Mineral-scale Sr isotope variation in plutonic rocks – a tool for unraveling the evolution of magma systems

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Abstract

Isotope ratios of elements such as Sr, Nd, Pb and Hf can be used as tracers of magmatic sources and processes. Analytical capabilities have evolved so that we can now analyse isotope ratios *in situ*, and can therefore use isotopic tracers within single minerals to track the changing magmatic environment in which a given mineral grew. This contribution shows that Sr isotope ratios in feldspars that make up plutonic rocks will typically preserve initial isotopic variations provided precise and accurate age corrections can be applied. Variations in initial isotope ratio can give a core-to-rim record of magmatic evolution and can be used to diagnose open system events such as contamination and magma recharge and mixing.

New single grain Sr isotope data are presented from the Dais Intrusion, Antarctica, which reflect an open system origin for the crystals. The crystal cargo appears to be aggregated and assembled during transport and emplacement. This model, as opposed to a magma body crystallising post emplacement, may be more applicable to plutonic rocks in general, and is testable using the *in situ* isotopic determination methods described here.

Key words

Differentiation, Feldspars, Isotope ratios, Cooling histories, Crystal Isotope Stratigraphy

1. Introduction; Principles of isotopic microsampling; can the approach be applied to plutonic systems?

Convergence in our understanding of volcanic and plutonic processes and the link between them has become an exciting prospect. Crystals provide that link. They record pre-eruption processes that reflect the architecture and connectivity of subvolcanic plumbing systems, and the degree to which magmas interact with the lithosphere during storage and transport within the system. Eruption of a magma aliquot from the system preserves the state of the magma system at that time – crystals transported by the erupted magma can be examined to ascertain whether the magma experienced contamination and/or recharge before eruption, and if so how much/ how often? The crystals remaining behind in sub-crustal reservoirs after the system becomes inactive end up as plutonic rocks, and may provide a more complete record of the evolution of the system.

Crystal phases in a wide range of volcanic rocks have been shown to exhibit considerable diversity in initial isotope ratios (e.g. Ramos and Reid, 2005; Tepley et al., 2000; Knesel et al., 1999). This suggests that crystals commonly grow from magmas undergoing open system differentiation, and are mechanically juxtaposed during or prior to eruption. The isotopic compositions of core-rim traverses across crystals and included minerals and melts can be integrated to provide an effective history of magmatic processes (where core compositions and textures record earlier events and those of the rims represent magma compositions immediately before/during eruption – Figure 1). This approach, termed *crystal isotope stratigraphy*

(CIS) by Davidson et al. (1998) demonstrates that many magmatic crystals are **not** true "phenocrysts". Elemental and isotopic observations, along with petrographic and textural observations indicate that many crystals have originated from cumulate deposits of earlier magmatic episodes (Dungan and Davidson, 2005) which have been remobilized and, in some cases, subsequently overgrown. The great advantage of working in volcanic systems is that they represent a "snapshot" of magma evolution, with rapid cooling on eruption effectively freezing in the elemental, isotopic and textural information. While CIS has proved to be very powerful in volcanic systems, we know that the slow cooling holding crystalline material at high temperatures which characterizes plutonic system causes re-equilibration of textures and chemistry. The question is whether the isotopic information which can potentially be used to unlock differentiation processes is still retained at the length scale of crystals in plutonic rocks (Figure 1).

Gagnevin et al. (2005a,b) considered the extent to which K-feldspar megacrysts in granites from Elba might retain their original Sr and Pb isotopic ratios rather than diffusively re-equilibrating. They found that timescales of >2 myrs (Pb) and 20-100 myrs (Sr) would be required to produce the observed isotopic profiles by diffusive equilibration. The long duration of these timescales relative to processes such as cooling and crystal growth, along with the fact that the timescales inferred from Pb and Sr isotope systematics respectively do not agree, suggests that diffusion did not generate the observed isotopic variations in the Elba granite.

We can generalize such considerations to different phases and compositions. A simple consideration of diffusion systematics suggests that, at least for Sr isotopes in typical plutonic phases from plutonic rocks (such as feldspar and pyroxene), if isotopic diversity exists at the mineral scale, it ought to be retained. Figure 2 shows the Sr equilibration lengthscale with time, of plagioclase and clinopyroxene at a variety of temperatures. The shaded bar represents typical grain sizes in plutonic rocks (~1.5-15 mm; 2 x ***a***). At magmatic temperatures up to 1100°C we can expect gabbroic rocks with grain sizes>1.5 mm to retain any initial isotopic heterogeneity for >1000 years. The time at which phases are effectively held at high temperature is a function of factors such as wallrock temperature (a function of depth of emplacement) and, most importantly, magma volume. Large volumes of magma might be expected to cool over timescales far in excess of 1000-10,000 years. On the other hand, slower cooling rates generally lead to larger crystals – which in turn would take longer to fully equilibrate.

We might also expect compositional effects to be important. Differentiated magmas are likely to crystallize feldspars lower in anorthite content, with higher diffusivities at a given temperature. In this case the trade-off is that more differentiated magmas crystallize at lower temperatures. Thus An_{60} plagioclase at 900°C has similar diffusivity to pure anorthite at 1100°C. The addition of water will also lower liquidus temperatures, leading to lower diffusivities, and typically result in larger crystals so that the extent of diffusive equilibration of individual grains is reduced still further.

2. Practical considerations – what to microsample and how?

In order for CIS to be successfully employed as a monitor of magmatic evolution a number of factors need to be considered;

1. Concentrations of elements of interest (Sr, Nd, Hf, Pb, Os) need to be sufficiently high that isotopic ratios can be determined accurately and precisely on the sub-grain scale. In this context the precision required must clearly fall within the range of isotope ratios initially present. Whole rock isotope ratios from a sample suite can be useful in suggesting whether or not isotope heterogeneity at the mineral scale is likely.
2. Diffusivities of species of interest in minerals at likely liquidus-solidus temperatures must be sufficiently slow that primary variations in isotope ratio are preserved.
3. Parent-daughter ratios should be as low as possible in order to minimize age correction errors.
4. Mineral grains need to be sufficiently large and abundant that several samples (minimum core-rim) can be analysed by whatever technique is chosen.
5. In order to provide as complete a record as possible, minerals that crystallize over a significant fraction of the solidus-liquidus range are ideal.
6. Minerals should ideally display clear petrographic features (chemical

zoning, dissolution surfaces, inclusion bands etc.) that can be integrated with isotopic microsampling.

When all of these factors are considered and weighed against each other, we find that Sr isotope ratios in feldspars provide an ideal tool to illuminate petrogenetic processes in plutonic rocks. This is because most plutons contain feldspar (plagioclase feldspar in mafic plutons, plagioclase and alkali feldspar in silicic bodies); it crystallizes over a wide P-T range and provides clear textural features that reflect changing crystallization environments; it contains high concentrations (100s to 1000s of ppm) of Sr, and, at least in plagioclase feldspar, Rb/Sr ratios are low.

