

Mineral isochrons and isotopic fingerprinting: Pitfalls and promises

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ABSTRACT

The determination of accurate and precise isochron ages for igneous rocks requires that the initial isotope ratios of the analyzed minerals are identical at the time of eruption or emplacement. Studies of young volcanic rocks at the mineral scale have shown this assumption to be invalid in many instances. Variations in initial isotope ratios can result in erroneous or imprecise ages. Nevertheless, it is possible for initial isotope ratio variation to be obscured in a statistically acceptable isochron. Independent age determinations and critical appraisal of petrography are needed to evaluate isotope data. If initial isotope ratio variability can be demonstrated, however, it can be used to constrain petrogenetic pathways.

Keywords: geochronology, igneous rocks, isotope geochemistry, isochrons.

INTRODUCTION

As isotope studies of igneous rocks become more detailed and the precision and accuracy of analytical methods improve, it has become increasingly clear that isotope heterogeneity is common among the constituent components (e.g., Simonetti and Bell, 1993; Geist et al., 1988; Davidson and Tepley, 1997) (Fig. 1). Initial isotope ratio variations among minerals are the consequence of multistage petrogenetic processes, and mineral-scale isotope data provide new insights into how magma systems evolve. Processes such as crustal contamination, partial assimilation, and magma recharge can, in principle, be identified from core-to-rim traverses of single minerals or from melt inclusions, provided that the components involved are isotopically distinct (Davidson et al., 1998).

The occurrence of significant isotope variation among mineral phases in Holocene volcanic rocks questions a fundamental tenet in isochron geochronology—that the initial isotope composition of the analyzed phases is identical. If variations in isotopic composition are common among the components (crystals and melt) of zero-age rocks, should we not expect similar characteristics of older rocks? We explore the consequence of initial isotope variability and the possibility that it may compromise geochronological interpretations.

INITIAL ISOTOPE RATIOS AND ISOCHRONS

Given a large range in Rb/Sr ratio, representative of, for example, the minerals in a granite, we can show that variations in initial isotope ratio that are entirely analytical (Fig. 2A) predictably lead to a nearly perfect isochron when aged for 20 m.y. (mean square of weighted deviates, MSWD = 0.097). If we simulate in the initial ratio a real petrogenetic variation of ~1500 ppm—comparable with ranges commonly found in volcanic rocks (Fig. 1)—then 20 m.y. of aging produces an errorchron age of 20.6 ± 0.95 Ma (Fig. 2B), which is within error of the 20 Ma age used. Thus, a random but real variation in initial ratio translates into a degradation in the precision of the isochron, but has a limited effect on the age.

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Figure 2C presents real data from a single lava dome of the Taylor Creek Rhyolite (Knesel et al., 1999). Measured isotopic data on single sanidine crystals describe a good positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$. If this correlation has age significance, then an age of 20 Ma is indicated (although the high MSWD should lead to the suspicion that this not a true isochron). However, if the same data points are aged for 200 m.y. rather than 20, the MSWD is reduced from 195 to 0.00016 (Fig. 2D), so interpretation as an isochron is not simply a matter of whether the initial isotopic ratios are scattered or not, but is also a function of age.

The emplacement age of the Taylor Creek Rhyolite is well constrained from argon isotope dating and paleomagnetic studies at 27.92

