On the sources of uranium in some Scottish Caledonian granites

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ABSTRACT. The lead isotope systematics, zircon uranium concentrations and whole-rock rubidium concentrations of 11 Scottish Caledonian granites are examined for clues to the origin of their uranium. A positive correlation between U in zircon and initial lead isotope ratios suggests that U and Pb were derived from the same source which, as some of these granites contain their U in inherited zircons, is likely to have been within the crust. It is argued, therefore, that most of the uranium in these granites had a crustal derivation but lead isotope ratios indicate that any Lewisian contribution was minor in comparison with those from postulated Grenville, Morarian or Caledonian metamorphic reservoirs. However, additional data are required before this conclusion can be extended to include uraniferous Caledonian granites such as Cairngorm.

THE Caledonian granites of the British Isles have classical field relationships and geochemistry (e.g. Read, 1961; Nockolds, 1940; Nockolds and Mitchell, 1946) and calc-alkaline or alkali-calcic characteristics of magmas near present day destructive plate margins but, despite their being the biggest intrusive suite in Britain, very little isotopic or precise trace element research was published on them until the late 1970s. The intrusions emplaced c.400 Ma ago in end Silurian/early Devonian times are the most important volumetrically. They have been subdivided on several different criteria, using intrusive style (Read, 1961), geophysics (Brown and Locke, 1979), and age (Pankhurst and Sutherland, 1981). The c.400 Ma-old granites have initial $^{87}Sr/^{86}Sr$ in the range 0.703–0.709 (Halliday et al., 1979) and the interpretation of these and other data has varied between a largely mantle- or subcontinental lithosphere-derived origin to one of mainly continental crustal origin (see Pidgeon and Aftalion, 1978; Halliday et al., 1979; Pankhurst, 1979; Leake et al., 1980; Brown and Locke, 1979; Harmon and Halliday, 1980; Hamilton et al., 1980). Simpson et al. (1979) have published data on the content and mineralogy of uranium (using delayed neutron and fission track methods) for several of these granites in an attempt to define which granites are urani-

ferous and why. It was their conclusion that granites not associated with uranium enrichment were generated within the crust while uranium-rich granites were 'derived from subcontinental lithosphere under-plated on to pre-existing Precambrian basement' and 'uranium enrichment by scavenging of subcontinental lithosphere' was 'considered important'. They based these conclusions on the low initial $^{87}Sr/^{86}Sr$ ratios of the uraniferous granites, the occurrence of uranium away from mineralization in resistate primary minerals such as zircon, their high contents of incompatible elements and low K/Rb ratios of the uraniferous granites and their postulated large volumes which they regarded as necessitating a mantle/lower crustal source region. Low $^{87}Sr/^{86}Sr$ initial ratios of the c.400 Ma-old granites do not necessarily preclude a significant crustal input. Many of the granites (including those studied in this paper) have Sr concentrations of up to 2000 ppm and some with lower Sr contents may well be differentiates of such magmas. Contamination of juvenile magmas with typical crustal materials may therefore have little effect on the $^{87}Sr/^{86}Sr$ ratio. The presence of inherited zircons in some of these granites (Pidgeon and Aftalion, 1978) provides evidence that old continental crust formed a constituent of the magma. Since uranium is strongly partitioned into zircon it is a reasonable hypothesis that at least some of the uranium in such granites may be derived from the crust. This study sets out to test this hypothesis and evaluate how important it is as a process. It must be pointed out that the granites studied here are mostly those of low uranium content attributed by Simpson et al. (1979) to derivation from a crustal source; the uraniferous Caledonian granites which Simpson and co-workers studied were Cairngorm, Weardale and Etive (Starav) for which we have no U–Pb isotopic data. Furthermore these intrusions have low Sr concentrations for example Cairngorm has a mean Sr content of 67 ppm (Plant et al., 1980) and in this and other respects is similar to the nearby Hill

of Fare intrusion, which has low $^{87}Sr/^{86}Sr$ initial ratios and no detectable inherited zircons (Pidgeon and Aftalion, 1978; Halliday et al., 1979). The Lochnagar intrusion which is similar but has a higher Sr content forms a part of this study and further isotopic work is needed to demonstrate the correctness of any extrapolation that is made to the Cairngorm intrusion.

Lead isotopes have been used widely as tracers in igneous and ore petrology to determine the age, U/Pb ratio, and hence the likely site of the source region. Blaxland et al. (1979) published the first common lead isotope work on the Scottish Caledonian granites, and this study relies heavily on these data plus those of Pidgeon and Aftalion (1978), van Breemen et al. (1979), and Halliday et al. (1979).

