

To analyze Sr isotopes using laser ablation, we suggest starting with previously determined mass spectrometer settings, laser settings, and collector configurations. A program should then be initiated to evaluate all potential elemental and molecular interferences and create appropriate correction procedures. Once done, users should analyze “known” samples with previously determined Sr isotope ratios. Modern marine carbonates are commonly used to evaluate measurement accuracies as modern seawater 87Sr/86Sr is well-known. Overall however, there is a dearth of reference materials for laser ablation applications, thus it is commonly easiest to analyze potential target materials using micromilling, chromatography, and TIMS or purified solution MC-ICPMS to obtain accurate Sr isotope ratios of reference materials. Reproducing “known” results will give users a means in which to evaluate measurement...
accuracy and reproducibility and an opportunity to test correction procedures for a range of materials. Such tests should be done for each type of material to be analyzed (i.e., carbonate, plagioclase, clinopyroxene, apatite, etc) and will be useful for evaluating at which concentration levels potential interferences can be accurately corrected (e.g., Rb/Sr ≤ 0.05).

**Sr isotope applications.** Studies measuring $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of minerals using laser ablation sampling encompass a wide range of applications. Carbonates, for example, offer a generally Sr-rich mineral with few interferences. For evaluating analytical accuracies and precisions associated with carbonates, shells characterized by modern marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are commonly measured (e.g., Christensen et al. 1995; Outridge et al. 2002; Ramos et al. 2004; Woodhead et al. 2005). Alternative methods include directly comparing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured using laser ablation sampling to results determined on purified samples, including freshwater otoliths, acquired using micromilling and TIMS (Barnett-Johnson et al. 2005). For otolith studies, spot and raster sampling have been used to document sequential changes in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that correlate to fish movements from freshwater to marine environments (e.g., Woodhead et al. 2005), between freshwater environments (e.g., Outridge et al. 2002), and within natal rivers of origin (e.g., Barnett-Johnson et al. 2008).

Studies identifying the natal rivers of fishes include Atlantic croaker (Thorrold and Shuttleworth 2000), tropical shad (Milton and Chenery 2003), barramundi (McCulloch et al. 2005), and California salmon (Barnett-Johnson et al. 2005). Barnett-Johnson et al. (2008) also correlated the spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with distinctive microtextural features indicative of wild or hatchery origins (Barnett-Johnson et al. 2007) to evaluate wild and hatchery salmon population dynamics in California offshore marine fisheries. This study demonstrated that natal rivers associated with both wild and hatchery fish could be accurately determined using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured by laser ablation sampling. The combination of otolith studies to date offers a foundation in which individual otolith growth rings can be used to estimate times associated with fish movements through different freshwater environments prior to outmigration to marine environments. These time constraints may aid in evaluating ecological and biological factors to ensure the greatest chance for successful marine migration and future reproduction of endangered anadromous fish species.

In contrast to otoliths, Bizzarro et al. (2003) focused on analyses of magmatic apatite and carbonate phenocrysts to identify open-system processes affecting alkaline igneous rocks of the Sarfartoq province (Greenland). This study successfully combined variable textural and mineral $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions, and concluded that similar $^{87}\text{Sr}/^{86}\text{Sr}$ variations in both apatite and carbonate crystals result from coeval crystallization occurring during continuous modification of the host magma as a result of magmatic recharge. Magmas acquired variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that originated from melts added to the magma reservoir from a range of subcontinental lithospheric- and plume-related carbonate-rich mantle components. Similar processes occurred throughout the history of the Sarfartoq province.

For plagioclase, early studies focused on identifying and tracking open-system processes reflected in $^{87}\text{Sr}/^{86}\text{Sr}$ variations retained in phenocrysts from basalts at Long Valley, California (USA) (Christensen et al. 1995) and El Chichón (Mexico) (Davidson et al. 2001). Christensen et al. (1995) used $^{87}\text{Sr}/^{86}\text{Sr}$ ratios acquired by laser ablation sampling to demonstrate that plagioclase phenocrysts, which otherwise were characterized by uniform major element compositions, retained variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios resulting from magma mixing associated with post-caldera basaltic magmatism at Long Valley. Additionally, Davidson et al. (2001) used laser rastering to measure $^{87}\text{Sr}/^{86}\text{Sr}$ profiles along traverses across plagioclase phenocrysts from El Chichón, an arc-related volcano. These traverses were shown to be generally symmetric, were correlated to textural features revealed by Nomarsky imaging, and demonstrated differential rim and core $^{87}\text{Sr}/^{86}\text{Sr}$ signatures confirmed by micromilling and TIMS. El Chichón variations resulted from sequential growth of plagioclase cores in magma with higher $^{87}\text{Sr}/^{86}\text{Sr}$ and growth
Figure 10. Sr ion beam intensity, $^{84}\text{Sr}/^{86}\text{Sr}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ transect profiles of an otolith. Profiles reflect marine (0.70916) and freshwater (0.70653) $^{87}\text{Sr}/^{86}\text{Sr}$ signatures. Such profiles can be used to identify the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of natal rivers and track fish outmigration to marine environments, immigration to freshwater environments, or migration between freshwater environments. [Reproduced by permission of The Royal Society of Chemistry, from Woodhead et al. (2005), *Journal of Analytical Atomic Spectrometry*, Vol. 20, Fig. 2, p. 26].
of rims in magma with lower $^{87}\text{Sr}/^{86}\text{Sr}$. For both studies, not only were the effects of open-system processes such as magma mixing identified, but the isotope compositions of the different mixed magmas were constrained.