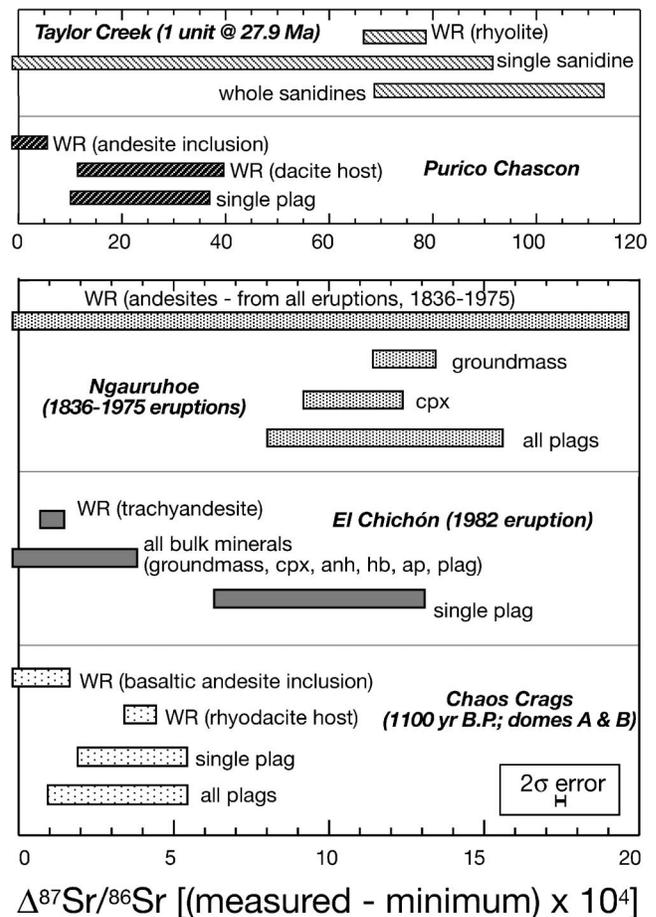
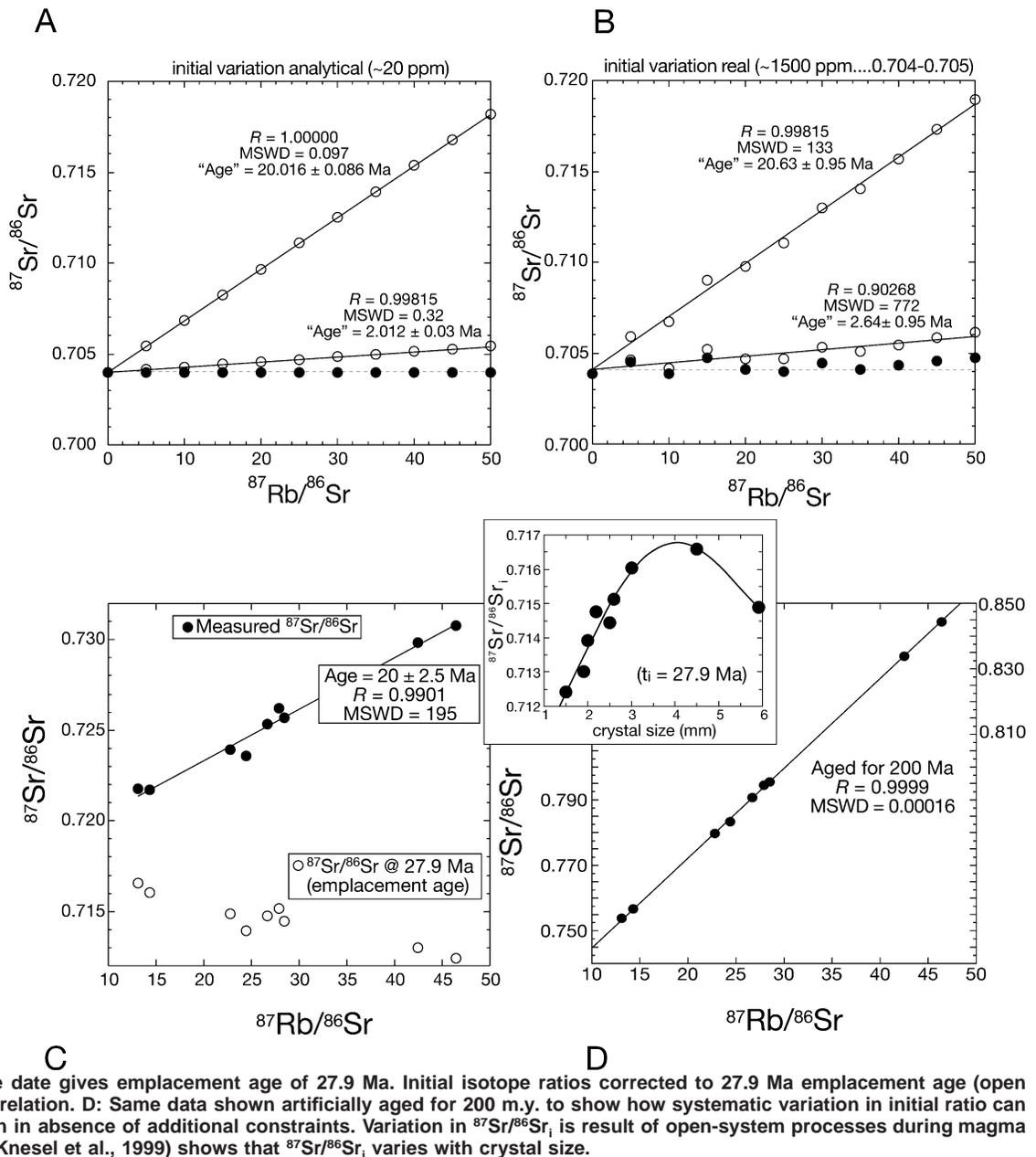


