The Geochemical Cycle of Uranium [and Discussion]

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The geochemical cycle of uranium

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If the uranium content of the mantle is based on data from basalts, a homogeneous mantle would contain about 10 parts U/10^9. This gives a similar mass of uranium in mantle and crust. Sea floor processes may enrich the surface layers of basalt in uranium but do not significantly change the mass of uranium subducted in basalts. If pelagic sediments are subducted, they contribute a significant mass of uranium to the mantle. Present rates of andesite production do not seem adequate to return all subducted uranium to the crust but andesites may make a significant contribution to uranium which eventually appears in granitic rocks. Uranium transport and accumulation in sediments may be dominantly biochemical. The problem of uranium distribution in the mantle during evolution of the Earth is unresolved. The main models of crustal evolution suggest continual depletion, early depletion, or early depletion followed by slow replenishment; a constant mantle composition seems unlikely.

Introduction

The past two decades of geological research have clearly shown, and in part quantitatively documented, the fact that the Earth is convecting. The pattern and style of present convective motions is commonly termed 'plate tectonics'. A fundamental conclusion of plate tectonics (Hallam 1976) is that the mass of crust is conserved, or that the new crust created by igneous materials rising from the mantle must be returned to the mantle in almost equal quantities. If this is so (and one may question any exactly steady-state model (Fyfe 1976*b*)) it implies a very significant cycling of mantle material through the crust–hydrosphere–atmosphere system. Such a process may lead to large-scale geosphere mixing. Given present rates of basalt production, and assuming that past rates were greater and related to past heat production, then something like 15% of the mass of the mantle may have been at or within 10 km of the surface during Earth history.

The recognition of the mechanism of plate tectonic phenomena requires that models of global geochemistry reflect such mixing. At present we are in a period when such considerations are in progress and, in many cases, established treatments of geochemical cycles require various degrees of revision. The classic Goldschmidt models of element partition between the main geospheres must be revised to accommodate the influences of large-scale convection. Recent work with elements such as calcium, magnesium, potassium and hydrogen has shown the potential importance of such mixing processes in estimating global distribution of the elements.

In this paper I wish to examine some of the information for uranium. The geochemical cycle of uranium is not only important in terms of global heat production, but gaps or inconsistencies in geochemical balance may point to similar gaps in our knowledge of potential resources. Appreciation of processes associated with plate tectonic phenomena has drastically changed resource estimates for metals such as copper, nickel, cobalt.

Uranium distribution in the Earth

Brewer (1951) discussed the general factors which influence the equilibrium distribution of the elements in a homogeneous body. For any component, i, in a mixture i, j, k . . ., the general equation for equilibrium distribution in a gravitational field can be written:

$$\mathrm{d}\mu_{\mathrm{i}} = 0 = \left(\frac{\partial \mu_{\mathrm{i}}}{\partial T}\right)_{P,N,h} \mathrm{d}T + \left(\frac{\partial \mu_{\mathrm{i}}}{\partial P}\right)_{T,N,h} \mathrm{d}P + \left(\frac{\partial \mu_{\mathrm{i}}}{\partial h}\right)_{T,P,N} \mathrm{d}h + \sum^{\mathrm{j}} \left(\frac{\partial \mu_{\mathrm{i}}}{\partial N_{\mathrm{j}}}\right)_{P,T,h,N_{\mathrm{k}}} \mathrm{d}N_{\mathrm{j}},$$

where μ_{i} is the chemical potential of species i and h is the position in the gravitational field. For most species in a body with the dimensions and temperature distribution of the Earth, two terms tend to dominate. These are the position in the gravitational field and the final term of the above equation which describes chemical interactions. Brewer emphasized that if a light major component like oxygen is enriched upwards, then a heavy element like uranium, with a great chemical affinity for oxygen, will follow the oxygen gradient and also be enriched upwards.