In contrast to smaller volcanic systems, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of plagioclase obtained using laser ablation sampling were also used to 1) confirm the presence of a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ variations in all major formational units of flood basalts erupted on the Columbia Plateau (USA) and 2) constrain the processes associated with continental, plume-related volcanism. Early-erupted Imnaha basalts, previously thought to result from melting of Yellowstone plume mantle without significant external inputs, exhibited a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in plagioclase phenocrysts while host basalts exhibited only subtle variations (Eckberg et al. 2006). The overall range of $^{87}\text{Sr}/^{86}\text{Sr}$ variations, best observed in plagioclase, originated from plume-related magma interacting with either accreted fluid-fluxed subcontinental mantle/crust or cratonic crust encountered during ascent (Wolff et al. 2008). Where magmas interacted with fluid-fluxed materials, plagioclase $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were lower than plume-related signatures. Where magmas interacted with cratonic crust, presumably while residing in crustal chambers, plagioclase crystals retained highly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Further plume-related magmatism on the Columbia River plateau generated Picture Gorge basalts and the volumetrically immense Grande Ronde basalts. Both whole-rocks and plagioclase crystals from these formations retained wider ranging $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in comparison to earlier-erupted Imnaha basalts. These variations resulted from more extensive interactions with either fluid-fluxed accreted materials (Picture Gorge basalts) or greater amounts of assimilation of cratonic crust (Grande Ronde basalts) and reflected the same processes affecting Imnaha basalts, but on a massive scale. Interestingly, laser ablation analyses of plagioclase crystals were key in identifying the processes that influenced isotopic and trace element signatures of early erupted magmas, processes that would greatly influence the geochemical and isotopic nature of future eruptions of large-volume flood basalts such as those comprising the Grande Ronde formation.

In addition to tracing the sources and processes generating Columbia River flood basalts, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured using laser ablation sampling were also used to evaluate crystal residence times for all major Columbia River basalt formations (Ramos et al. 2005). Results indicated that most plagioclase phenocrysts, and where available clinopyroxene, reflected 1) disequilibrium with host melts and 2) phenocryst incorporation into large-volume flood basalt magmas at varied times prior to eruption, some less than five years prior (Fig. 11).

Open-system processes influencing the products of the 1915 Lassen volcano (USA) eruption were also evaluated by Salisbury et al. (2008). This study pursued an integrated approach using crystal size distributions (CSDs), textural, and in situ analyses including $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured by laser ablation sampling. Andesite- and dacite-hosted plagioclase crystals with $^{87}\text{Rb}/^{86}\text{Sr}$ ratios as high as 0.20 were successfully analyzed. Sequential trough analyses documented subtle core to rim $^{87}\text{Sr}/^{86}\text{Sr}$ variations that resulted from the complex interplay of a range of dacite, andesite, and basaltic andesite magmas. Phenocrysts of plagioclase, with uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, were thought to have experienced simple crystallization histories over 100s to 1000s of years in a dacitic magma chamber. Microphenocrysts, however, grew over months in an environment in which andesite and basaltic andesite were mixed, while microlites reflected equilibrium growth during ascent and eruption from the resulting hybrid magma. This study exemplified the utility of integrating a range of chemical and physical parameters to understand the histories of individual eruptive episodes of arc volcanoes.

For clinopyroxene, Schmidberger et al. (2003) targeted individual crystals from a single mantle xenolith and documented a large range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This range resulted, at least partially, from the infiltration and reaction with kimberlitic host melt during magmatic ascent but may have also been largely present before magmatism. If so, highly variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
Inter- and Intracrystalline Isotopic Disequilibria

present at the single xenolith scale would indicate direct evidence for mantle heterogeneity at small scales.

Although not all-inclusive, these studies reflect the broad utility of $^{87}$Sr/$^{86}$Sr isotope analyses obtained using laser ablation samples in a microspatial isotope context. The potential for these analyses to address new questions associated with biological and petrological fields is extensive and future studies will undoubtedly use such analyses in even more creative ways.

**Pb isotope technique.** In contrast to Sr, Pb isotopes measured using laser ablation have far fewer apparent interfering elements or molecules. By introducing thallium into the sample stream via a nebulizing spray chamber prior to the sample entering the torch of the mass spectrometer, analytical precisions associated with Pb isotope ratios are increased substantially as a result of mass fractionation correction using $^{203}$Tl/$^{205}$Tl normalization (Horn et al. 2000). As a result, Tl normalized Pb isotope ratios sampled using laser ablation attain precisions and accuracies that approach those of double-spike TIMS measurements although some variances have been documented (Thirwall 2002). Alternatively, sample-standard bracketing can be effectively used, commonly using NBS610 glass as a standard. Thus, laser ablation sampling offers an opportunity to acquire accurate and precise Pb isotope ratios in a highly time-efficient fashion.