Figure 1. Mineral-scale isotope variations—expressed as Δ function, where $\Delta = (\text{measured isotope ratio} - \text{minimum measured isotope ratio})$ —among whole rocks (WR) and minerals from example cases to illustrate wide ranges recorded among minerals. References: Chaos Crags—Tepley et al. (1999); El Chichón—Tepley et al. (2000); Ngauruhoe—Hora (2003); Purico Chascon—Davidson et al. (1990) and Tepley (1999); Taylor Creek Rhyolite—Knesel (1998) and Knesel et al. (1999). Minerals: plagioclase—plagioclase; cpx—clinopyroxene; anh—anhydrite; hb—hornblende; ap—apatite. In all five cases feldspar comprises ~5%–35% of the rocks examined.

Figure 2. A: Simulated isochrons showing effect of aging minerals with wide range in Rb/Sr ratio, but constant initial $^{87}\text{Sr}/^{86}\text{Sr}$ (~20 ppm range randomly imposed to represent analytical error). **B:** Minerals with same range in Rb/Sr, but real variation in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (~1500 ppm, comparable with ranges observed in natural systems, equivalent to ~0.704–0.705; see Fig. 1). Note that for given age, isochron degrades as scatter in initial ratio is increased (cf. A and B). Note also improvement in R and mean squares of weighted deviates (MSWDs) with age (cf. 2 and 20 Ma isochrons in each case). Variations are imposed by taking arbitrary $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.704 and adding $0.001R$, where R is a random number between 0 and 1 generated in Microsoft Excel. Ages and MSWDs calculated by using ISOPLOT (model 3) (K. Ludwig—<http://www.bgc.org/klprogrammenu.html>). In Figures 2 and 3, errors of 1% and 30 ppm, respectively, were used on $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in determining MSWDs. **C:** Correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios described by single K-feldspar crystals from unit WHC/2 of Taylor Creek Rhyolite. Slope corresponds to age of 20 Ma, whereas argon isotope date gives emplacement age of 27.9 Ma. Initial isotope ratios corrected to 27.9 Ma emplacement age (open circles) define negative correlation. **D:** Same data shown artificially aged for 200 m.y. to show how systematic variation in initial ratio can lead to convincing isochron in absence of additional constraints. Variation in $^{87}\text{Sr}/^{86}\text{Sr}_i$ is result of open-system processes during magma differentiation; inset (from Knesel et al., 1999) shows that $^{87}\text{Sr}/^{86}\text{Sr}_i$ varies with crystal size.



± 0.04 Ma (Duffield and Dalrymple, 1990). The discrepancy between the apparent Rb-Sr age and the argon age is due to the feldspar crystals having different $^{87}\text{Sr}/^{86}\text{Sr}_i$ at time, $t = 27.9$ Ma. Moreover, Knesel et al. (1999) showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of single feldspar crystals from the Taylor Creek Rhyolite varies with the crystal size (Fig. 2D, inset), consistent with observed core-to-rim variations in selected larger crystals. If the feldspar crystals are plotted at zero age, a clear negative correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ is seen (Fig. 2C). This case demonstrates that a systematic relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ at $t = 0$ may result in a good isochron fit, even though the age obtained is meaningless.

PETROGENETIC INFORMATION FROM ISOCHRON DATA?

The case of the Taylor Creek feldspars raises the question of whether initial ratio data for ancient rock components can be extricated from isochrons and subsequently used to gain additional constraints on processes such as contamination that may have occurred during magma differentiation. For the Taylor Creek Rhyolite, high-quality argon isotope data giving a younger age allow us to conclude that the isochron

is fictitious and, therefore, that initial heterogeneity in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios characterizes the feldspar crystals.

