Reports

Strontium Isotope Fractionation in the Kiglapait Intrusion

Abstract. *The initial ratio of strontium-87 to strontium-86 rises systematically from 0.70395 to 0.70662 over the upper 10 percent of the Kiglapait layered intrusion. This ratio is strongly correlated with potassium and rubidium. Contamination, exchange, and magma mixing fail to account for the increase, which is ascribed to the imperfect retention of radiogenic strontium-87 in feldspar-like structural units of the melt inherited from the magma source. These accidents in chemical discrimination persist most readily in anhydrous melts.*

It is not expected that ^{87}Sr and ^{86}Sr will be fractionated in high-temperature igneous processes because they have such a small mass difference and the same chemical properties. Indeed, the high correlation coefficients of innumerable strontium isochron diagrams (*1*) imply the lack of strontium isotope fractionation in most systems studied. Nonetheless, because a small fraction of ^{87}Sr is the daughter product of the radioactive decay of ^{87}Rb, the possibility of fractionation arises if this radiogenic strontium (^{87}Sr* hereafter) fails to become entirely dissociated from the sites of its parental rubidium and other alkali elements such as potassium and sodium. In this event, ^{87}Sr* could be fractionated passively by the processes of fractional crystallization that actively concentrate alkalies in magmas. Such a case has never been convincingly demonstrated and is commonly regarded as extremely unlikely because of the relatively high experimental diffusion coefficient (D) for cations in basaltic melts, $\sim 10^{-7}$ cm^2/sec, which leads to characteristic transport distances $X \sim (Dt)^{1/2}$ of 2 cm/year (where t is time) (*2*). Here I describe a situation in which the hypothetical fractionation mechanism cannot be lightly discarded.

The Kiglapait intrusion is a large Proterozoic body of layered igneous rocks in Labrador (*3*), very strongly fractionated from troctolite in the lower zone (LZ) to ferrosyenite at the top of the upper zone (UZ). The roof contains a downward-grown upper border zone (UBZ). The calculation of the bulk composition and successive liquid compositions has been described by Morse (*4*).

Precise analytical data for 12 rocks have been furnished by Simmons and Lambert (*5*) and are reproduced in Table 1. The initial isotopic ratio ^{87}Sr/^{86}Sr (Sr^0 hereafter) at ^{87}Rb/^{86}Sr = 0 was calculated for an age of 1.4×10^9 years (*6*). A constant value for Sr^0 of 0.70395 from 0 to 90 volume percentage solidified (PCS) (Fig. 1) is followed by two stages of remarkably logarithmic-linear increase in Sr^0 with decreasing liquid fraction remaining (F_L). The total abundances of ^{87}Sr and ^{86}Sr at 1.4×10^9 years were calculated from the well-established variation curve for total strontium (*7*) and the indicated initial ratios. These calculations yield the value of Sr^0 for the total intrusion, 0.70404, and the liquid variation curve for Sr^0 shown by the dotted line in Fig. 1. This curve is drawn on the assumption that there is continuous growth of Sr^0 in the liquid, but, since each point represents the sum over all overlying rocks, the curve can also be used to discuss episodic contamination events, as described below. Sample KI 4086 comes from a part of the UBZ stratigraphically and isotopically equivalent to the LZ at 80 PCS. The data show a systematic increase of Sr^0 with increasing stratigraphic height and PCS.

The extra ^{87}Sr in the upper rocks cannot have been grown in place. The calculated crystallization time for the Kiglapait intrusion is about 10^6 years (*4*). With rubidium = 1.08 parts per million (ppm) (*8*) and strontium = 330 ppm (*7*) in the intrusion, the time required to raise Sr^0 from the lowest observed value of 0.70395 to the ratio for the total intrusion, 0.70404, is about 630×10^6 years, an impossibly long time for crystallization.

Even if we presume surroundings having abundant ^{87}Sr, not known to exist, exchange by meteoric water is contraindicated by the normal igneous oxygen isotope (δ^{18}O = +6 per mil) that occur throughout the intrusion (*9*). Moreover, the UBZ has the same δ^{18}O as the uppermost ferrosyenites, yet a very much lower Sr^0: 0.7040 as opposed to 0.7066. Parallel differences in δ^{18}O and Sr^0 would be expected in an exchange or contamination process (*10*).