**Figure 12** illustrates results from six separate $50 \times 250 \mu m$ troughs analyzed from a single Valles caldera potassium feldspar crystal using the ThermoFinnigan Neptune™ (Wolff...
Analyses of isotope ratios involving the more abundant $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$ isotopes average 2.1095 and 0.8701 for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ respectively, with all individual analyses lying within in-run error of these averages. To evaluate accuracy, the crystal was then dissolved, Pb was purified using anion exchange chromatography, and the sample was analyzed using Tl-doping following the procedures of Wolff and Ramos (2003). Results for this crystal are 2.1096±0.00002 and 0.8701±0.0001 for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, respectively. For potassium feldspar, laser and single crystal results yield identical $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios and attest to the accuracy of laser ablation, Tl-normalized Pb isotope measurements.

To evaluate ratios normalized to less abundant $^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ average 17.80, 15.49, and 37.55 respectively for the same six laser ablation analyses. These ratios are characterized by poorer measurement precisions, as reflected by two decimal place precisions, as a result of much lower $^{204}\text{Pb}$ ion intensities. And unlike larger peaks, $^{204}\text{Pb}$ is corrected for interfering $^{204}\text{Hg}$ which is present in minor amounts presumably as impurities in He or Ar carrier gases. In addition, very minor signals originate from the potassium feldspar crystal itself, potentially near the crystal surface. To minimize such surface contributions for both Hg and Pb, ~3 µm of the surface was ablated along the targeted sampling area prior to analysis. To correct for Hg, $^{202}\text{Hg}$ is monitored and used to calculate $^{204}\text{Hg}$ contributions using the $^{202}\text{Hg}/^{204}\text{Hg}$ ratio measured in separate Hg solutions. Results for the single crystal analysis are 17.802±0.002, 17.489±0.002, and 37.555±0.005 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ respectively. Thus, laser ablation measurements relative to $^{204}\text{Pb}$ have poorer overall analytical precisions but still lie within in-run error of the single crystal results, again demonstrating measurement accuracy for potassium feldspar.
In contrast to Sr, Pb contents of most magmatic materials are substantially lower. In this case, the Pb content of the potassium feldspar is generally between 10-15 ppm, a concentration level that still yields highly accurate and precise $\frac{^{208}\text{Pb}}{^{206}\text{Pb}}$ and $\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$ ratios and highly accurate and relatively precise $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$, $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$, and $\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$ ratios. In contrast to the Tl normalized analytical procedure described above, Simon et al. (2007) pursue a sample/standard bracketing methodology that normalizes laser ablation results to nebulized NBS981 solutions to correct for mass bias. This procedure is reserved, however, for measuring ratios involving the larger $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$ isotopes from potassium feldspars and related glasses from Long Valley rhyolites where interferences are presumed to be minor. Further studies by Kent (2008) evaluate Pb isotope accuracy, reproducibility, and interference corrections using both Faraday and ion multipliers, and sample/standard bracketing using standard/reference glasses.

**Pb isotope applications.** There are a range of studies that focus on Pb isotopes analyzed using laser ablation. Below, selected studies are reviewed that either focus on uncommon radiogenic materials or materials characterized by common Pb isotope signatures. Studies targeting highly radiogenic materials such as zircon are not included. For example, Willigers et al. (2002) obtained Pb ages using laser ablation sampling, including $^{204}\text{Pb}$ results using an ion multiplier, for apatite, monazite, and sphene. While sphene ages diverged from those determined by TIMS, apatite and monazite ages were within error of TIMS results for equivalent mineral separates. These authors attributed this sphene age discrepancy to the presence of interferences across the Pb mass spectrum, although individual interferences were not identified.

For materials characterized by common Pb isotope ratios, Mathez and Waight (2003) used laser ablation sampling to determine $\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$ and $\frac{^{208}\text{Pb}}{^{206}\text{Pb}}$ ratios of sulfide and plagioclase crystals to evaluate the evolution of the Bushveld Complex (South Africa), a large layered mafic intrusion. These authors found Pb isotope disequilibrium between sulfides and plagioclase, and between plagioclases from different layers of the intrusion. For sulfide-plagioclase pairs, sulfides typically had lower $\frac{^{208}\text{Pb}}{^{206}\text{Pb}}$ and higher $\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$ ratios than plagioclases that were attributed to the addition of Pb from surrounding country rocks. Pb isotope variations between plagioclase crystals from different layers of the mafic intrusion resulted from the inputs of multiple sources of Pb during crystallization. Different Pb isotope ratios between sulfides and plagioclase however, resulted from Pb addition to sulfides after temperatures dropped below those needed for Pb exchange in plagioclase. And, these different Pb sources were thought to have obliterated any potential mantle isotopic signatures of the mantle sources associated with the original magma.