The potential pitfalls in obtaining true ages outlined here apply equally to phaneritic intrusive rocks. Preservation of mineral-scale initial isotopic heterogeneity (as opposed to the object of the geochronologists' interest: differential ingrowth of radiogenic daughters over time at temperatures well below the solidus) in plutonic rocks requires (1) slow diffusion, the rates of which depend on the element and mineral of interest, and (2) relatively rapid cooling—or, more strictly, low integrated temperature-time histories relative to the half-life of the isotopic system used. The cooling history will depend on the volume of magma involved and its starting temperature, which in turn is a function of its composition. Evidence for heterogeneous initial ratios on a mineral scale was reported by Waight et al. (2000) for Lachlan granites (southeast Australia), by Tepley and Davidson (2003) for Rum gabbros (northwest Scotland), and by Cox et al. (1996) for the Shap Granite (northwest England). In the case of the Lachlan granites, covariation between Nd and Sr isotope ratios in core-to-rim profiles of megacrysts argues that variations are due to crystallization from magma(s) in

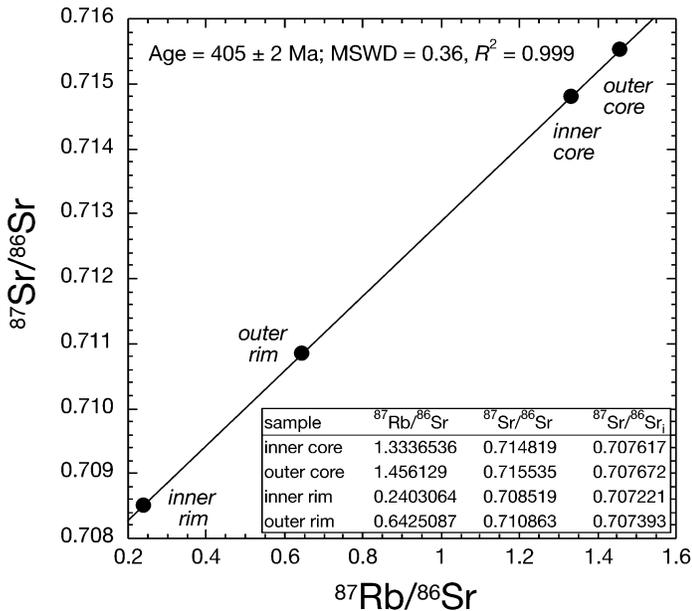


Figure 3. Isochron from single plagioclase-rimmed K-feldspar megacryst from Shap Granite, northwest England. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios measured by dynamic peak hopping on Micromass Sector mass spectrometer. NBS 987 values for $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245$ and 0.710231 . $^{87}\text{Rb}/^{86}\text{Sr}$ was determined by isotope dilution using mixed Rb-Sr spike. Data are from Perloth (2002). MSWD—mean square of weighted deviates.

which isotope compositions were changing as a result of open-system processes. In the case of Rum gabbros, plagioclase core-to-rim differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios cannot be easily explained by any age effects because the Rb/Sr ratio is low and the rock is young (60 Ma); once again, open-system processes during crystallization must be invoked to impart isotopic heterogeneity to the mineral population.

Figure 3 shows an isochron from a single megacryst from the Shap Granite. The late Caledonian Shap Granite is renowned for its

mafic enclaves with K-feldspar megacrysts, many of which are rimmed with plagioclase. The presence of mafic inclusions in both plutonic and volcanic environments is commonly cited as evidence for interaction between magmas of different compositions (e.g., Bacon, 1986; Holden et al., 1987; Davidson and Tepley, 1997). Cox et al. (1996), in a detailed isotopic study of the Shap Granite, concluded that the megacrysts originated in the granite and were mechanically incorporated into a mafic magma that now forms the inclusions. The plagioclase rims were grown from this mafic magma. The single crystal isochron of Figure 3 gives an age of 405 ± 2 Ma, broadly consistent with the Caledonian emplacement age. However, both the zircon age (390 ± 6 Ma; Pidgeon and Aftalion, 1978) and the K/Ar (biotite) age (397 ± 7 Ma; Rundle, 1992) are significantly younger than the isochron age of Figure 3.

The initial ratios for two core and two rim samples corrected for 397 m.y. (the K/Ar emplacement age) of radioactive ingrowth of ^{87}Sr are distinct from each other. The two core samples both give $^{87}\text{Sr}/^{86}\text{Sr}_{397} = 0.70739$. The plagioclase rim data are significantly lower, $^{87}\text{Sr}/^{86}\text{Sr}_{397} = 0.70717$ and 0.70726 . This distribution of $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios suggests that a lower $^{87}\text{Sr}/^{86}\text{Sr}$ mafic magma picked up the megacrysts from a high $^{87}\text{Sr}/^{86}\text{Sr}$ granite magma and that the plagioclase rim overgrowths were formed from the more mafic magma.