Contamination can be evaluated with the aid of Fig. 1. In a simplified contamination model, the liquid has Sr^0 = 0.70395 until 90 PCS, at which point the contaminant is injected, raising Sr^0 for the remaining liquid to 0.7051. This solution is unsatisfactory, as the ratio in the liquid must still somehow evolve along the dotted curve in Fig. 1. To avoid this problem, consider that the contaminant is injected at the roof and mixes gradually back into the main magma. Then, however, the contaminant must share the unusual bulk chemistry of the uppermost Kiglapait intrusion (*11*), and the mixing process must yield the remarkable regularity shown by the data, mimicking the regular exponential growth expected only of fractionation. Numerically, contamination fares badly also. A rubidium-rich crustal melt similar to the radiogenic (Sr^0 = 0.7264) pink Operngeviksoak granite (*12*) can raise the Sr^0 of the system only to 0.7041 before accounting for all the rubidium in the intrusion at 90 PCS. A 10 percent contami-

Table 1. Rubidium and strontium isotopic data for rocks of the Kiglapait intrusion (*5*).

Sample No.	PCS	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr	Sr^0 = ^{87}Sr/^{86}Sr (at 1.4×10^9 years)
KI 3109	9	0.007744	0.70412	0.70397 ± 8*
KI 3224	21	0.007546	0.70410	0.70395 ± 7
KI 3034	72	0.01273	0.70422	0.70396 ± 7
KI 3369	89.3	0.02066	0.70432	0.70390 ± 7
KI 4142	92.8	0.01552	0.70477	0.70445 ± 7
KI 4145	95.5	0.01440	0.70541	0.70512 ± 8
KI 3379	98.6	0.02200	0.70600	0.70556 ± 9
KI 4123	99.4	0.04654	0.70665	0.70572 ± 8
KI 4119	99.6	0.02763	0.70638	0.70582 ± 8
KI 4079	99.9	0.06297	0.70745	0.70618 ± 9
KI 4077	99.985	0.3038	0.71272	0.70662 ± 19
KI 4086	(UBZ, ~ 80)	0.03791	0.70480	0.70405 ± 10

*The uncertainty refers to the last significant figure, calculated on the assumption that there was no covariance with maximum uncertainties of 2.0 and 0.01 percent for ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr, respectively. All errors are 2σ.

nant (*6*) injected at 90 PCS will yield the correct bulk and isotopic compositions if rubidium = 5.6 ppm, strontium = 458 ppm, and Sr^0 = 0.710 in the contaminant and rubidium = 2.2 ppm, strontium = 238 ppm, and Sr^0 = 0.704 in the residual Kiglapait magma at 90 PCS. Such a strontium-rich, rubidium-poor contaminant is unlike any known country rock or reasonable low-melting fraction thereof near the intrusion. The exercise ascribes all the increment in strontium and rubidium at 90 PCS and thereafter to the contaminant and none to intrinsic enrichment of the magma by fractional crystallization that must have occurred; it fails to account for the exponential growth in Sr^0 after 90 PCS and is subject to the back-mixing problems mentioned above.

Under the contamination hypothesis, the exponential growth of Sr^0 to the very end of crystallization would require accelerated ingestion of country rock, but this is mechanically impossible because the late-stage residual magma was shielded from the roof rocks by the downward-grown UBZ. Moreover, it is thermally unlikely that assimilation would increase with falling temperature rather than the opposite.

Magma mixing is a process conceptually like contamination. Acceptable characteristics for the contaminant are reached only when it acquires the unusual chemical properties of the Kiglapait UZ itself, and these include low rubidium, K/Rb = 1750, strontium = 260 ppm, high FeO/MgO, critical silica undersaturation, vanishingly low H_2O, and a nearly flat pattern of rare-earth elements (*13*). The FeO enrichment of the uppermost Kiglapait rocks is extreme [FeO = 18.6 percent (by weight), MgO = 0.08 percent (*11*)] and known only as a product of protracted fractional crystallization. The proposed contaminant reduces to a rare liquid very like the fractionated Kiglapait liquid itself but with high Sr^0. Such a solution only buries the problem and requires special pleading.