The concentrations of U, Th and Pb in Earth 'reservoirs' increase in the order mantle, lower continental crust, upper continental crust. This is shown in Table I where present-day concentrations

TABLE I. Present-day concentrations of U, Th, and Pb in earth reservoirs according to Doe and Zartman (1979)

Reservoir	Average Concentrations (ppm)			
	U	Th	Pb	U/Pb
Mantle	0.055	0.19	0.40	0.14
Lower Crust	0.62	3.6	6.5	0.095
Upper Crust	3.65	12.1	19.9	0.18

as estimated by Doe and Zartman (1979) are given. The lower crust is thought to be depleted in U relative to Pb and relative to its concentration in the upper crust because granulite-facies rocks uplifted from lower crustal depths are commonly U depleted (Heier and Adams, 1965) and because the heat contribution from the lower crust and upper mantle is uniform over very large areas (Roy et al., 1968). This means that, unlike absolute concentrations, U/Pb ratios in the Earth increase from the lower continental crust to the mantle to the upper continental crust (Table I).

Fig. 1 shows part of the two-stage terrestrial lead isotope evolution curve of Stacey and Kramers (1975) based on galena data from large conformable ore deposits. Also plotted are the recently determined Pb isotope data for the Lewisian (Chapman and Moorbath, 1977) and for the Scottish Caledonian granites (Blaxland et al., 1979; van Breemen et al., 1979). The granite data are initial ratios determined on K-feldspars. The Lewisian

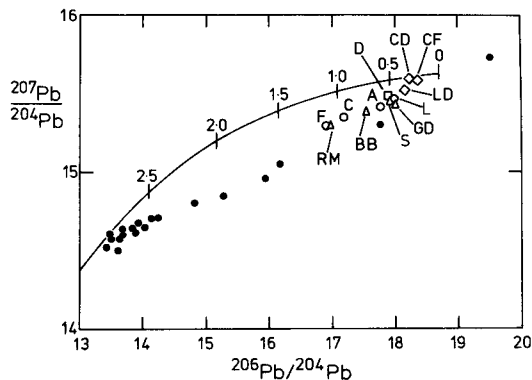

FIG. 1. Pb isotope data for K-feldspars from Scottish Caledonian granites (open symbols) (from Blaxland et al., 1979, and van Breemen et al., 1979) and for Lewisian samples (filled circles) (from Chapman and Moorbath, 1977) plotted relative to two-stage terrestrial Pb isotope evolution curve of Stacey and Kramers (1975). The curve is subdivided at 0.5 Ga intervals. Diamonds—Southern Uplands; square—Midland Valley; circles—Grampian Highlands; triangles—Northern Highlands; CF—Cairnsmore of Fleet; CD—Criffell-Dalbeattie; LD—Loch Doon; D—Distinkhorn; L—Lochnagar; GD—Glen Dessary; S—Strontian; A—Aberdeen; BB—Bonar Bridge; C—Cruachan; RM—Ross of Mull; F—Foyers.

data are present day ratios of whole-rock samples because no U and Pb concentration data were reported. However, by comparison with previous studies of the Lewisian in which concentration data were presented (Moorbath et al., 1969) and from the consistent linear array of the data, it is reasonable to assume that the Pb isotope ratios 400 Ma ago would plot only slightly to the left of those shown. It can be seen immediately from the fields of data that the Scottish Caledonian granites can, at the most, have a relatively minor component of Lewisian-derived Pb in them unless it is unusually radiogenic. It is not possible to say from these data alone that the linear array of the granite data reflect mixing of mantle-derived Pb with Pb directly derived from Lewisian basement as suggested for Skye (Moorbath and Welke, 1969). For example a more complex process of mixing of Pb from crustal rocks of differing ages and histories which may have carried a Pb isotope memory in the form of Lewisian-derived sedimentary detritus may be more accurate. However, the data do show (and Blaxland et al. (1979) pointed this out) that the Southern Uplands granites contain Pb that is more radiogenic than that found further north, which lends support to the interpretation of seismic evidence that there is a fundamental difference between the basement on either side of the Southern Uplands Fault (Bamford et al., 1978).