Pb isotope ratios of Bishop Tuff-hosted potassium feldspars obtained by Simon et al. (2007) were used to confirm that feldspar crystals grew from magmas associated with the Bishop Tuff, not magmas related to precaldera glass mountain lavas. Similar to Wolff and Ramos (2003), Simon et al. (2007) used Pb isotopes of potassium feldspar to discount the possibility that the Bishop Tuff resulted from long-lived rhyolitic magmatism and instead concluded that the Bishop Tuff more-likely resulted from the accumulation of many small, different magmas. In addition, Pb isotope ratios defined linear trends between young Long Valley basalts and local evolved crust undermining any potential for accurate age determinations using Rb/Sr isotopes.

In addition to igneous applications, Tyrrell et al. (2007) utilized the efficiency of laser ablation sampling to analyze a large suite of potassium feldspar crystals to trace sediment provenance associated with the breakup of Pangea. Potassium feldspar crystals in selected Triassic and Jurassic sandstones were targeted to identify crystal populations based on Pb isotopes. Both sandstones had two main populations of crystals with the Jurassic sandstone also having one additional outlier population. Crystals from each population were found together independent of facies and stratigraphic position. Isotope ratios from these distinct populations were compared with potential source rocks found throughout the North Atlantic region. Sources were then either discounted or included and paleodepositional directions were
determined for sediments contributing to these sandstones. In addition to constraining sediment transport directions, dispersal distances were also determined, as well as identification of different sediment sources associated with different periods of North Atlantic rifting.

Pb isotopes analyzed using laser ablation sampling also aided geologic structure-based studies. Connelly and Thrane (2005) utilized laser ablation sampling to rapidly measure a large suite of potassium feldspar crystals from currently adjoining early Proterozoic orthogneiss terranes in west Greenland to evaluate a potential suture zone between them. These authors focused on initial Pb isotope ratios of potassium feldspars to distinguish whether these terranes shared similar magmatic sources and were thus related. Two populations of feldspars were present, each with distinctive initial Pb isotope ratios, which suggested that these orthogneiss bodies did not originate from similar mantle/crustal sources. As a result, these authors concluded that a cryptic suture must be present between the two west Greenland orthogneiss terranes.

Overall, Pb isotopes sampled using laser ablation offer an accurate means in which to acquire data in a time-efficient manner. Current applications attest to the potential utility of Pb isotopes results measured using laser ablation sampling for a wide variety of scientific applications in the earth sciences.

**MICROANALYTE ANALYSIS**

**Single crystal analyses**

*Technique.* Together with micromilling, single crystal isotope analyses target a limited sample microspatially (i.e., a single crystal) but unlike micromilling, single crystals usually contain low overall amounts of analyte because either the crystal is small or the crystal is characterized by low analyte concentrations. In addition to single crystals, multi-crystal samples may also be targeted using the same technique because many multi-crystal samples (e.g., quartz) also have low analyte abundances. For Sr and Pb isotopes, olivine and quartz best demonstrate the utility of single crystal analyses.

Olivine, \((\text{Mg,Fe})_2\text{SiO}_4\), and quartz, \(\text{SiO}_2\), are found in a wide variety of igneous rocks and have little tolerance for incorporating Sr or Pb into their respective mineral structures as a result of elemental size and charge considerations. As a result, both typically have very low Sr and Pb concentrations. In contrast, mineral or melt inclusions captured during olivine or quartz growth may contain significant amounts of Sr and/or Pb. The generally small size of these inclusions, however, may require large amounts of host mineral to obtain minimal analyte abundances. For olivine, inclusions of basaltic melt can contain Sr concentrations ≥1000 ppm. If, for example, melt inclusions account for 1% of the total weight of an olivine crystal and contain 1000 ppm Sr, a 1 mg (0.001 g) single crystal would yield ~10 ng of Sr, an amount easily analyzed using TIMS. If, however, the crystal contained only 0.1% melt inclusions, a 1 mg crystal would yield ~1 ng of Sr. A ~1 ng Sr sample can still be analyzed to a reasonable precision (\(^{87}\text{Sr}/^{86}\text{Sr} ≤ 0.0001\)) using TIMS but uncertainty of whether the measured isotope ratio reflects that of melt inclusions magnifies as the amount of Sr contamination resulting from the digestion and purification process becomes a greater percentage of the total amount of analyte analyzed. This “processing” contamination is measured as a total process blank. If such blanks can be limited to ≤10 pg Sr, small (~1 ng) samples can be analyzed successfully while maintaining blank levels of ≤1%. Maintaining low blank levels is the most critical aspect of accurately analyzing single crystals, or small micromilled samples, characterized by low analyte abundances. While Sr samples as small as 0.5 ng can be successfully analyzed (e.g., Wolff et al. 1999), uncertainties in blank corrected ratios increase dramatically when processing blanks exceed 1% of total analyte.
For quartz crystals from high-silica rhyolites, captured melt inclusions may have low Sr but high Pb concentrations. Current studies targeting comendites and pantellerites from Baitoushan volcano (Ramos et al. 2007, 2008) determine quartz-hosted melt inclusion Sr concentrations of ≤1 ppm while Pb concentrations are ≥40 ppm. These quartz crystals are characterized by high melt inclusion contents, typically >20%. For a 3 mg quartz crystal, the Sr yield would be <0.6 ng while the Pb yield would be >24 ng. While analyzing 0.6 ng of Sr is challenging, especially given that associated blank would have to be ≤6 pg to maintain a 1% blank contribution, analyzing 24 ng of Pb is easily accomplished using solution MC-ICPMS in conjunction with Tl-normalization (Wolff and Ramos 2003). Thus, single quartz crystals could be analyzed for Pb isotopes but multiple crystals would be required for Sr isotope analyses.