Sr isotope ratios at the mineral scale have been variously measured by ion microprobe (SIMS), laser ablation ICP-MS (LA-ICP-MS) or mechanical extraction (microdrill) followed by chemical separation and thermal ionization mass spectrometry (TIMS). Each method has its advantages and disadvantages, which will not be discussed at length here. We have chosen to employ microdrilling, chemical separation and TIMS. The methodology is explained in detail by Charlier et al. (2006). The main advantage of this approach is that we can analyse very small samples (down to 1 ng of Sr) with precisions on $^{87}Sr/^{86}Sr$ of better than 30 ppm (Figure 3). The main disadvantage is that it is very time-consuming, requiring skill and care to maintain blanks at levels of <<1% (which typically translates to ~10 pg of Sr).

SIMS analyses, by virtue of small spot sizes and consequent small ion beams and much poorer precision, cannot compete with the TIMS method for Sr isotope ratios - although it can be used to great advantage in other applications, such as U-Th-Pb in zircons where very small spot sizes are required (e.g. Charlier et al., 2005). The low precision is compounded by the inability to resolve ^{87}Rb from ^{87}Sr, and thus adequately account for isobaric interferences.

LA-ICP-MS has been embraced as a technique for isotopic analysis and has been used successfully in analyzing U-Th-Pb isotopic compositions in zircons, and Pb isotope compositions in alkali feldspars (Gagnevin et al., 2005). However, in the analysis of Sr isotope ratios it may not be possible to obtain the excellent precision afforded by TIMS because of difficulties in adequately correcting the ^{87}Sr/^{86}Sr ratio for isobaric interferences (Waight et al., 2002); especially the ^{87}Rb contribution at mass 87. Davidson et al. (2001) showed that Rb/Sr corrections can be made to LA-ICP-MS analyses if less than ~0.2, and if carefully calibrated using known standards. Even so, the precision on the measured ^{87}Sr/^{86}Sr deteriorates as Rb/Sr increases. Ramos et al., (2004) present a more optimistic assessment of LA-ICPMS, demonstrating that ^{87}Sr/^{86}Sr$_i$ ratios with precisions of ~200 ppm can be obtained on samples with Rb/Sr up to 0.08. Both Ramos et al. (2004) and Davidson et al. (2001) agree that the laser can be used effectively where the dynamic range in ^{87}Sr/^{86}Sr is large relative to the precision that can be obtained as constrained by Sr contents, Rb/Sr and analytical procedures.

This potential problem of Rb interference is even more acute with ancient plutonic samples where an age correction (and therefore precise and accurate Rb/Sr) is needed.

3. Mineral-scale Sr isotopic heterogeneity in mafic-ultramafic intrusions

The arguments above give us confidence that relatively small volumes of basaltic magma emplaced and crystallized at relatively shallow levels in the crust where ambient wallrock temperatures are low should escape significant Sr isotopic re-equilibration. An ideal case study to test whether initial $^{87}Sr/^{86}Sr$ variations are preserved at the mineral scale would therefore comprise a large dyke, sill or small plagioclase-phyric intrusion from which bulk rock isotopic heterogeneity has already been established.

3.1. The Dais Intrusion, Dry Valleys, Antarctica

The Dais Intrusion in the Dry Valleys of Antarctica is part of the laterally extensive Basement Sill. The Sill has been shown to vary up-section in chemical and isotopic composition (Marsh, 2004; Foland and Marsh, unpublished data). It was emplaced into granitic country rocks as part of the c. 180 myr Ferrar Dolerite magmatic episode associated with Gondwanaland breakup. Marsh (*op. cit.*) interprets the Sill, along with associated superjacent sill intrusions, as the high level expression of a crust-crossing mush column supplying crystal-charged magma to high level intrusions. This magma-mush column is believed to have supplied contemporaneous volcanoes of the Kirkpatrick Basalts, which may have lain above the present erosion level. The Dais Intrusion represents the thickest expression of the Sill. Here, a laterally extensive tongue of orthopyroxene gabbro (the opx-tongue) which is present throughout the Basement Sill, is expressed as layered gabbro.

Isotopic microsampling through the Dais Intrusion, which represents the greatest expression of the opx tongue in the Basement Sill, has been employed to test the hypothesis that the opx tongue reflects transport and emplacement of an allochthonous crystal cargo, rather than *in situ* crystallization of a liquid (or series of liquids). If crystallized *in situ*, mineral phases within the same sample (within a few mm of each other) would be expected to share an identical initial Sr isotopic ratio. If crystals grew at deeper levels (possibly from isotopically contrasting liquids), then juxtaposed during transport and emplacement, neighbouring crystals would exhibit diversity in initial isotopic ratios. These scenarios are, of course, end members of a spectrum of possible mechanisms. Isotopically variable crystal cargoes could be deposited and then consolidated by growth from intercumulus liquids. In such cases we might expect intercumulus phases to be isotopically similar, or crystal overgrowths to reflect a common intercumulus composition, much as many crystals in volcanic rocks have rims in equilibrium with the host groundmass. In any case there is a fundamental requirement to integrate isotopic microsampling with careful petrographic observations.

The data are given in Table 1 and illustrated in Figure 4. The methodology of isotopic microsampling is described in detail by Charlier et al. (2006). Pertinent points of note in the context of this contribution are;

1. There is a trade-off between Sr concentration and sample size needed for precise analysis (> 1 ng Sr; see Figure 3). The Basement Sill gabbro is relatively poor in Sr (<100 ppm bulk rock) with the bulk of the Sr partitioned into the plagioclase (Table 1). Sample sizes – particularly of pyroxene – need to be larger than those used in most of our previous studies. A 60 micron cylindrical drill was used to sample multiple pits in the crystal cores, recovering 0.1-1.5 mg of sample, corresponding to 5-160 ng of Sr (cf Figure 3). This corresponds to a much coarser sampling strategy than we typically employ using cylindrical-tipped drills (Charlier et al. 2006).
2. The sample age (177 Ma; Elliot et al., 1999) means that an age correction is necessary. Rb/Sr ratios were therefore measured by aliquoting 10% of the sample solution and measuring Rb and Sr contents on a Finnigan Element2 ICP-MS. Samples were weighed after drilling - weighing errors might lead to inaccurate Rb and Sr contents, although the effects of weighing errors can be ignored in the age correction as the Rb/Sr ratio was measured on the same solution with the same instrument calibration.