Uranium concentrations of zircons from most of the granite complexes for which common Pb data are available have been determined by Pidgeon and Aftalion (1978), Halliday et al. (1979) and van Breemen et al. (1979). In all cases more than one zircon fraction and, in the case of Strontian, more than one intrusive phase, have been analysed. These U concentration data, as available, have been averaged for each complex and are plotted against the initial Pb isotope ratios of the K-feldspars in fig. 2. In some instances the zircons and K-feldspars have been extracted from the same rock sample. It can be seen that there is an increase in both $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ initial ratios with U concentration in the zircons. The correlation coefficients are greater than 0.7.

Ludwig and Silver (1977) have shown that some Precambrian K-feldspar contains unsupported radiogenic ^{206}Pb apparently derived by migration from external U-rich sites. However three factors suggest that this is not the cause of the correlations observed in fig. 2. First, the rocks are mainly post-tectonic and have not been affected by subsequent alteration or metamorphism. Secondly, Blaxland et al. (1979) reported that one sample (the Loch Doon separate with quite radiogenic Pb) was given a thorough acid wash treatment which resulted in no significant change in Pb-isotopic composition. Thirdly, the Pb in the zircons varies greatly in $^{207}Pb/^{206}Pb$ because some have marked inherited (Precambrian) isotopic components. If lead had been leached from the zircons and transplanted into K-feldspar there should be a significant difference in the relative distribution of points between the upper and lower isotopic plots in fig. 2 whereas, in fact, they are strikingly similar.

It therefore has to be concluded that the correlation between initial Pb isotopic composition in K-feldspar and U content of zircons reflects a correlation in the magmas at the time of emplacement. Several implications follow from this. The correlations suggest that the source(s) of U in the zircons are also the source(s) of the Pb in the magma. Although we do not have the data to tell us how much of the uranium in the whole rocks is attributable to zircon, Simpson et al. (1976) reported that the U is chiefly concentrated in zircon and other resistate phases. From the mineral separation yields on which these analyses are based it is reasonably certain that zircon is dominant among these phases. The U whole-rock data of Simpson et al. (1979) include some mainly low-uranium intrusions covered in this study (Foyers, Strontian, Doon, Fleet) and others for which U–Pb zircon data are available. Uranium loss from these zircons is probably not very great because U substitutes readily in the zircon structure, and
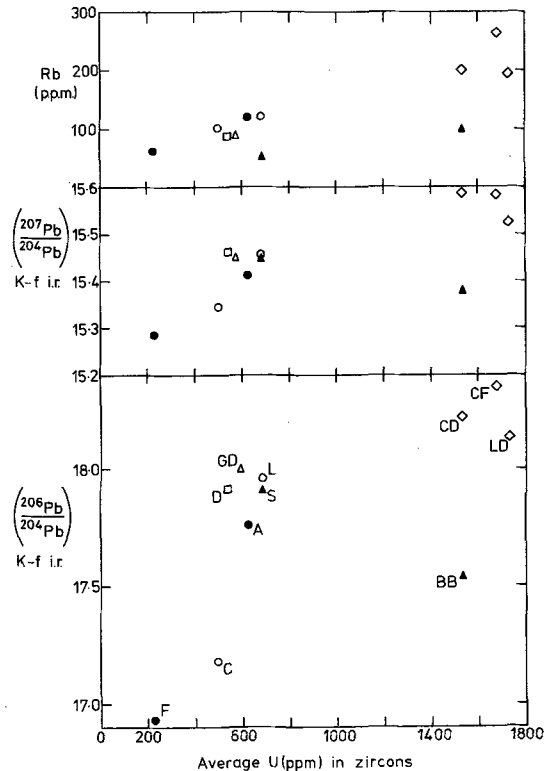

FIG. 2. Pb isotope initial ratios of K-feldspars and whole-rock Rb concentrations plotted against the average U concentration of analysed zircons from the same granites. Symbols as for fig. 1 except that filled symbols refer to intrusions with some Pb isotope memory in the zircons.

because it is rare to find zircons with $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios which plot above the concordia curve. Also, since Pb in zircons can remain disequilibrated during a cycle of assimilation, partial melting and subsequent cooling, it is reasonable to assume that U does also. This is supported by the frequent observation of core/rim structures and zoning in zircons from granites, suggesting that equilibrium is not commonly attained during this cycle. Simpson et al. (1976, 1979) concluded that uranium redistribution takes place at the magmatic stage and, in some hydrothermally-affected granites, after cooling. It is possible, therefore, that U whole-rock values may not be as diagnostic as U contents of zircons in identifying which granites have been derived from uranium-rich sources.