The above equation would be valid for an essentially one phase (say liquid) Earth. In a largely crystalline Earth with major phase changes in different depth zones, any such simplistic model must be questioned. Further, if convection and heat and mass transfer via partial fusion occur, our confidence in such an approach is further diminished. Realistic thermodynamic calculations become almost impossible.

Recent considerations of energy sources for the core dynamo, and the recognition of alkali metal sulphide minerals in meteorites (djerfisherite, $\mathrm{K(Cu, Na)\,(FeNi)_{12}S_{14}}$) have led to the suggestion that an element such as potassium could be present in the metallic core (see Stacey 1977). Such a view is quite contrary to the normal classification of potassium as a lithophile element. Burns & Fyfe (1966) have discussed the problems of unique classification of geochemical behaviour of elements. In fact, such behaviour is dependent on local bulk composition and crystalline state (phase changes). A reaction which illustrates such surprises is, for example,

$$\mathrm{2ThO_2 + 3FeS \longrightarrow Th_2S_3 + Fe_3O_4},$$

which has a ΔG° of $-6.26\ \mathrm{J\ mol^{-1}}$. In such a system, thorium is chalcophile.

My conclusion is that, given the present state of the art, the distribution of any element in the Earth will be constrained by observation and not by theoretical considerations alone. For the heat producing elements, there are also constraints imposed by our knowledge of heat production (see Clarke & Turekian 1979, this volume). However, for many elements, even common elements such as hydrogen, our knowledge of concentrations and distribution in the deep Earth is inadequate.

The basic geochemical cycle

Today, we are approaching a realistic model of how the Earth functions. Any treatment of the geochemical cycle for an element must consider:

(*a*) New crust formation by heat and mass (basalt) transfer from the mantle. At present this process occurs dominantly at the ocean ridges and to a lesser extent (say 1%; Burke & Wilson 1976) at hot spots. In addition there are minor contributions from exotic magma types such as kimberlites and leucitites, etc. While the above crustal additions are well documented, some less well understood processes may be involved in crustal underplating and may cause vertical motions inside continental blocks.

(*b*) The new crust created at ocean ridges is quantitatively removed at subduction zones. The oceanic crust subducted has been modified by sea water convective cooling. It is generally considered that subduction proceeds to depths of 600–700 km but the limiting depth is not certain and subduction to deeper levels is not impossible.

(*c*) Some components of the subducted material are returned to higher levels. This process is associated with igneous processes above subduction zones and the blueschist metamorphism and metasomatism. Our detailed knowledge of such processes is again inadequate.

(*d*) Erosion off the continents feeds the ocean reservoir. As the residence time of most elements is short (less than 1 Ma), there is rapid cycling from continent to ocean to spilite and sediments.

(*e*) Some sediment may be subducted and returned to the mantle. This proposition (see below) involves one of the greatest gaps in our present consideration of global balance of the elements. It is vital to our understanding of the distribution of heat-producing elements.

URANIUM IN THE MANTLE

There are many approaches to the overall abundance of uranium in the deep Earth. These may be based on evidence from meteorites, cosmic abundance data, heat production, or even the Earth itself. Here, I will restrict myself to evidence from the Earth.

By far the largest and most significant samples of mantle materials we see are the ridge and hot spot basalts. The ratio of the two is something like 100 : 1 and it is generally considered that the depth of origin of the hot spot basalts is greater than that of the ridge basalts.

Recently Arndt (1977) has discussed some general features of the mechanics of partial melting. To collect a magma, a significant degree of partial melting and hence permeability must be generated. As any consideration of the chemistry of melting processes shows, a minor element (at 1 part/10^6 or less) will tend to be collected in early melt fractions. An exception would involve oxides with very high melting temperatures. The general behaviour of uranium in igneous processes clearly shows that it is not an exceptional element. Comparison of U–Th–Zr clearly reflects their fusion behaviour (UO_2, melting point 2176 °C; ThO_2, 3050; ZrO_2, 2700).