The data from Table 1, representing drilled cores of crystals, are plotted on a parent-daughter (“isochron”) diagram on Figure 4a. The age-corrected Sr isotope ratios are highly scattered, suggesting that the rocks were isotopically heterogeneous on the mineral scale when emplaced. The scatter cannot be attributed to an error in the age (which simply defines the isochron slope), and is unlikely to be due to random (and unusually large) errors in the measured Rb/Sr ratios. Figure 4b shows that even within a single sample (A292) there is considerable initial isotopic heterogeneity among mineral phases. For the two rocks with a single mineral analysed, the isotopic ratio of the mineral in A285 is not the same as that of the whole rock, while that of A377 is within the (propagated) uncertainty. The bulk rock isotopic data then are likely to simply reflect the contributions of the different mineral phases weighted by their modal abundances and Sr contents. The initial isotope heterogeneity in the Dais Intrusion indicates that crystals (pyroxene *and* plagioclase; Figure 4) have grown in an open system (variable ^{87}Sr/^{86}Sr) and been mechanically transported/ juxtaposed - consistent with the opx tongue representing an allochthonous crystal cargo.

3.2. The Rum Intrusion, NW Scotland

The Rum intrusion in northwest Scotland is a relatively thick pile of mafic and ultramafic cumulate rocks. Whole rock isotopic variations reported by Palacz (1984) are interpreted as reflecting open system magmatic evolution, with progressive crustal contamination of resident magmas punctuated by recharge by ultramafic mantle-derived magmas. CIS enables us to distinguish whether crystallization took place *in situ* from a series of variably-contaminated liquids, or whether the crystals in a given layer were transported and deposited there following evolution at different times and/or places in the magmatic system. Tepley and Davidson (2003) document mineral-scale isotopic heterogeneity consistent with the latter mechanism. Initial isotopic diversity between mineral phases, and within individual plagioclase grains increases up-section within a layer. Isotopic diversity is likely the result of variable degrees of contamination at a boundary layer where wall-rock assimilation and concomitant crystallization (i.e. AFC) is most likely to occur.

As discussed above, the extent to which isotopic ratios equilibrate over a given lengthscale within (and among) mineral phases depends on diffusivity – which itself is a function of temperature and mineral type. The Eastern Layered Series from which Tepley and Davidson took the samples for their 2003 study is >700m thick (Emeleus and Bell, 2005). A significant volume of mafic/ ultramafic magma might be expected to hold minerals at high temperature for a long time. The cooling *rate* is therefore the key criterion dictating the lengthscale over which isotopic equilibration occurs in a given mineral type. We can therefore use the lengthscales over which isotopic diversity is preserved to constrain cooling rates. If diffusivity is expressed as a function of time;

$$D = D_o e^{\frac{E_a}{RTf(t)}} \qquad (1)$$

(where D = diffusivity, D_0 and E_a are the frequency factor and activation energy respectively, both of which are specific to the element of interest and phase of interest, R = the gas constant, T = temperature and t = time)

Then it can be integrated to define a lengthscale parameter ***P***;

$$P = \int_{t_o}^{t} D(t)dt \qquad (2)$$

Such that the mean path length (***a***) for diffusional equilibration is;

$$a = \sqrt{P} \qquad (3)$$

This approach, described by Reddy et al. (1996) is illustrated in Figure 5a using simple cooling algorithms. In the Rum rocks core-rim isotopic ratios in plagioclase over 1-2 mm distance are distinct, indicating that cooling was faster than c. 0.05°C per year. A caveat is that diffusional closure was effectively complete within about 3000 years. This can be seen on Figure 5 where the dot on each curve represents the time at which the temperature has fallen to 1000°C. After this there is no further increase in the equilibration length – diffusion is only effective at the highest temperatures, over the first 300°C of cooling.

Figure 5b illustrates a similar exercise for the Basement Sill, Antarctica, discussed above. In this case the simple geometry constrains the cooling rate so a 1-D conductive cooling model can be constructed to estimate cooling rates at various distances from the contact and for different country rock temperatures. Considering the slowest possible cooling rate with hot country rocks (500°C) and at the centre of the thickest accumulation, diffusive equilibration is likely to have occurred only over <0.3mm for An_{60} (even less for more anorthitic plagioclase). Note that cooling at the contact is effectively instantaneous – resulting in virtually no diffusive re-equilibration. However, if the magma convects, cooling rates away from the contact will be less variable, and cooling of the interior would be much faster than shown here. Cumulative emplacement of the magma as multiple thinner sheets, or increased advection of heat into the surrounds through convective cooling of the wallrocks via hydrothermal circulation would reduce the extent of diffusive re-equilibration. Flowing magma through the sill over significant periods of time could increase it – although the considerations of Figure 2 suggest that this period of time would need to be >>1000years. The simple calculation suggests that any mineral-scale initial Sr isotopic heterogeneity is likely to be preserved and lends encouragement for more detailed study than the pilot survey shown in Figure 4.

A comparison of the Basement Sill and Rum examples suggests that the vertical extents of the magma systems during emplacement were of the same order of magnitude. At the Basement Sill, a well-exposed architecture and intrusion geometry allows us to calculate the effects of cooling on the preservation of isotopic systematics. At Rum we are less sure of the emplacement history – the magma might have been emplaced as "one shot" into the volume it now occupies and the crystallized products organized themselves into layers subsequently, or it could have been intruded as a series of sheets, emplaced into cooled and (partially) crystallized earlier products (Bedard et al., 1988). The preservation of isotopic heterogeneity in this case can be inverted to constrain cooling history. The relatively rapid cooling rate inferred (Figure 5) is similar to (within an order of magnitude) that of the Basement Sill. The volumes of magma involved at Rum were likely significantly greater than the cumulate layers now observed (Henderson and Gijbels, 1976) but must have at least been sufficiently small and cooled sufficiently fast to fulfill the criteria for preserving isotopic heterogeneity documented in Figure 5a. Thus the isotopic heterogeneity is more consistent with emplacement as multiple sheets rather than a single volume of magma. Emeleus et al., (1996) note that field and petrographic evidence is also consistent with multiple intrusion.

Isotope microsampling at the mineral scale in plutonic rocks can therefore not only record open system magma evolution, but can also constrain the cooling rates of the system. This means that it could, in principle, help us to constrain the emplacement mechanisms of plutons. Judicious choice of mineral (Figure 2) and isotopic species could be made to cover different cooling timescales and samples taken from different parts of the intrusion relative to carefully-mapped contacts. The degree of isotopic equilibration can be related to cooling rates, and cooling rates can then be matched to model results for different geometries and intrusion rates or frequencies. Thus cases where isotopic equilibration has occurred over significant lengthscales would indicate slow cooling, which in turn would require larger masses of magma emplaced, rather than the progressive assembly of smaller masses over time (Figure 6). Quantification of cooling rates might then be related to textural criteria to gain a better general understanding of temperature-time pathways in intrusive bodies. This might be particularly useful for granites (*s.l.*) where field and petrographic observations cannot easily distinguish the emplacement architecture and suggestions that assembly was via dikes or sheets (e.g. Petford et al., 2000) remain, at present, speculative.