In support of the idea of fractionation during crystallization is the extremely regular exponential growth of Sr^0, similar to that shown by potassium and rubidium in the UZ (Fig. 1). The efficiency with which ^{87}Sr is conserved to residual liquid, assuming fractionation, is easily obtained from the initial and final points of the liquid curve in Fig. 1. For the Rayleigh equation

$$R = R_0 F_L^{K_D - 1}$$

where R is the final ratio (Sr^0 = 0.70662); R_0 is the initial ratio (Sr^0 = 0.70404); F_L is the fraction liquid at 99.985 PCS, that is, 0.00015; and K_D is the compound distribution coefficient Sr^0 (whole rocks)/Sr^0 (liquid), we obtain K_D = 0.9996 (*14*). In other words, 4 out of every 10^4 atoms of ^{87}Sr are conserved to the liquid. If we assume that only radiogenic $^{87}Sr^*$ atoms are involved in the fractionation process, and calculate that 71 in 10^4 atoms of ^{87}Sr are radiogenic, having evolved in the earth from Sr^0 = 0.699 to 0.704 (*15*), then 4/71 or 6 percent of the radiogenic atoms are reliably conserved to the liquid.

There is strong correlation between Sr^0 and both potassium and rubidium in the Kiglapait rocks but not with Rb/Sr because of independent variations in the strontium concentration (*7*). Among known chemical parameters of the intrusion, only potassium and rubidium (Fig. 1) are inflected both at 90 PCS and near 96 PCS; this suggests a causal relationship between Sr^0 and potassium or rubidium. Both of these elements reside mainly in feldspar.

The weight of evidence appears to leave no alternative but some mechanism of conserving $^{87}Sr^*$ preferentially (to a small degree) in the magma during fractional crystallization. Since feldspar is overwhelmingly the chief carrier of total strontium, any successful fractionation mechanism must have involved either feldspar crystals or the feldspathic network–forming component of the magma. Some partially resorbed plagioclase feldspar crystals are seen near the top of the intrusion (*3*), but they are sporadic in occurrence and hence unlikely to account for the uniform growth of Sr^0 even if they were sufficiently abundant. A preferable hypothesis is that radiogenic ^{87}Sr is passively carried in the feldspathic regions of the melt structure (*16*) as fossil ^{87}Rb that has not been entirely equilibrated with other structural regions of the melt or with the crystals being formed. In crystalline feldspar, strontium is coupled to aluminum residing in diffusion-resistant tetrahedral sites, and a similar coupling in feldspar-like structural regions of the melt is to be expected.

Although the proposed mechanism could have operated on contaminants introduced near 90 PCS, if it can operate on contaminants it can operate just as well on the uncontaminated magma. Because of the severe chemical restrictions on the nature of a possible contaminant, the fractionation mechanism more likely operated on the magma throughout its history. This conclusion raises the question of whether magmas or indeed their source regions are always fully equilibrated on a local scale in their strontium isotopic composition, for, if a site specificity for radiogenic strontium can be maintained for 10^6 years in a dry melt, it can surely be maintained longer in a dry crystalline source. The vanishingly low H_2O content of the Kiglapait intrusion (*14*) would tend to favor the proposed carrier mechanism, which would probably not operate in the presence of appre-