To undertake low blank single crystal or micromilled Sr isotope measurements, a method of column chromatography must be pursued which offers an opportunity to attain total process blanks of generally less than ~20 pg. Two methods are prevalent: 1) a stripping method using Sr spec™ resin and 2) a chromatographic method using standard cation exchange resin. The first uses a small volume of Sr spec™ resin loaded onto ~1 ml shrink-fit Teflon columns with a frit inserted at the column tip (e.g., Davidson et al. 1998; Charlier et al. 2006). This method removes unwanted ions by flushing the resin with ~3N HNO₃ and removing Sr with pure ultrafiltered water. Total process blanks using this method can be <10 pg (e.g., Harlou et al. 2005).

During the Wolff et al. (1999) study, the presence of organic ion signals that appeared at both Sr and Rb masses was identified in samples processed using batches of Sr spec™ resin made prior to 1998. As a result, pyrex columns with high aspect ratios (height/width >25) were designed that use ~0.5 ml of 200-400 mesh cation exchange resin to undertake low blank Sr chromatography. These small-volume, high-aspect ratio columns were fitted with microporous frits and minimized blank while maximizing Rb/Sr chemical separations. The procedure for Rb and Sr sequestration was essentially the same as larger cation exchange columns commonly used for whole-rock purifications, but the resin and eluant volumes were dramatically reduced. These small-volume columns were used to undertake column purifications of quartz and potassium feldspar crystals (Wolff et al. 1999; Knesel et al. 1999) and plagioclase, clinopyroxene, amphibole and olivine crystals (Ramos and Reid 2005) and maintained blanks that were typically <20 pg and commonly <10 pg.

To obtain low blanks using either Sr spec™ or cation exchange resins, the resins must be extensively pre-cleaned prior to use and all acid components used in the digestion and chromatography procedures must be fresh and doubly distilled. Normally these acids are distilled the night before use and extracted directly from the distillery. In addition, 3 ml Teflon digestion vessels are used and must be cleaned extensively. All should undergo cleaning in Teflon bottles containing distilled aqua regia that sit on a warm hot plate for more than a week. All pipette tips and bottles containing distilled acids should be cleaned prior to undertaking chemistry. For pre-cleaning cation exchange resin, a ~20 ml disposable Bio Rad Econo-column™ is filled with resin and flushed with freshly distilled 2.5N HCl, 6.0N HCl, and ultrafiltered H₂O for at least two days prior to use. For Sr spec™ resin, hot water is commonly flushed through the resin in a similar fashion.

To determine the total amount of Sr in the samples to be analyzed, isotope dilution using a high-purity Rb/Sr spike is required. Spikes should be added to samples and blanks prior to undergoing digestion. A high Rb/Sr spike and a low Rb/Sr spike are commonly used depending on the Rb/Sr ratio of the target material (e.g., plagioclase would require low Rb/Sr spike and potassium feldspar would require high Rb/Sr spike). For crystals from high-silica rhyolites (e.g., potassium feldspar and quartz), a spike with very high Rb/Sr may be required. Isotope dilution results will 1) yield Rb and Sr concentrations and ⁸⁷Rb/⁸⁶Sr ratios for age dating or age correction if required and 2) allow for the determination of total analyte abundances so that samples can be stripped of blank contributions. Such contributions will be minor with
blanks that are <1% of the analyte but may become more significant when blanks exceed 1%. For actual blank measurements, minimal amounts of spike should be used (commonly ~1 µL) so that pre-spiked $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of blank can be determined and samples can be corrected for the effects of blank. It may also be useful to determine blank $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from samples collected from flushing greater amounts of acid (i.e., greater than used in normal column chromatography) through columns without adding spike. Accurately constraining the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the blank will be critical for correcting samples in which blank exceeds 1% of the total analyte.

For analyses of small samples, thermal ionization mass spectrometry (TIMS) is usually preferred to MC-ICPMS. Loading of samples requires TaO$_2$ and dilute phosphoric acid that must also be devoid of Sr (see Charlier et al. 2007). Standard loading procedures include adding 1 µL of TaO$_2$ suspended in a solution of 5% nitric acid and 1 µL of 5% phosphoric acid. Filaments for analyses should be made of rhenium and brought to temperatures that exceed normal Sr analytical conditions and be manually checked for Sr and Rb signals in the mass spectrometer prior to loading. Commonly, filaments have to set at high temperatures to allow for all Sr and especially Rb to be depleted. Care should be used for analyzing small Sr samples and NBS987 Sr standards should be analyzed at similar concentration levels to evaluate mass spectrometer analytical accuracy and reproducibility at low analyte levels.