Recent work of Aumento (1979, this volume; Aumento, Mitchell & Fratta 1976) on young sea floor rocks and work on Archaean basalts (Condie, Viljoen & Kable 1977) indicates the extreme care required in the sampling and determination of the original uranium content of sea floor basalts. In general, uranium is added to basalts by sea floor alteration. Here I shall use data from Aumento *et al.* (1976) and a primary uranium content of 0.1–0.2 part/10^6. This value compares well with data summarized in Carmichael, Turner & Verhoogen (1974). Data on individual minerals in such basalts (all in the order of 1 part/10^9) also show that much uranium may be on grain boundary phases and hence in the late liquid fractions and therefore also easily mobilized.

If we turn to hot spot basalts, data in Wedepohl (1974) indicate similar to higher values than those for ridge basalts (0.2–0.9 part/10^6). If these magmas originate at greater depth, there is here no evidence for significantly different uranium contents in this deeper mantle. I am reluctant to use data from continental basalts as the chances of crustal contamination (see Armstrong *et al.* 1977) are too great. I also consider that values from kimberlites (see Brookins *et al.* 1977) are so high (0.5–18 parts/10^6) that they can have no general significance for the mantle. They do show that parts of the mantle have highly anomalous chemistry, perhaps related to residual fragments of a former subduction process.

What degree of partial melting is responsible for the final basalt magmas? I do not see an adequate answer to this problem but here I will assume that an upper limit might be near 10% and no more. If we assume that most of the uranium is concentrated in the basaltic products of a rising plume, then we obtain a mantle uranium content in the order of 0.01 part/10^6. Such a 'guess' can hardly be better than a factor of four and depends on models of magma separation and the range of concentrations in unaltered basalts.

Given the mass of the mantle as 4×10^{24} kg, then the uranium content of a homogeneous mantle would be in the order of 4×10^{16} kg. I can see no other data that can be provided by Earth-bound geochemistry.

We may compare the above figure with Cameron's (1966) cosmic abundance data. Cameron gives uranium as 0.042 relative to silicon at 10^6 (atoms). As the Earth has a silicon content of about 15% (Mason 1966), this would give a uranium content of the Earth of about 3×10^{17} kg. The mantle figure above thus appears low on this basis, but is similar to Gast's (1972) estimate. Clark (1979, this volume) discusses the significance of mantle uranium in terms of heat production.

URANIUM IN THE CRUST

One of the striking features of uranium in the crust is the large number of separate minerals (over 100) known for this element whose overall abundance is in the order of 2 parts/10^6. This shows how difficult it is to accommodate uranium in common minerals of the crust and correlates with the mobility in the surface environment. Mason (1966) gives an average crustal abundance of about 2 parts/10^6 which gives the crustal uranium mass as about 3×10^{16} kg, a figure close to the above mantle abundance. This conclusion was also reached by Gast (1972). The similarity of the uranium mass in essentially continental crust and the mantle implies that heat production in the mantle may be significantly changed if the mass of such crust has changed with time and hence there must be great significance associated with the evolution of continental crust (see below).

RATES OF U ADDITION AND SUBDUCTION

The modern ocean floor spreading process requires that new ocean floor crust (basalt) is added at a rate of about 3×10^{13} kg a^{-1}. From figures given above this implies an annual addition of uranium of 3–6;10^6 kg a^{-1}. The present mantle reserve could obviously supply this addition indefinitely at the present extraction rate. It is interesting to reflect that if the rate of basalt extraction was much greater in the past (say five times) and in proportion to past heat production, and if early basalts were more like lunar basalts, then a few hundred million years would suffice to move most of the uranium to the surface.

We must now turn to the return flow and subduction process. Aumento and coworkers (1976; 1979, this volume) have clearly shown that during the sea floor hydrothermal cooling process, uranium is fixed in basalts. This observation is further confirmed by the observations of Ku (1969) that uranium in the Red Sea brines is at lower concentrations than in average sea water. Some sea floor basalts contain uranium up to 4 parts/10^6. In a general way, uranium addition can be correlated with the degree of potassium addition, hydration etc. and increases with distance from the ridge axis. Is the process significant to the overall uranium balance?