CAN ISOCHRON QUALITY BE USED TO EVALUATE INITIAL $^{87}\text{Sr}/^{86}\text{Sr}$ RATIO HETEROGENEITY?

The problems of unraveling the isotopic effects of aging from those of primary isotopic heterogeneity have been addressed frequently (e.g., Zheng, 1989; Powell et al., 2002), but always in the context of producing the most accurate and reliable age information. We argue here that if ages can be independently determined, then any variations in initial ratio—effectively residual after age correcting each sample—can provide important petrogenetic constraints.

The validity of an isochron is often justified on the basis of the MSWD, which is effectively a measure of how well points fit the correlation line. Brooks et al. (1972) suggested that in order to be considered a satisfactory isochron, MSWDs must be <2.5 . However, note that (1) for a given data set the MSWD deteriorates as the errors

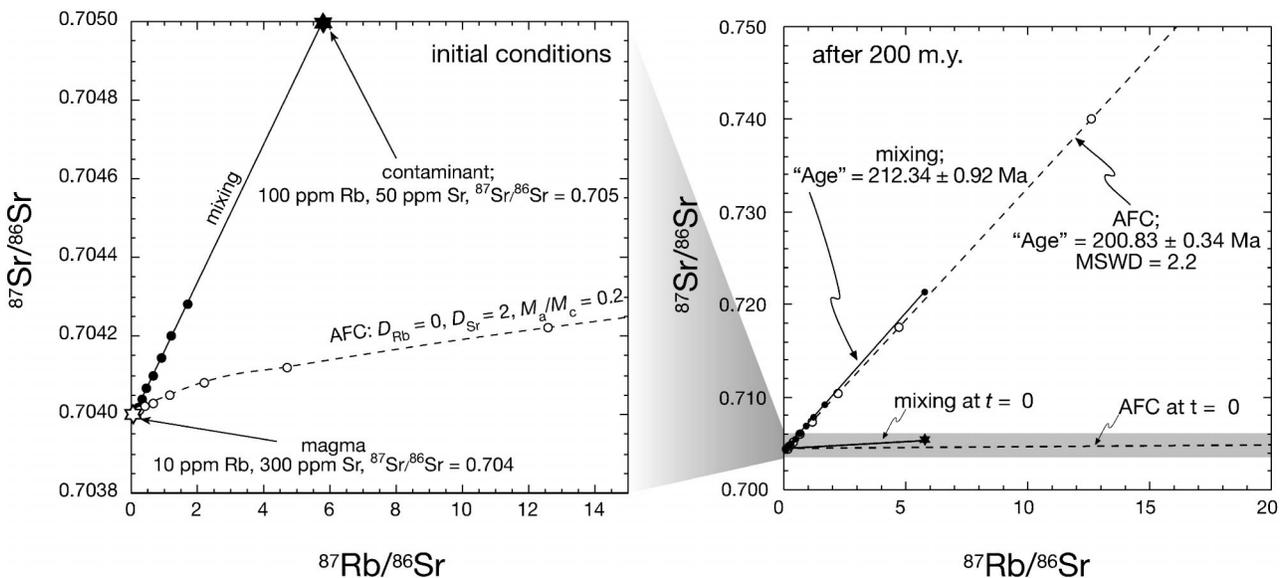


Figure 4. Illustration of potential effects of petrogenetic processes in causing variations of $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios (realization made some time ago; e.g., see Briquieu and Lancelot, 1979). Left panel is zoomed from shaded bar on right panel. Model simulates interaction of magma with crust through mixing or assimilation–fractional crystallization (AFC). In case of mixing, linear correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ is obtained. With aging, this correlation gives precise isochron (for these simulated data, mean squares of weighted deviates [MSWD] = 0), but erroneous age. Case of AFC gives age much more similar to true age of 200 Ma, because slope of $^{87}\text{Sr}/^{86}\text{Sr}_i$ vs. $^{87}\text{Rb}/^{86}\text{Sr}$ is shallower than that for mixing case. D_{Rb} , D_{Sr} = Rb and Sr bulk distribution coefficients, M_a/M_c = rate of mass assimilated to mass crystallized.

on the data points decrease (it effectively becomes less easy to pass the correlation line within the error bars) and (2) for a given isochron the MSWD improves as slope (age) increases (the significance of the latter observation has been illustrated for the case of the Taylor Creek feldspars in Figs. 2C, 2D).