For Pb purifications, anion exchange resin and 1N HBr can be used in similarly small columns as that used for Sr microchemistry. Resin again needs to be pre-cleaned prior to use and HBr needs to be doubly distilled to maintain low blanks. Teflon cleaning procedures should be followed as described for Sr and columns should be cleaned accordingly. Additional chromatography procedures may also be used. Studies associated with single zircons have also been successful in purifying Pb while minimizing blank, thus select procedures from these studies could also be pursued. Ultimately, Pb isotope analyses should be undertaken using either double-spiking and TIMS or MC-ICPMS. Alternatively, Tl-doping or standard sampling bracketing can be used with MC-ICPMS.

Sr and Pb applications. Single crystal isotope analyses were used in a range of applications. The earliest focused on a wide variety of minerals to identify and constrain the effects of open-system processes and discriminate between competing models describing the petrogenesis of S-type rhyolites from Italy (Feldstein et al. 1994). Two separate rhyolites were involved: a more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ endmember and a less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ endmember. Single crystal analyses included plagioclase, potassium feldspar, biotite, and cordierite, in addition to glass. For plagioclase, textural evidence was also integrated with isotope results. Coarse and medium, highly sieved plagioclase crystals with low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined to be associated with clinopyroxene megacrysts and mafic enclaves, materials not directly related to host rhyolites. All other plagioclase crystals had higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and were considered phenocrystic. These phenocrystic plagioclase $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were generally lower than those of phenocrystic potassium feldspar crystals but higher than accompanying glass (assumed to reflect the melt component). In addition, individual biotite crystals retained initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that spanned most of the total observed range in both rhyolitic glasses and crystals. Thus, a complex petrogenetic history was involved. Feldstein et al. (1994) concluded that this history included crystallization of phenocrysts occurring at a mixing interface between two layers of rhyolitic magma in which minerals grew in an environment that offered a range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Additionally, diffusion modeling was used to constrain possible crystal residence times and suggested that this process occurred relatively quickly (<10,000 years) as much of the observed isotopic heterogeneity would have been eliminated if time periods were longer. This study exemplified the use of single crystal isotope analyses to evaluate the petrogenetic history of highly complicated rocks involving a range of melt and mineral components derived from multiple sources.
More recent studies targeting large rhyolitic magma systems included Wolff et al. (1999) and Knesel et al. (1999). These studies used Sr isotopes of single potassium feldspar crystals to evaluate open-system processes affecting Bandelier Tuff and Taylor Creek (New Mexico, USA) rhyolites. Wolff et al. (1999) focused on linear trends defined by potassium feldspar crystals in the Otowi member of the Bandelier Tuff (Valles caldera). These trends could either have been Rb/Sr isochrons or mixing lines (line "A" in Fig. 13 defined by potassium feldspars). If isochronous, results suggested extensive residence of Bandelier high-silica rhyolitic magma for ~270,000 years prior to eruption. Alternatively, linear trends could have also resulted from two-component mixing without age significance.

To further discriminate between these possibilities, Wolff and Ramos (2003) evaluated similar potassium feldspar crystals using single crystal Pb isotope analyses. Single crystal Pb isotope results also defined a linear array that, if isochronous, yielded an age in excess of 10 Ma, an age that far exceeded any reasonable magma residence time. Thus, Pb isotope variations must have resulted from mixing. Sr was highly depleted (~3 ppm) in Valles magmas compared to Pb (~40 ppm), therefore Sr isotopes must have been modified long before Pb isotopes given any reasonable contaminant (e.g., local crustal lithologies), and both must then have resulted from mixing not aging. Thus, results from combined single crystal Sr and Pb isotopes undermined the possibility of long-lived magma residence at Valles caldera and called into question similar assessments for other large rhyolitic magma systems. Additional work focused on $^{87}\text{Sr}/^{86}\text{Sr}$ variations in glasses from glomerocrysts and melt inclusions in quartz. Overall, results suggested mixing (Fig. 13) between three magmatic components: 1) magmas with crustal Sr and Pb isotope signatures, 2) magmas with more-mantle like Sr and Pb isotope signatures, and 3) minor amounts of local Proterozoic crust. Mixing between these components resulted in a complex array of Sr and Pb isotope variations that may be typical for large rhyolitic magma systems.