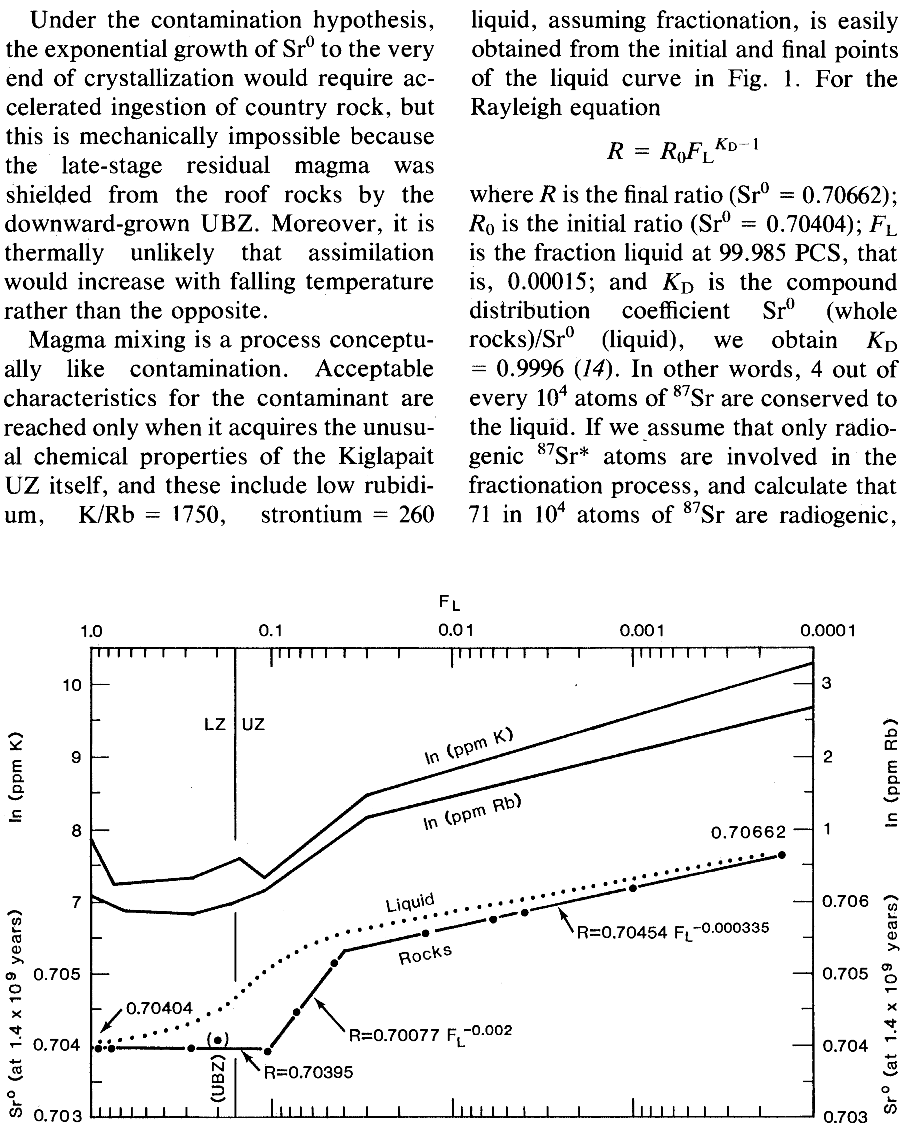

Fig. 1. Strontium isotope initial ratios (Sr^0) for rocks of the Kiglapait intrusion 1.4 × 10^9 years ago, plotted against the volume percentage solidified (PCS). The upper abscissa is the fraction of liquid remaining (F_L). The upper two curves show the variations of potassium and rubidium in rocks of the intrusion (*8*). Abbreviations: LZ, lower zone; UZ, upper zone; UBZ, upper border zone. The UBZ sample locality is topographically above the UZ in the stratigraphically inverted UBZ; this sample is correlated to the 80 PCS level on the basis of its plagioclase feldspar composition.

ciable H_2O, known to act as a catalyst in feldspar diffusion experiments (*17*).

Passive upward fractionation of $^{87}Sr^*$ probably occurred in the Kiglapait intrusion through the agency of rubidium-bearing feldspar-like parcels in the melt, acting as carriers of radiogenic strontium. The probability with which radiogenic strontium was regularly conserved to the residual magma is 0.06 (in other words, 94 percent of the $^{87}Sr^*$ escaped from its carrier and equilibrated with the main magma and contemporary crystals). Such a process can be expected only in dry systems, among which are many layered mafic intrusions (*18*) and mid-ocean ridge basalts (*19*). Some of the poorly understood strontium isotopic variations in such rocks may have arisen from the carrier fractionation mechanism, but the evident inefficiency of the process deserves emphasis: crystallization of 90 percent of the system would increase Sr^0 from 0.7040 only to 0.7051, according to the Kiglapait liquid curve. Somewhat greater efficiency would result from the crystallization of olivine without feldspar, causing a more rapid increase in alkalies than occurred in the Kiglapait magma.