There are many elements for which fixation in the spilitization process appears significant: S, CO_2, H_2O, K, etc. All of these processes require circulation of an appropriate volume of sea water and this in turn is related to the energy available to drive convection. Three energy terms are important in this process: (*a*) energy from the cooling igneous rocks; (*b*) energy from exothermic reactions, hydration, oxidation, CO_2 addition (Fyfe 1974); (*c*) mantle heat flow.

All of these processes provide similar quantities of energy and a total input of 20 EJ/km; (20×10^8 J/km;) (the annual production) is not unreasonable (see also Wolery & Sleep 1976). The mass of sea water which could be heated to 100 °C is thus in the order of 5×10^{14} kg for each 3×10^{13} kg of basalt, a ratio of about 20 : 1. It follows that for significant fixation (and assuming that fixation dominates over extraction), the concentration of a species in sea water must be at least 0.05 of the concentration in primary basalts; in this case the concentration in the basalt could be doubled.

Uranium in sea water is present at about 1 part/10^9 level, in basalt 100 parts/10^9. It is thus difficult to see that the level of uranium in basalt is much changed by such interaction. Significant changes in upper layers are possible, but not for the entire ocean floor crust. But the converse holds and the basalts can act as a sink for sea water uranium.

It should be noted that for an element such as potassium, the ratio for sea water to basalt concentration is near 0.2 so that major change is possible. In fact a twofold to threefold increase in potassium seems possible and correlates with observations of Aumento *et al.* (1976). In such a process we see the intermediate step in the eventual subduction of a 'continental' element.

Recently, Sibley & Vogel (1976) have discussed the general features of calcium balance in sediments. They state: 'Pelagic sediments, in contrast to other sediments, are not usually recycled; most are subducted and therefore act as a geochemical sink. Models for the chemical evolution of the Earth's crust may need to take into account the fact that vast amounts of pelagic material are subducted and that the chemistry of these pelagics changes with time.' Such a statement, when viewed in the light of the mass involved, opens up one of the greatest unknowns and problems of geochemical balance.

The idea that massive quantities of sediment may be subducted was first contemplated by Gilluly (1971). I think that one of his major statements is worth quotation:

> It has been argued that these lighter rocks – the basalts and sediments – could not have been dragged far down a subduction zone into the much denser mantle. But many arguments seem to show that huge volumes of both sediment and basalt are so dragged. First, and perhaps less convincing, is the widespread occurrence along subduction zones of blue schist, eclogite, and aragonite marbles, associated in melanges with such low-density rocks as chert and shale. The mineral paragenesis indicates deep burial, but both dense blueschist and light chert have gone down to depths of several tens of kilometres and been returned to the surface. The common occurrence of ophiolites high in the sialic crust of many ranges also demonstrates that not all rocks are disposed in the Earth's gravity field in strict accordance with their density.
>
> But a much stronger argument, and one that seems to me unassailable, if the plate tectonics model is accepted, is this: if the westward drift of the Americas has really gone on, the American plates must have overridden those to the west for fully 1500 km. Indeed, if the absence of any subduction zone between the Mid-Atlantic Ridge and the continents to the east means what several of the plate advocates think it does, that is, that the ridge has