Knesel et al. (1999) also focused on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of potassium feldspar crystals derived by both single crystal and micromilling analyses. This study integrated crystal size parameters from Taylor Creek rhyolites to constrain the evolutionary history of a single dome from another

![Figure 13. Single crystal feldspar, quartz separates, and glass $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ results from pumice and pumice hosted glomerocrysts of the Bandelier Tuff. Variations result from mixing 1) highly-evolved, rhyolitic magmas with crustal isotope characteristics with 2) highly-evolved, magmas with more mantle-like $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ characteristics (double-headed, bold arrow indicated by “A”). In addition, crystals and glasses that diverge to the upper left of this diagram (dashed arrows indicated by “B”) originate from melt, present as glass in glomerocrysts or melt inclusions in quartz, that has also incorporated local Proterozoic crust after mixing (Wolff and Ramos 2004).](image-url)
large rhyolitic magma system. **Figure 14**a shows that as individual crystal size increased, initial $^{87}\text{Sr} / ^{86}\text{Sr}$ values increased to a maximum and then decreased to a minimum. Interestingly, initial $^{87}\text{Sr} / ^{86}\text{Sr}$ profiles of variably sized sanidine crystals showed the same pattern, in this case core-to-rim, of increasing to a maximum then decreasing to a minimum with the added observation that the smallest crystals lacked the initial increasing trend (Fig. 13b). Knesel et al. (1999) postulated that these trends resulting from crystal growth initially in a magma chamber contaminated by incongruent melts of crustal components with higher $^{87}\text{Sr} / ^{86}\text{Sr}$ (initial increasing $^{87}\text{Sr} / ^{86}\text{Sr}$ trend) followed by progressive recharge of a similar composition magma with lower $^{87}\text{Sr} / ^{86}\text{Sr}$ (decreasing $^{87}\text{Sr} / ^{86}\text{Sr}$ trend). Larger, presumably older crystals found throughout the chamber grew during contamination and magma recharge events and recorded sequentially increasing and then decreasing initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios from core to rim, whereas smaller, presumably younger crystals grew during the magma recharge phase only and recorded only decreasing initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios. In this study, the combined use of micromilling, single crystal, and crystal size techniques proved to be critical to identifying a complex petrogenetic history.

In contrast to successful studies focused primarily on single potassium feldspar crystals, additional mineral and melt components were used by Ramos et al. (2007) to evaluate magma generation processes at Baitoushan volcano (China/North Korea). At Baitoushan, minerals and melt obtained from at least three recent (<10 ka) comendite and pantellerite eruptions reflected disequilibrium at many levels. **Figure 15** illustrates potassium feldspar and pumice fragment $^{87}\text{Sr} / ^{86}\text{Sr}$ variations found in highly-evolved, alkali-rich comendite and trachyte components comprising the 980 AD eruption which emitted ~100 km$^3$ of volcanic material. Initially the

**Figure 14.** a) Initial $^{87}\text{Sr} / ^{86}\text{Sr}$ versus crystal size in sanidines from the Taylor Creek Rhyolite complex. This diagram illustrates increasing then decreasing initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios in crystals with decreasing size. Smaller crystals do not record increasing initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios because they reflect later growth in a magma chamber that was initially contaminated by wallrock melt with high $^{87}\text{Sr} / ^{86}\text{Sr}$ and then progressively fluxed with rhyolitic magma with low $^{87}\text{Sr} / ^{86}\text{Sr}$. b) Diagram of changing $^{87}\text{Sr} / ^{86}\text{Sr}$ values in three micromilled sanidine phenocrysts of different sizes. The largest crystal showed increasing $^{87}\text{Sr} / ^{86}\text{Sr}$ near the core to a maximum $^{87}\text{Sr} / ^{86}\text{Sr}$, and then decreasing $^{87}\text{Sr} / ^{86}\text{Sr}$ from the middle of the crystal to the rim. Smaller crystals recorded only portions of this trend owing to later growth in the magma chamber. [Used by permission of Oxford University Press, from Knesel et al. (1999), *Journal of Petrology*, Vol. 40, Fig. 4 and 7, p. 779 and 781].
eruption produced comendite, while the final stages were comprised of trachyte. For comendites, potassium feldspar crystals retained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which were both higher and lower than accompanying pumices while the reverse was seen in trachyte components where potassium feldspar crystals retained a limited range in $^{87}\text{Sr}/^{86}\text{Sr}$ while trachyte pumices spanned most of the range of comendite potassium feldspars. These relationships reflected the complex interplay of highly-evolved magmas and most-likely resulted from the mixing of a range of melt and mineral components which were not directly identified in the eruptive products.

In addition to the 980 AD eruption, a pantellerite was erupted from Baitoushan at ~0 AD. This pantellerite retained a range of mineral components including potassium feldspar, clinopyroxene, and quartz. These different components retained a range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that were different than accompanying ratios of pumices (Fig. 16A). Melt, as reflected by pumice, generally defined a ~400 ka isochron that suggested an extended magma residence age. Mineral components, however, did not lie along this trend and reflected more consistent, less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In contrast, comendites have potassium feldspar crystals that retain even greater $^{87}\text{Sr}/^{86}\text{Sr}$ variations than trachytes that are both higher and lower that accompanying comendite pumice fragments. Results reflect open-system magmatic processes most-likely involving a range of highly-evolved, variably radiogenic magmas rather than variably enriched crustal materials.