It would not be too surprising if the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ initial ratios correlated with the $U/^{204}Pb$ ratios of the rocks regardless of

the sources involved. However to show a correlation with absolute U concentration (assumed to be equivalent to that in zircon) places strong constraints on the source of the U because, as already pointed out, the U concentration does not correlate with U/Pb ratio for the three 'reservoirs' (mantle, lower crust, and upper crust), the U concentration of the lower crust being more than a factor of 10 times greater than in the mantle but the U/Pb ratios being lower. Some of these granites (with filled symbols in fig. 2) have inherited Pb isotope systematics in the zircons. We know from this that they have, at least in part, been derived by the disaggregation of continental crust, the zircon content and Pb concentration of mantle rocks being very low. As these samples have definitely derived some of their U and Pb from the continental crust and plot on the same trend as samples lacking a Pb-isotopic memory in their zircons it is difficult to see how very much of the U and Pb in any of the granites studied here could be derived directly from the mantle or subcontinental lithosphere. Fractional crystallization can be expected to concentrate U in the melt phase and hence it might be argued that highly fractionated mantle-derived magmas would have higher U concentrations. It is difficult to test this critically in any unambiguous way. The U contents of eighteen 'mantle-derived' acid rocks (granophyres, felsites, obsidians, and dacites) from Iceland give an average of 3.2 ± 1.3 ppm (1σ) (Welke et al., 1968), much lower than in many of the Scottish granites. However, it is difficult to assess the potential U concentration in a granite that has been derived from melting of altered oceanic crust or U-enriched sub-continental lithosphere since we have no unambiguous control to compare with and no way of estimating the U content of such a hypothetical source. However we can argue from circumstantial evidence that such a mechanism is unlikely. Oxygen isotope data for these rocks suites (Halliday et al., 1980, 1981; Harmon and Halliday, 1980) suggest that if the magmas have been derived from the mantle or sub-continental lithosphere they have interacted with the crust to varying degrees. Also the chemistry of the samples varies considerably. Focusing on the cluster of points representing Lochnagar, Distinkhorn, Strontian and Aberdeen in fig. 2; there are, within this group, ranges of $\delta^{18}O$ from 7.1 to 10.5 ‰ and of rock type from tonalite to leucogranite. Yet these all have approximately the same Pb isotopic composition and U content in zircon. In the case of Aberdeen and Strontian these zircons are, in part at least, inherited from the crust together with some Pb and U. The clustering of the data for these intrusions is readily explained if crustal reservoirs are dominating the U and Pb concentrations of the magmas, regardless of the ultimate source of the parent magma since it would require minimal interaction with the crust to affect the Pb and U contents drastically. On the other hand the data in fig. 2 coupled with the range in rock type require, not just extreme coincidence, but also non-systematic behaviour of U during fractional crystallization if the uranium concentration is largely a function of fractional crystallization of magma derived from subcontinental sources.

Also plotted in fig. 2 are the Rb concentrations of whole rocks from the granites. Where analyses for the same sample were not available, the data for that phase of the intrusion have been averaged (Halliday et al., 1979, 1980; van Breemen et al., 1979). There is a general increase in Rb in whole rocks with U in zircon. This is as expected since Rb and U enrichment/depletion processes are often coincident. That the correlation is not perfect is also not surprising since (a) as already pointed out these 'granites' vary in rock type and equilibrium between zircon and liquid during fractional crystallization was probably not always attained and (b) the crust which these granites have sampled is very variable.

A plot of $^{87}Sr/^{86}Sr$ initial ratios against initial $^{206}Pb/^{204}Pb$ (not shown) displays no correlation or sign of a systematic relationship. The $^{87}Sr/^{86}Sr$ initial ratios vary between 0.704 and 0.708 with the exception of Aberdeen which has an initial $^{87}Sr/^{86}Sr$ of c.0.712. There is no independent information on the Pb isotopic composition of the mantle underneath Scotland 400 Ma ago. The two samples with lowest $^{87}Sr/^{86}Sr$ initial ratio ($\simeq 0.704$) are from Distinkhorn and Glen Dessary. They have similar Pb isotopic compositions (figs. 1 and 2) and as they are geographically widely separated it may be that these are unmodified mantle Pb isotope initial ratios. However as already pointed out it is an odd coincidence that these data should plot in the same position in fig. 2 as data for granites that have incorporated crustal material.