The simulation of Figures 2A and 2B shows that a random variation in $^{87}\text{Sr}/^{86}\text{Sr}_i$ translates into increased MSWD at a given age. In principle, however, the age is still geologically meaningful, even if it may not be acceptable on the basis of statistical tests. If, however, the initial variation is systematic (e.g., due to open-system mixing or contamination), then isochrons are generated that can be very good (based on low MSWD), but the ages are geologically meaningless. In such a case, if the real age is known, then the variation in $^{87}\text{Sr}/^{86}\text{Sr}_i$ can be used to illuminate petrogenetic processes of mixing or assimilation-fractional crystallization (AFC) that were involved in petrogenesis (Fig. 4). The general principles illustrated in Figure 4 are valid for a series of differentiated magmas (whole rocks or glasses, or minerals, and core-to-rim profiles of single minerals) that crystallized during open-system differentiation, although additional scatter may be introduced in the case of minerals if Rb and Sr distribution coefficients vary significantly or nonsystematically with melt evolution. In the models of Figure 4, both the mixing and AFC scenarios aged for 200 m.y. would be statistically acceptable as isochrons and, in the absence of evidence to corroborate or refute the interpretation, would be assigned chronological significance. Independent determination of the true 200 Ma age allows the $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio to be used as evidence for mixing or AFC during petrogenesis. Isotope data from two or more systems are useful in this regard; it is highly unlikely that open-system processes acting to produce a range in, for example, $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios would produce identical isochron ages, given the different respective half-lives of ^{87}Rb and ^{147}Sm as well as the different fractionation behaviors of Rb-Sr and Sm-Nd. Petrographic criteria such as mineral disequilibrium and trace element indicators of contamination should be used in conjunction with the isotopic data in assessing the degree to which the $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio reflects primary open-system magma behavior versus postcrystallization ingrowth of ^{87}Sr .

SUMMARY

1. The common observation of significant variation in $^{87}\text{Sr}/^{86}\text{Sr}_i$ among components of zero-age rocks suggests that the assumption of a constant $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio in isochron analysis of ancient rocks may not be valid in many instances.

2. Statistical methods may not be able to distinguish between constant or variable $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios, particularly as rocks become older or if the $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio is correlated with the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio as a consequence of petrogenetic processes.

3. Independent ages are needed to evaluate rock-component isochrons. If they do not agree, then the age-corrected $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios of the rock components (minerals, melt inclusions, groundmass) may constrain differentiation mechanisms such as contamination and mixing.

ACKNOWLEDGMENTS

The Shap sample was provided by S. Caunt. Discussions with K. Knesel, R. Powell, D. Morgan, G. Pearson, and C. Macpherson helped focus the manuscript. F. Tepley and K. Knesel were instrumental in developing this line of research with Davidson. Research was supported by National Science Foundation grant EAR-980523, the University of California, Los Angeles, Academic Senate and Natural Environment Research Council grant NER/A/S/2000/01008.

REFERENCES CITED

Bacon, C.R., 1986, Magmatic inclusions in silicic and intermediate volcanic rocks: *Journal of Geophysical Research*, v. 91, p. 6091–6112.
Briqueu, L., and Lancelot, J.R., 1979, Rb-Sr systematics and crustal contami-

nation models for calc-alkaline igneous rocks: *Earth and Planetary Science Letters*, v. 43, p. 385–396.