4. Mineral-scale Sr Isotopic heterogeneity in granite intrusions

The lower temperatures of crystallization of evolved magmas suggest, on the basis of arguments above, that initial Sr isotopic heterogeneity should be easily preserved. However, more evolved magmas, and the phases which crystallize from them, are typically enriched in Rb and a precise and accurate correction is needed in order to distinguish Sr initial isotope heterogeneity with confidence.

We have studied a sample of the Shap Granite of NW England (Davidson et al., 2005) on the basis of its potential as an analogue to inclusion-bearing evolved volcanic magmas. In the latter, petrographic evidence, inclusion morphology and field relationships commonly indicate that minerals have been exchanged between the host and inclusion magmas (e.g. Eichelberger, 1978; Clynne, 1999). CIS, where applied, has confirmed this to be the case (Davidson et al., 1990, Davidson and Tepley, 1997, Tepley et al., 1999). The Shap Granite is noted for the abundance of mafic inclusions (“enclaves” in the terminology of some; e.g. Vernon, 1984) and the abundance of K-feldspar megacrysts. The megacrysts can be found commonly in the mafic inclusions where they are rimmed by plagioclase. Although alternative mechanisms have been proposed (Caunt, 1987 suggested that they were metasomatic in origin), petrographic observation suggests that the megacrysts grew originally in the granite magma and were mechanically transferred into the inclusion magma, where an overgrowth of the new equilibrium feldspar composition, plagioclase, was added. This can, in principle, be tested if the inclusions and host magmas from which the megacrysts grew had different initial isotopic compositions (Cox et al., 1996).

Figure 7 shows the Rb and Sr isotopic data for the core and rim of a single plagioclase-rimmed K-feldspar megacryst. The excellent correlation on the isochron diagram might encourage interpretation of the data as a single crystal isochron with an age of 405 Ma. However, isochronous relationships are predicated on the basis of all phases sharing a common initial Sr isotope ratio. Published ages for the Shap Granite are somewhat younger (zircon = 390±6 Ma; Pidgeon and Aftalion, 1978; K/Ar (biotite) = 397±7; Rundle, 1992). **IF** a younger age is accepted then the core and rim initial isotopic ratios are isotopically distinct (Davidson et al., 2005), as illustrated in the cartoon of Figure 7. The high $^{87}Sr/^{86}Sr_i$ core and lower $^{87}Sr/^{86}Sr_i$ rim is consistent with growth of the core in a contaminated granitic magma, followed by transfer into a more mafic, lower $^{87}Sr/^{86}Sr_i$ magma from which the plagioclase rim was grown. Recent volcanic rocks from Chaos Crags, California, exhibit similar relationships (Tepley et al., 1999; Figure 7).

Being able to distinguish whether an ancient evolved rock exhibits mineral-scale initial isotopic heterogeneity depends on the range of $^{87}Sr/^{86}Sr_i$, and its total uncertainty. The total uncertainty, in turn, depends mainly on the magnitude of the Rb/Sr ratio (and uncertainty on this measurement), and the age (and uncertainty on the age) of the sample (i.e. how well the age correction can be made - see Seibel et al. (2005) for discussion, and Figure 8). Recent volcanic samples for which age correction is not an issue typically show variations in $^{87}Sr/^{86}Sr_i$ of the order of 1500 ppm. At this level, isotopic variations in young rocks are easily distinguished since typical modern instrumentation returns precisions on

$^{87}Sr/^{86}Sr$ of better than 20 ppm. However, age correction may easily compromise such precision (Figure 8b) as errors on ages are typically 1%, and on the Rb/Sr ratio from which the correction is projected may be 0.5-3% depending on the analytical technique used. Compromise of initial isotope ratios may be particularly severe if alteration has changed the Rb/Sr ratio by adding or subtracting either element from the system at some time between crystallisation and analysis. Careful petrography accompanied, if possible, by stable isotope determinations are needed to evaluate this potential problem.

Note that for high Rb-Sr systems (granites) in cases of very slow cooling, minerals close progressively to Rb and Sr diffusion over timescales which are significant relative to the ingrowth of radiogenic Sr. This effectively disturbs isochronous relationships. The variations in calculated $^{87}Sr/^{86}Sr_i$ among different minerals in this case may reflect redistribution of Rb and Sr during cooling as $^{87}Sr/^{86}Sr$ is changing (Ganguly and Ruiz, 1986; Giletti, 1991), rather than real initial variations due to open system petrogenetic processes such as suggested at Shap. At cooling rates greater than ~200°C per million years isotopic compositions are effectively quenched in (Giletti, 1991) and for cases such as those modelled in Figure 5 with cooling rates >10,000°C per million years and mineral closure temperatures typically >>500°C, the issue is not relevant. In the deep crust, where cooling through blocking temperatures might be controlled by slow processes such as uplift, isotopic redistribution during cooling may be significant. Here again CIS approaches may find a use. The concept of using closure temperatures to define cooling rates (Giletti, 1991) was developed independently of spatial information (other than a general idea of grain “size”). Large single mineral grains with slow-diffusing species can be microsampled in the same way as described for Figure 5, and cooling rates so determined can be checked against the closure temperature method.

Waight et al. (2000) were perhaps the first to apply microisotopic approaches to granitic rocks. They showed that both $^{87}Sr/^{86}Sr_i$ and $^{143}Nd/^{144}Nd_i$ variations are preserved in feldspar megacrysts from 395 Ma granitoids of SE Australia. They used isotopic variations to confirm the suspicion, based on previous petrographic and elemental observations (e.g. Vernon, 1986), that megacrysts were transferred between granite host and mafic inclusion. Most importantly, however, the complementarity of variation between $^{87}Sr/^{86}Sr_i$ and $^{143}Nd/^{144}Nd_i$ lends confidence that Rb/Sr isotopic systematics can be relatively robust in plutonic systems, at least where slow cooling effects and extensive hydrothermal alteration can be discounted.

The link between volcanic and plutonic systems is emphasized when large plutons are effectively mobilized and eviscerated *en masse.* The 5000 km^3 Fish Canyon Tuff of Colorado is considered to be an example of such an event. Preservation of mineral-scale initial isotope heterogeneity in the Fish Canyon Tuff (Charlier et al., 2004) offers the prospect of understanding the timescales and mechanisms of pluton assembly and evolution.