A further implication of the crustal dominance in the Pb and U data is that the trend of the data in fig. 1 does not simply reflect mixing between Pb of sub continental origin and Lewisian Pb. Some crustal reservoir with more evolved compositions was involved. From the geophysical data of Bamford et al. (1978) and the reconstruction by Shackleton (1979) it is reasonable to assume that the reservoirs are Grenville, Morarian, and Caledonian metamorphic rocks, the lower parts of which reached granulite-facies grade during orogenic events. The basement presumably underwent simultaneous U depletion. Confirmatory evidence for U depletion events in the Scottish crust sub-

sequent to Lewisian times comes from U concentrations in zircons and monazites from Morarian and Caledonian pegmatites (van Breemen et al., 1974, 1978). The Morarian zircons in particular are, as far as the author is aware, the most U-rich zircons analysed from granitic rocks in Scotland with between 3000 and 6000 ppm U. These pegmatites formed during orogenic events and probably represent low-degree partial melts of undepleted metasedimentary crust, not previously metamorphosed to high grades or precipitates from H_2O-rich fluids which have scavenged U from the crust.

It is of interest that the U content of the Foyers zircons analysed are lower than have been reported for any zircon sample analysed from Scottish rocks with the exception of Scourian pyroxene granulites (Pidgeon and Bowes, 1972). Similarly the average uranium whole-rock concentration for Foyers is among the lowest of the Caledonian granites analysed by Simpson et al. (1979). This suggests that the Foyers magmas sampled granulite facies crust but the Pb isotope data indicate that this was not the Lewisian. It also follows (not too surprisingly) that U-rich granites do not derive their U from granulite-facies crust unless the U is concentrated by fractional crystallization.

Clearly there is a great deal more systematic work to be done relating initial Pb isotopic composition to Zr, U, and Pb concentration in whole-rock samples and the U concentration of the contained zircons, as well as carrying out analyses of type crustal reservoirs. However despite the limitations of the data presented here, they do strongly suggest that the U in the Scottish Caledonian granites studied here is chiefly derived from the crust. Further support for this comes from a recent study of the Kilmelford diorite complex (Halliday, Rickard, and Harmon, in preparation) in which U concentration is found to correlate positively with $^{87}Sr/^{86}Sr$ initial ratio (fig. 3). Whilst not debating the point that U can be concentrated by fractional crystallization, it does appear that the chief source of U in these granites is in the continental crust. This does not contradict the view of Simpson et al. (1979) so far as granites such as Foyers, Strontian, and Aberdeen are concerned that these 'were derived by crustal ultrametamorphism and partial melting' but it is less consistent with the view that the late U-rich granites in the British Caledonian (not studied here) derive their high U by the scavenging of sub-continental lithosphere. Although the most U-enriched granite they studied was Cairngorm, for which there are no published U–Pb isotopic data, their conclusion that uranium was derived from the mantle is very hard to substantiate on the basis of the geochemistry that is available (Brown et al., 1979). The high Rb/Sr ratios, low Zr concentrations and marked negative Eu anomalies are suggestive of zircon and plagioclase crystal fractionation. Without a knowledge of the parent magma and the degree of uranium enrichment by crystal fractionation, it is impossible to say whether the source of the uranium in these late granites was in the mantle or the crust. Further work is likely to reveal a more complicated picture for a diagram such as fig. 1 because of the complex history of Scottish crustal evolution prior to the formation of the c. 400 Ma-old granites.
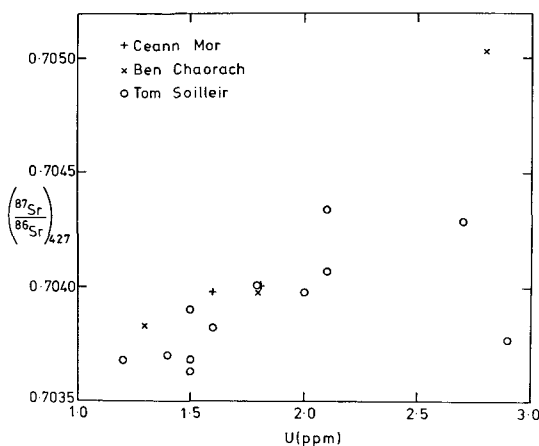
Fig. 3. The initial $^{87}Sr/^{86}Sr$ ratio plotted against U concentration in whole-rock samples of the Kilmelford diorite complex (Halliday, Rickard, and Harmon, in preparation).

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