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13. Major element data are from Morse (*11*); H_2O data are from H. D. Huntington [*J. Petrol.* **20**, 625 (1979)]; and rare-earth element data are from L. A. Haskin and S. A. Morse [*Trans. Am. Geophys. Union* **50**, 335 (1969); unpublished data].
14. A K_D of 1.0 results in no fractionation, that is, a slope of zero.
$$\begin{aligned} K_D - 1 &= D^{WR/L}_{^{87}Sr} - D^{WR/L}_{^{86}Sr} \\ &= 1.047269 - 1.047683 \end{aligned}$$
from the decomposed data for the strontium isotope abundances.
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Asian Dust: Seasonal Transport to the Hawaiian Islands

Abstract. *Analyses of atmospheric particles collected at Mauna Loa Observatory in Hawaii from February 1979 through September 1982 reveal strong influxes of Asian dust in the spring of each year. Concentrations of a typical crustal element, aluminum, are more than an order of magnitude greater between February and June than during the remainder of the year (71 ± 51 versus 6.7 ± 2.3 nanograms per cubic meter). The mass of crustal material transported during the relatively short dust episodes accounts for an average of 80 percent of the total yearly mass of atmospheric particles at 3400 meters on Mauna Loa.*

Transport of vast quantitites of Sahara desert dust eastward across the Atlantic Ocean to Bermuda has been known since the late 1960's (*1, 2*). Strong evidence now exists for transport of large quantities of Asian dust westward across the North Pacific (*3–7*). Mauna Loa Observatory (MLO), at an altitude of 3400 m on Mauna Loa mountain on the island of Hawaii, is an excellent site from which to observe this dust. Bodhaine *et al.* (*3*) observed increases in aerosol light scattering (b_{sp}) at MLO from $\sim 1 \times 10^{-7}$ to $\sim 1 \times 10^{-5}$ m^{-1} each spring since 1974, indicating a huge increase in concentration of particles with diameters in the range 0.1 to 1 μm. The site is far enough away from Kilauea volcano that the wind patterns usually do not carry volcanic emissions to the observatory. Other researchers have also used MLO to observe these dust episodes (*5, 7*).

There has been a need for long-term monitoring of these dust events as well as the normal nondust conditions to establish a baseline of aerosol mass and detailed composition in the Northern Hemisphere at a remote site (*3, 8*). As in all studies of aerosol composition, care must be taken to eliminate contamination of samples by locally produced aerosols. Concentrations of major elements are important in categorizing an aerosol's composition as marine, crustal, or anthropogenic. With the addition of trace elements, one should be able to further categorize sources. Trace elements may discriminate between possible sources of dust—for instance, between arid regions (sedimentary material) and Hawaii (basalt). This report presents results from a 4-year study of particle composition at MLO.

The 3400-m altitude of MLO places it well above the mean trade wind inversion layer height of 1800 m (*9*). The inversion greatly restricts mixing of the free troposphere with air below the inversion (*10, 11*). Concentrations of marine particles, which can mask analysis for many trace elements at sea-level collection sites, are reduced at MLO. Continental crustal material is suppressed by the large distances to North America (3800 km) and Asia (more than 6000 km to Japan). For such crustal material to reach Hawaii, large quantities must be dispersed into the free troposphere with proper meterological conditions for long-range transport, as apparently happens during the Asian dust events (*5, 6*). Locally derived crustal material is a possible source of particles at MLO, but trace elemental analyses can be used to identify it. There are few sources of anthropogenic emissions on Hawaii, as no people live near MLO and few vehicles come to it.

Convectively induced mountain winds normally occur in a diurnal upslope-downslope pattern (*12*). Particles collected during daytime upslope flow should represent air from just above or below the trade wind inversion, depending on the altitude and strength of the inversion. This air could contain significant concentrations of local aerosols from weathered basalt, marine sources, or anthropogenic sources which have mixed through the inversion layer. By contrast, nighttime downslope winds bring air from above Mauna Loa to MLO. Such air has minimal contact with the mountain slopes and thus little opportunity to pick up local particles. Aerosols borne by these downslope winds should be representative of midtropospheric air in this region of the Pacific. To sample these winds at MLO, we constructed a digital sector analyzer-controller with help of