5. Conclusions

Isotopic variations at the mineral scale can, just as with volcanic rocks, be used to monitor magma evolution, processes and timescales in plutonic rocks. Contamination and magma mixing are reflected in core-rim variations of $^{87}Sr/^{86}Sr_i$ in feldspars. By defining a mean effective path length for diffusion based on an integrated diffusivity during cooling, the lengthscales over which isotopic re-equilibration is achieved in crystals can be used to constrain cooling histories. The caveats to these approaches are;

1. An assessment of the potential degree of isotopic re-equilibration should be made – for cases of exceptionally large, and therefore slow-cooling high temperature magmas variations in $^{87}Sr/^{86}Sr_i$ might be expected to re-equilibrate during cooling.
2. Age corrections will need to be made – as the age and Rb/Sr of the samples increase the likelihood of confidently identifying distinctions in $^{87}Sr/^{86}Sr_i$ decreases.
3. Potential alteration effects will need to be evaluated. Additional work using isotope systems that are less mobile (Sm-Nd, Lu-Hf) or minerals that are more “robust” (e.g. zircon) may be needed. However, this is offset against the advantages of using Rb-Sr on feldspar (large minerals, high Sr contents, low parent/daughter ratios).

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Figure Captions

Figure 1. Schematic representation of principles behind crystal isotope stratigraphy (CIS). Isotopic variation in a magma system due to processes such as magma recharge and contamination is recorded by crystals as they grow; panel (1) shows illustrative $^{87}Sr/^{86}Sr$ transects across feldspar crystals experiencing different evolutionary histories. In the plutonic system two additional complications need to be considered. Isotopic re-equilibration may occur (2) if crystals are held at sufficiently long temperature for a sufficiently long time (isotope profile evolves from t_0 to t_1 and t_2). The issue of what exactly "long" times and "high" temperatures are needed is addressed in the text and figures 2 and 5. (3) illustrates the additional complication of radiogenic ingrowth with time, which depends on the Rb/Sr in different crystal zones (which itself is fixed by partitioning controlled by magmatic processes). Correction for ingrowth to recover initial isotope variations (panel 1) and thereby deduce differentiation histories is addressed further in the text and Figure 7.

Figure 2. Equilibration lengthscale versus time - the curves show the time taken for Sr isotope ratios to reach 95% equilibration ($Dt/a^2>0.25$), where D = diffusivity (taken from Cherniak and Watson, 1994, for plagioclase, and Sneeringer et al., 1984, for diopside), a= lengthscale of equilibration and t = time.

Figure 3. Trade off between sample size and element concentration, illustrating masses needed to provide 1 to 100ng of the element. In the case of Sr 1 ng of Sr can be analysed precisely and accurately using TIMS. Samples <1ng see a deterioration in precision, and a progressive influence of blank corrections. To the right, bars indicate typical concentration ranges of Sr for common minerals that could be used for CIS (crystal isotope stratigraphy). Referring these to the graph on the left (shaded bands with dotted arrows) shows that we can confidently analyse sample masses <<0.1 mg. Sample volumes

are shown along the top, translated from masses using $\rho_{\text{mineral}} \sim 2.8$ gcm^{-3}, to enable simple evaluation of potential sample sizes in plutonic rocks (mineral sizes are typically >> 1mm^3).

Figure 4. a) $^{87}Sr/^{86}Sr_i$ vs Rb/Sr diagram for minerals of the Dais Intrusion (data in Table 1). Age of 177Ma is assumed for Ferrar dolerites magmatism (with which the Basement Sill is associated); Elliot et al., 1999. b) Comparison of mineral initial $^{87}Sr/^{86}Sr$ data from 3 rocks. Bars for whole rock compositions (WR) are unpublished data of Foland and Marsh. 2σ error is estimated propagated error (from method of Siebel et al., 2005)

Figure 5. a) (after Tepley and Davidson, 2003) Equilibration path length versus time for plagioclase feldspar (labradorite) in the Rum intrusion cooling from 1300°C. Curves represent linear (solid) and exponential (dashed) cooling rates where T = f(t) as defined on the diagram and input into equation 1 in the text. Filled circles indicate point on the curve where temperature has dropped to 1000°C – note that this effectively marks closure to diffusion. b) Equilibration path length versus time for plagioclase feldspar (labradorite) in the Dais Intrusion (Basement Sill), Antarctica. Cooling rates are constrained by 1-D conductive cooling model for hot interior of the sill 200m from the contact, starting at a liquidus temperature of 1100°C (Nick Petford, pers. com.). Two different country rock temperatures (T_{CR}) are used, resulting in different linear cooling rates (k).

Figure 6. Schematic illustration of how determination of degree (lengthscale) of isotopic re-equilibration in minerals can be used to constrain emplacement mechanisms. Cooling rate curves can be constructed as in Figure 5, requiring knowledge of diffusivity-temperature relationship in mineral of interest (Figure 2) and starting temperature of magma. The cartoon shows how the crystal isotope stratigraphy of minerals from the centre and margins of a large intrusive body might vary with mode of emplacement.

Figure 7. Sr isotope systematics of a plagioclase-rimmed megacryst from

a mafic inclusion in the Shap Granite of NW England. Inset shows a field photograph of an enclave with megacrysts, and the megacryst sampled (Perlroth, 2000). Cartoon (top right gives a possible interpretation of how distinct core and rim isotope ratios might be interpreted as an isochron with an erroneous age. Photos bottom right summarise results from the Chaos Crags inclusion-dacite system (Tepley et al., 1999) which can be considered as a simple modern analog.

Figure 8. Cartoon representing effects of age correction in compromising our ability to distinguish heterogeneity in $^{87}Sr/^{86}Sr_i$. The simple case of two samples ***L*** and ***H*** (low Rb/Sr and high Rb/Sr respectively) is considered where ***L*** and ***H*** may be two minerals or zones within a single mineral, having different $^{87}Sr/^{86}Sr_i$ as a result of magmatic processes. Error bars on $^{87}Rb/^{86}Sr_i$ are schematic – although typically they are >> 10 x the error on $^{87}Sr/^{86}Sr_i$ (within symbol size). a) as age increases (t_1-t_3) the error on the corrected $^{87}Sr/^{86}Sr_i$ of sample ***H*** increases, such that by t_3 it cannot be distinguished from sample ***L***. b) if error on the age is also taken into account, since age is proportional to the slope of the isochron, the error on the age-corrected $^{87}Sr/^{86}Sr_i$ of sample ***H*** increases. c) all other things being equal, a greater range in $^{87}Sr/^{86}Sr_i$ makes it more likely that initial isotopic heterogeneity will be detected in ancient samples.