**Figure 15.** Feldspar and pumice $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ results from the ~980 AD Baitoushan comendite eruption (Ramos et al. 2007, 2008). The eruption involved two distinct magma components: 1) a early-erupted, highly-evolved comendite and 2) a later-erupted, less-evolved trachyte. Unfilled squares and diamonds represent results from individual comendite potassium feldspar crystals and pumice fragments, respectively. Filled squares and diamonds represent results from individual trachyte potassium feldspar crystals and pumice fragments, respectively. Comendite and trachyte crystals and pumices retain distinct isotope characteristics. Trachyte potassium feldspar crystals define a linear trend (also in $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$) that results from 2-component mixing that does not involve comendite as a mixing endmember. Accompanying trachyte pumices are characterized by greater $^{87}\text{Sr}/^{86}\text{Sr}$ variations imposed after feldspar fractionation. In contrast, comendites have potassium feldspar crystals that retain even greater $^{87}\text{Sr}/^{86}\text{Sr}$ variations than trachytes that are both higher and lower that accompanying comendite pumice fragments. Results reflect open-system magmatic processes most-likely involving a range of highly-evolved, variably radiogenic magmas rather than variably enriched crustal materials.

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In contrast to rhyolites, Ramos and Reid (2005) identified assimilation processes occurring during basaltic magmagenesis at Pisgah Crater, California (USA) using single olivine crystals, in addition to plagioclase, clinopyroxene, and amphibole. This study clearly demonstrated that melt inclusions in olivine crystals from alkalic, continental basalts reflected both 1) the greatest overall Sr isotope variations of all magmatic components present and 2) sequentially increasing Sr isotope ratios in progressively erupted lavas. Results confirmed that basalts acquired a range of isotope characteristics that resulted from the incorporation of materials during residence at crustal depths (Glazner and Farmer 1992) and not as a result of the mixing of mantle-derived magmas (Reiners 2002). Further work by Mickiewicz (2007) combined crystal size distributions (CSDs) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained by micromilling to evaluate the crustal residence history and magma chamber dynamics associated with these basalts. This work also clearly identified individual sieve-textured plagioclase xenocrysts that retained highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that confirmed an origin involving crustal assimilation.

Figure 16. Rb-Sr and U-Pb systematics of minerals and pumices from the ~0 AD Baitoushan pantellerite eruption (Ramos et al. 2007). A) Illustrates differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of individual potassium feldspar crystals, individual clinopyroxene crystals, and a quartz separate (~20 crystals) as compared to accompanying pumice fragments. Quartz has high $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ (>1000) and lies to the left of this graph (as indicated by the arrow). Pumice fragments generally define a linear trend that, if isochronous, suggests ~400,000 years of magma residence prior to eruption. Potassium feldspar and clinopyroxene crystals, however, have relatively consistent $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are significantly lower than pumice fragments. B) Pb isotope results from the same crystals (except quartz symbols represent two individual crystals) that define a negative trend with all minerals and pumice fragments having variable signatures that cannot result from extended magma residence. Results are consistent with Pb addition after the bulk of crystallization of clinopyroxene and potassium feldspar, or the scavenging of crystals from unrelated magmas by the magma represented by pantellerite pumice fragments.
In contrast in igneous applications, Muller et al. (2000) used micromilling to mill out small pieces of synkinematic minerals (not milling them directly) from mylonites and dykes from the Eastern Alps. Using this technique, samples could be inspected prior to milling thick sections to ensure exclusion of mineral inclusions that could potentially impact Rb and Sr budgets. Although this study mainly targeted white micas that grew in pressure shadows of feldspar and andalusite during deformation, potassium feldspar, plagioclase, biotite, and andalusite were also included. Multiple white mica samples, and some additional minerals, were used to generate isochrons dating 1) mica formation resulting from mylonitization affecting their respective host rocks and 2) mica formation ages associated with small local dikes in the area. Most mylonitization ages were similar to nearby intrusion ages, suggesting that most white micas, and thus mylonitization, resulted from deformation due to pluton emplacement. In addition, dikes yielded similar ages as both intrusion and mylonitization ages. Thus, micromilling was successfully used to obtain portions of single crystals that required low blank chromatography to obtain dates of deformation related to local intrusive rocks.

Overall, single crystal isotope studies have proven valuable in addressing questions related to igneous and metamorphic petrogenesis and discriminating between potential models describing how volcanic and metamorphic rocks and minerals obtain their chemical and isotopic characteristics. Further studies will undoubtedly integrate even more chemical, textural, and size parameters to better identify and constrain the effects of processes involved in magmagenesis and metamorphism.

**SUMMARY**

As reviewed above, the utility of microscale isotope sampling is only beginning to be appreciated. Whether micromilling, single crystal analyses, or in situ analyses using SIMS or laser ablation sampling, these techniques offer vast potential for understanding a range of natural systems. Although this manuscript mainly focuses on applications targeting magmatic minerals and melt components, investigations of biological materials have also benefited greatly. As such, additional fields will also benefit from such isotope sampling techniques in the future. As has been the case for the last ~20 years, advances in both sampling systems and measuring technologies will continue, increasing the possibilities and range of opportunities to apply multiple isotope systems in scientific applications. Ultimately, these techniques will allow evaluations of natural systems in new and innovative ways, ways that are bound to expand our understanding of natural processes in revolutionary ways.

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