- Brooks, C., Hart, S.R., and Wendt, I., 1972, Realistic use of two-error regression treatments as applied to rubidium-strontium data: *Reviews of Geophysics and Space Physics*, v. 10, p. 551–577.
Cox, R.A., Dempster, T.J., Bell, B.R., and Rogers, G., 1996, Crystallization of the Shap Granite: Evidence from zoned K-feldspar megacrysts: *Geological Society [London] Journal*, v. 153, p. 625–635.
Davidson, J.P., and Tepley, F.J., III, 1997, Recharge in volcanic systems: Evidence from isotope profiles of phenocrysts: *Science*, v. 275, p. 826–829.
Davidson, J.P., de Silva, S.L., Holden, P., and Halliday, A.N., 1990, Small scale disequilibrium in a magmatic inclusion and its more silicic host: *Journal of Geophysical Research*, v. 95, p. 17,661–17,675.
Davidson, J.P., Tepley, F.J., III, and Knesel, K.M., 1998, Isotopic fingerprinting may provide insights into evolution of magmatic systems: *Eos (Transactions, American Geophysical Union)*, v. 79, p. 185, 189, 193.
Duffield, W.A., and Dalrymple, G.B., 1990, The Taylor Creek Rhyolite of New Mexico: A rapidly emplaced field of lava domes and flows: *Bulletin of Volcanology*, v. 52, p. 475–487.
Geist, D.J., Myers, J.D., and Frost, C.D., 1988, Megacryst-bulk rock isotopic disequilibrium as an indicator of contamination processes: The Edgecumbe Volcanic Field, SE Alaska: *Contributions to Mineralogy and Petrology*, v. 99, p. 105–112.
Holden, P., Halliday, A.N., and Stephens, W.E., 1987, Neodymium and strontium isotope content of microdiorite enclaves points to mantle input in granitoid production: *Nature*, v. 330, p. 53–56.
Hora, J.M., 2003, Magmatic differentiation processes at Ngaaurhoe volcano, New Zealand: Constraints from chemical, isotopic and textural analysis of plagioclase crystal zoning [M.S. thesis]: Los Angeles, University of California, 200 p.
Knesel, K.M., 1998, Strontium isotope systematics during melting in the continental crust [Ph.D. thesis]: Los Angeles, University of California, 240 p.
Knesel, K.M., Davidson, J.P., and Duffield, W.A., 1999, Open-system evolution of silicic magma by assimilation followed by recharge: Evidence from Sr isotopes in sanidine phenocrysts, Taylor Creek Rhyolite, NM: *Journal of Petrology*, v. 40, p. 773–786.
Perlroth, R., 2002, An investigation of crystal transfer between melts [M.S. thesis]: Los Angeles, University of California, 133 p.
Pidgeon, R.T., and Aftalion, M., 1978, Co-genetic and inherited zircon U-Pb systems in granites, in Bowes, D.R., and Leake, B.E., eds., *Crustal evolution in northwestern Britain and adjacent regions: Geological Journal Special Issue*, v. 10, p. 183–220.
Powell, R., Hergt, J., and Woodhead, J., 2002, Improving isochron calculations with robust statistics and the bootstrap: *Chemical Geology*, v. 185, p. 191–204.
Rundle, C.C., 1992, Review and assessment of isotopic ages from the English Lake District: British Geological Survey, Onshore Geology Series, Technical Report WA/92/38, 27 p.
Simonetti, A., and Bell, K., 1993, Isotopic disequilibrium in clinopyroxenes from nephelinitic lavas, Napak volcano, eastern Uganda: *Geology*, v. 21, p. 243–246.
Tepley, F.J., III, 1999, Plagioclase isotopic heterogeneities in continental volcanic arc rocks [Ph.D. thesis]: Los Angeles, University of California, 309 p.
Tepley, F.J., III, and Davidson, J.P., 2003, Mineral-scale Sr-isotope constraints on magma evolution and chamber dynamics in the Rum layered intrusion, Scotland: *Contributions to Mineralogy and Petrology*, v. 45, p. 628–641.
Tepley, F.J., III, Davidson, J.P., and Clynne, M.A., 1999, Magmatic interactions as recorded in plagioclase phenocrysts of Chaos Crags, Lassen Volcanic Center, California: *Journal of Petrology*, v. 40, p. 787–806.
Tepley, F.J., III, Davidson, J.P., Tilling, R.I., and Arth, J.G., 2000, Magma mixing, recharge and eruption histories recorded in plagioclase phenocrysts from El Chichón volcano, Mexico: *Journal of Petrology*, v. 41, p. 1397–1411.
Waight, T.E., Maas, R., and Nicholls, I.A., 2000, Fingerprinting feldspar phenocrysts using crystal isotopic composition stratigraphy: Implications for crystal transfer and magma mingling in S-type granites: *Contributions to Mineralogy and Petrology*, v. 139, p. 227–239.
Zheng, Y.-F., 1989, Influences of the nature of the initial Rb-Sr system on isochron validity: *Chemical Geology*, v. 80, p. 1–16.

Manuscript received 26 July 2004

Revised manuscript received 30 September 2004

Manuscript accepted 1 October 2004

Printed in USA