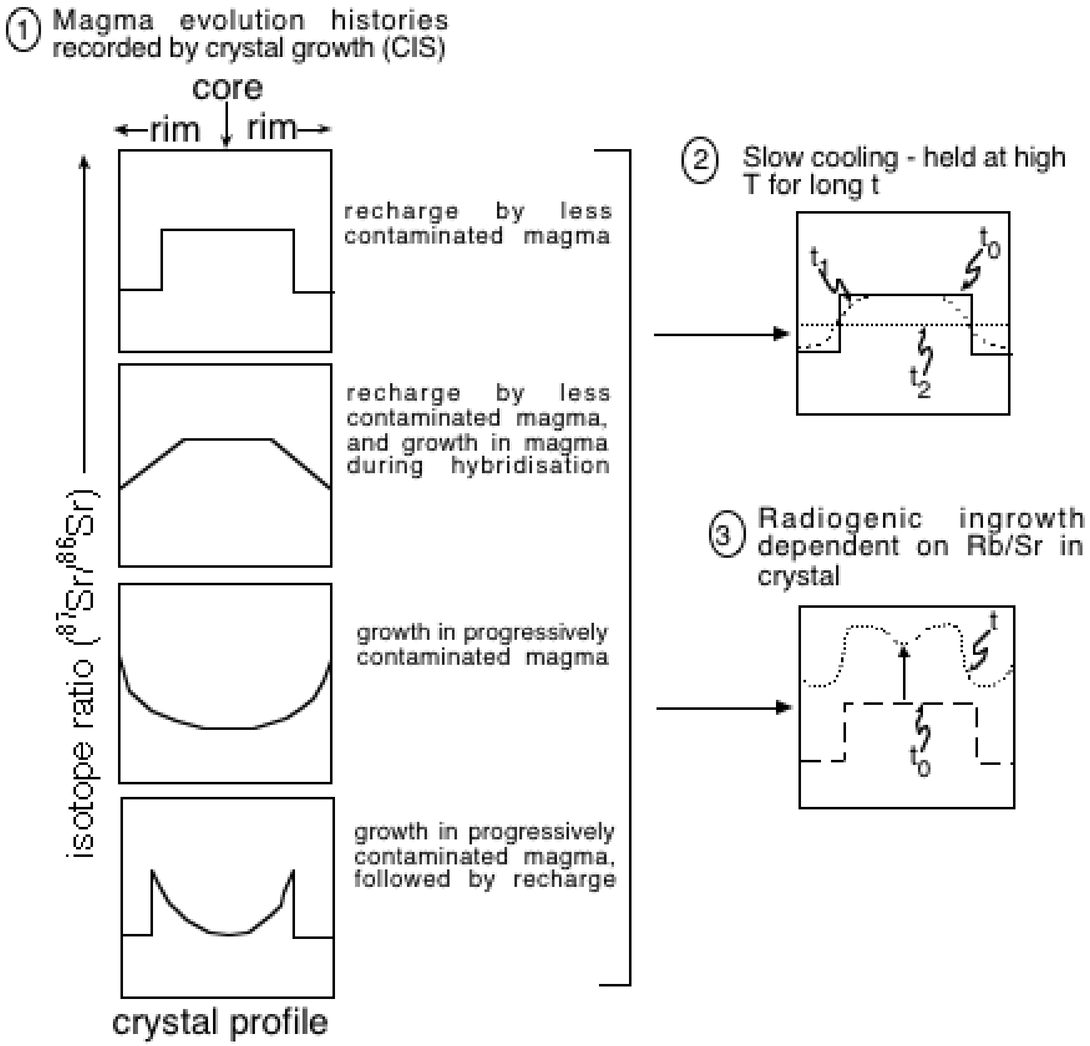
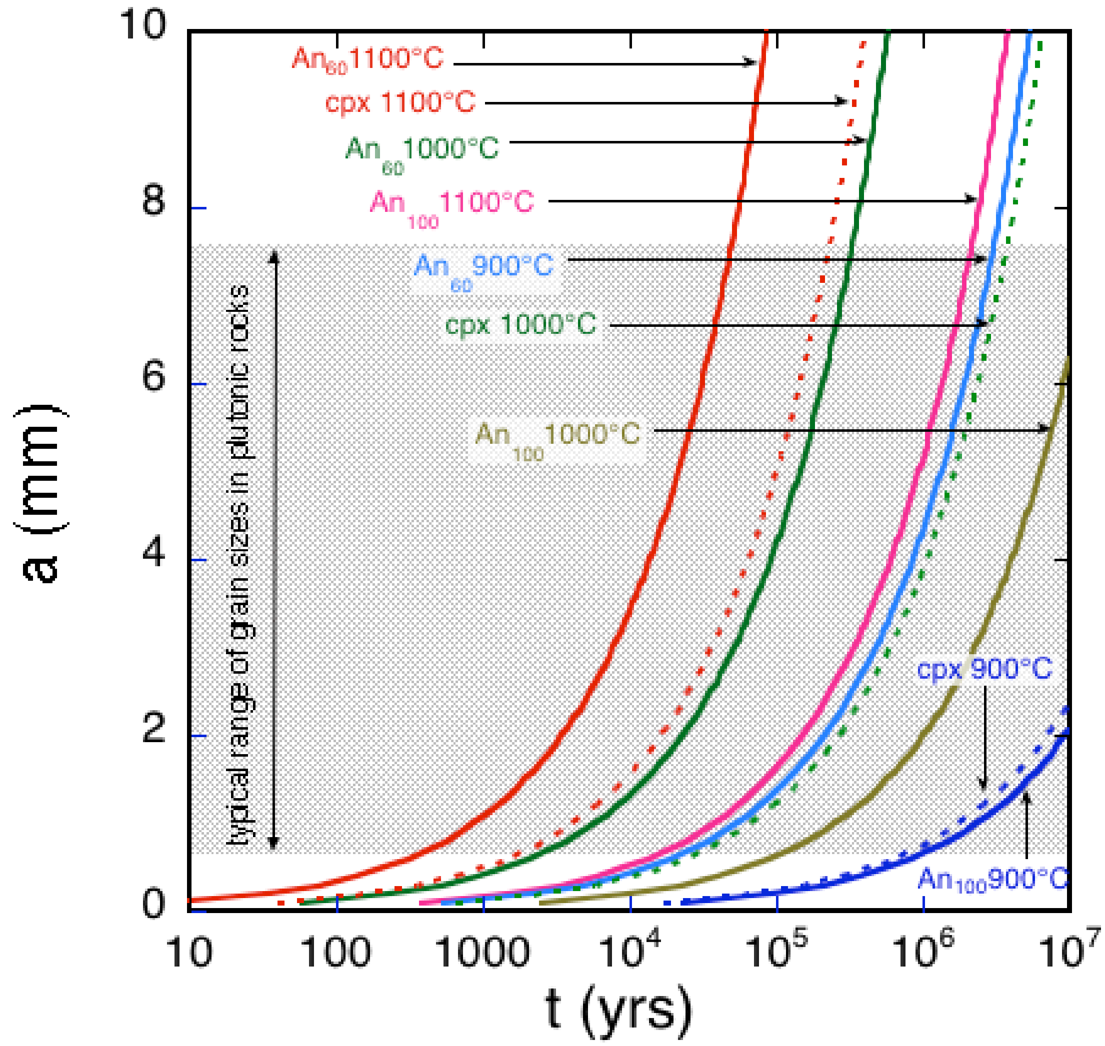

① Magma evolution histories recorded by crystal growth (CIS)
core
←rim rim→
isotope ratio ($^{87}Sr/^{86}Sr$)
recharge by less contaminated magma
recharge by less contaminated magma, and growth in magma during hybridisation
growth in progressively contaminated magma
growth in progressively contaminated magma, followed by recharge
crystal profile
② Slow cooling - held at high T for long t
t_1
t_0
t_2
③ Radiogenic ingrowth dependent on Rb/Sr in crystal
t
t_0

Figure 1


An60 1100°C
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An100 900°C
typical range of grain sizes in plutonic rocks
a (mm)
0
2
4
6
8
10
t (yrs)
10
100
1000
10^4
10^5
10^6
10^7

Figure 2

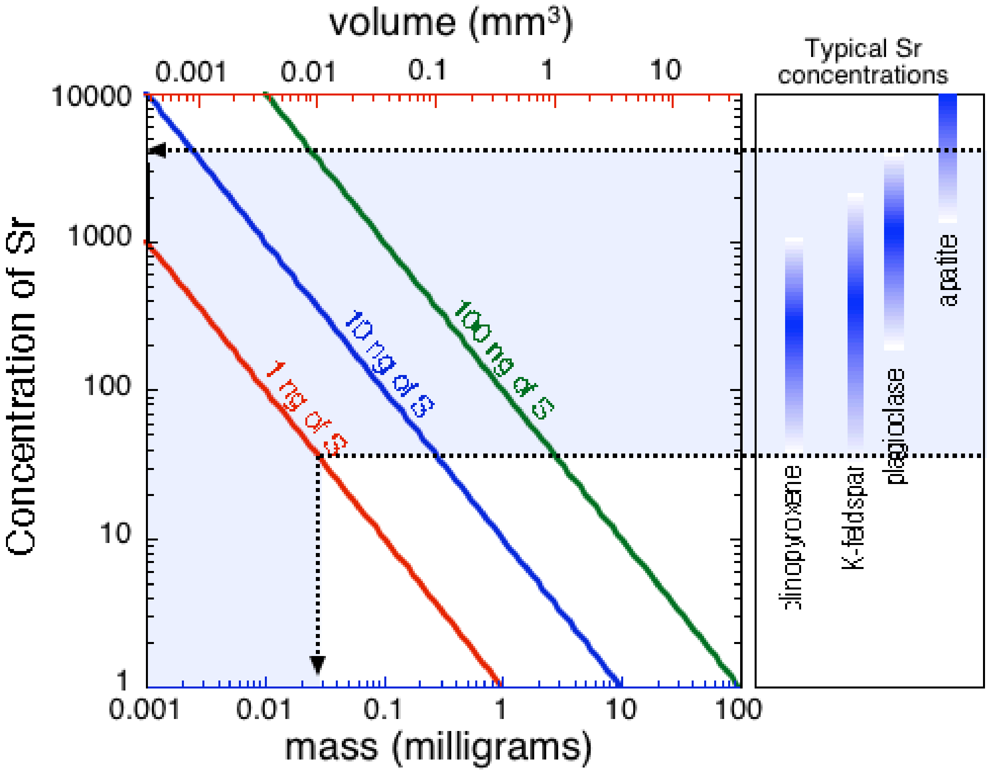

Figure 3

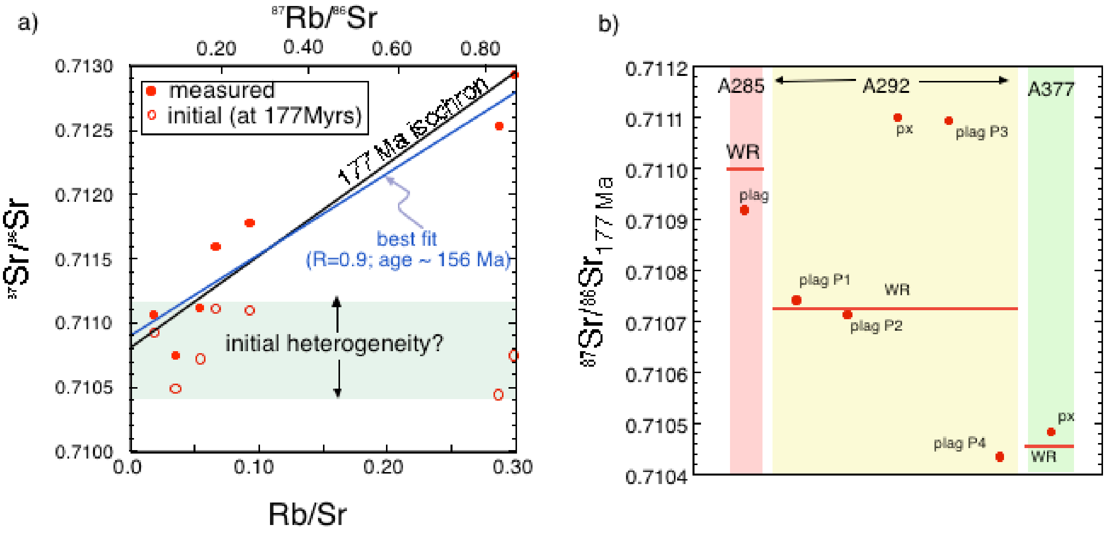

Figure 4

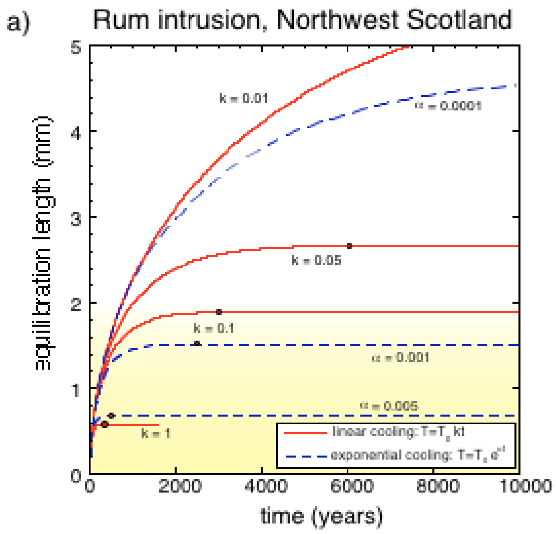

Figure 5

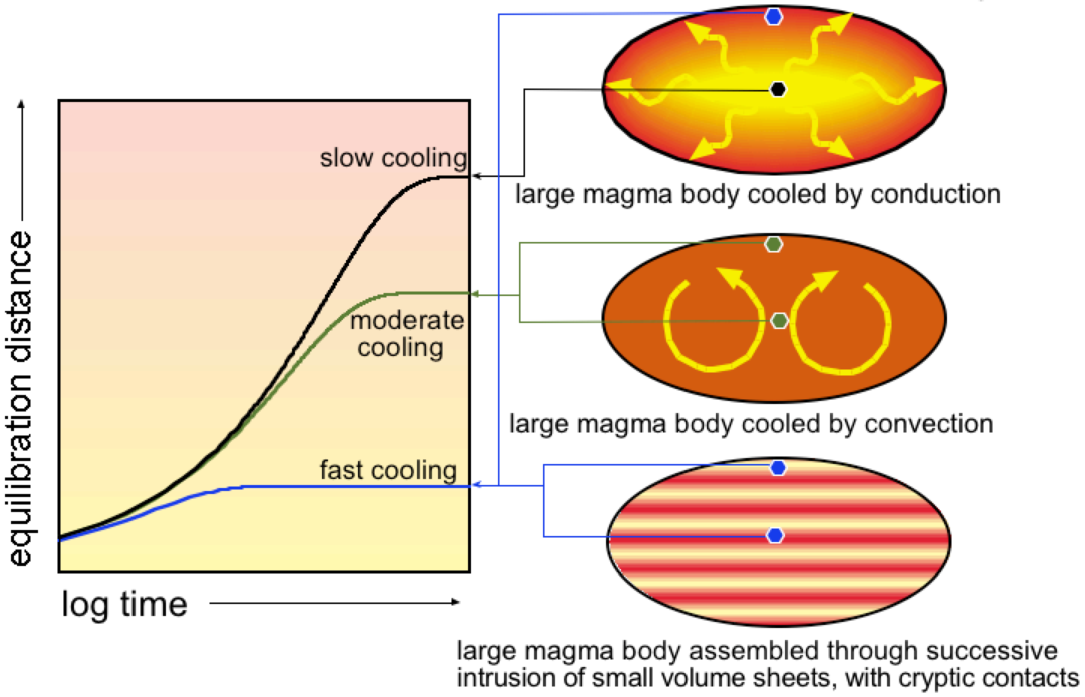

Figure 6

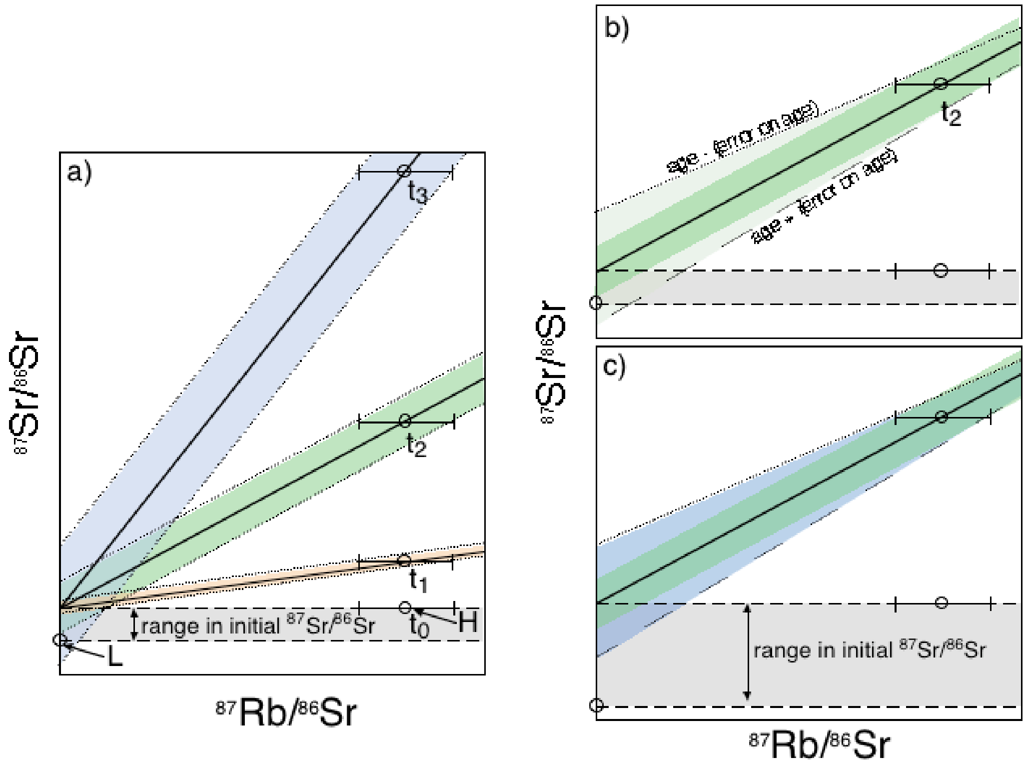
a)
t_3
t_2
t_1
t_0
H
L
range in initial $^{87}Sr/^{86}Sr$
$^{87}Sr/^{86}Sr$
$^{87}Rb/^{86}Sr$
b)
age - (error on age)
age + (error on age)
t_2
c)
range in initial $^{87}Sr/^{86}Sr$
$^{87}Sr/^{86}Sr$
$^{87}Rb/^{86}Sr$

Figure 8

Tables

Table 1. Sr isotope ratios of minerals (single mineral cores extracted by microdrilling; P = plagioclase C = clinopyroxene) from three samples; A285, A292, A377; in order up-section of the Dais Intrusion (=Basement Sill). Rb and Sr concentrations were measured by high resolution ICP-MS (Finnigan Element2).

	^{87}Sr/^{86}Sr$_m$[1]	Sample wt mg[3]	Rb	Sr	Rb/Sr[2]	^{87}Sr/^{86}Sr$_i$[1]
A292-P1	0.712919±12	0.156 (21 ng)	39.5	132.1	0.299	0.710741
A292-P2	0.711112±04	1.456 (161 ng)	6.0	110.4	0.055	0.710713
A292-C1	0.711589±16	0.621 (6 ng)	0.6	9.1	0.067	0.711100
A292-P3	0.711775±17	0.436 (67 ng)	14.4	154.0	0.094	0.711093
A292-P4	0.712526±09	0.355 (56 ng)	45.0	156.8	0.287	0.710435
A377-C1	0.710744±11	0.604 (29 ng)	1.0	29.1	0.036	0.710481
A377-P1	0.712419±08	0.387	-	-	-	
A285-P1	0.711059±42	0.088 (12 ng)	2.7	138.3	0.019	0.710919

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[1] m = measured, I = initial (corrected to t = 177 Ma)
NBS 987; ^{87}Sr/^{86}Sr = 0.710232 ± 6 (2σ, n = 4)

[2] Rb/Sr concentrations and ratios blank-corrected

[3] Numbers in brackets are amount of Sr, calculated from sample weight in mg and Sr concentraton