> pushed itself westward, away from Europe and Africa – the American plates have overridden those to the west by a distance equal to the full width of the Atlantic – 3000 km, not merely the half width.
>
> The oceanic crust averages about 1 km or so of sediment overlying 5 to 6 km of tholeiitic basalt. Accordingly, somewhere between 7500 and 15000 km^3 of basalt and about 1500 to 3000 km^3 of sediment have been overridden for *each km* length of continent–ocean interface. These are gigantic numbers. But that is not all that must be accounted for. Very considerable masses of Paleozoic and even Precambrian strata lay immediately off the west coast of North America, judging from the cutoff edges of such rocks along the southeastern Alaskan, Juan de Fucan, Klamath, and Transverse Range segments of coast. What happened to all these rocks? The sediments now offshore the Pacific Coast of the United States are less than a sixth as voluminous as those off the Atlantic, despite the roughly comparable areas tributary to the two coasts (Gilluly *et al.* 1970). The greater volume of Mesozoic and Cenozoic [Cainozoic] rocks on the west of the continent by no means equalizes the discrepancy.
>
> Obviously, if the sediments had been scraped off the downgoing slab, we should find them piled up against the west edge of the continent. According to Pakiser & Steinhart (1964), the average thickness of the crust under the Coast Range in California is about 20 km. If only 1500 cu km of sediment had been scraped off the diving slab, we ought to find a 75 km average width of Paleozoic, Mesozoic, and Cenozoic rocks piled up against the continent; if the drift did indeed equal the whole width of the Atlantic, the pile should be 150 km wide. But the Franciscan mélange is a mere fraction of this volume. It seems to me undeniable that most of the 1500 to 3000 cu km of sediment and virtually all of the 7500 to 15000 cu km of basalt per km of latitude have disappeared down the subduction zone – this despite the fact that when they started down, at least, they were much less dense than the surrounding material. How far down do they go? Even though under pressure there would doubtless be phase changes, with production of such minerals as kyanite in the sediments and with the basalts converting to eclogite, I doubt that they go all the way to the bottom of the zone. Probably they get heated up and drift off to form the magma pockets that many seismologists think characteristic of the low velocity zone – somewhere between 80 to 90 km to, say, 200 to 300 km.
>
> I therefore think that when we hypothesize about magma genesis along a subduction zone we are not restricted to pyrolite alone as the parental material – in fact, we are *compelled* to think otherwise.

I make no apology for this long quotation from one of the masters. At this Discussion Meeting it was apparent that such a proposition is not popular or does not sit comfortably with all workers. It is natural that it does not for it makes many things more complicated and less 'steady state'.

I wish to add one further recent comment from Garrels & Lerman (1977): 'About 75% of the new sediments are cannibalized from older sediments; 25% come from the weathering of crystalline rocks. The new sediments are apparently balanced by subduction of a comparable mass of sediment into the mantle, presumably accompanied by return of volatiles to the surface system. This balance permits treatment of the system as if it were closed, but truly so only if the subducted sediment had the same average composition as the newly created sediment.'

Let us assume that sediment subduction is a reality and examine what it means for the uranium balance. Pelagic sediments accumulate at a rate of 0.3–1 km^3 a^{-1}. The uranium content of pelagic sediments averages around 3 parts/10^6. We should perhaps also note that the Pb/U ratio of pelagic sediments is similar to that of igneous rocks. This cubic kilometre of such sediment would contain about 10^7 kg of uranium and if subducted would return more uranium to the mantle than the sinking basalt. Given the crustal mass of uranium, 3×10^{16} kg, this would be subducted in 3 Ga. Obviously, sediment subduction could change the uranium balance of the mantle.

It is also interesting to note that if spilites contain an average 0.4% potassium, and pelagic sediments 3% K_2O, then all continental potassium would be subducted in a period of the order of 1 Ga. Quite similar conclusions apply to the H_2O in the hydrosphere (Fyfe 1975) which is subducted in the metamorphic minerals of the descending ocean floor crust.

Returning to Gilluly (1971) there is the suggestion that the ratio of basalt: subducted sediment is in the order of 5 : 1 (not the 10 : 1 ratio discussed above). From Garrels & Lerman (1977) the ratio is given as 4 : 1 but with the sediment contribution variable by a factor of 4.

It appears to me, that unless we dismiss the evidence from sedimentary balance, we are forced to the conclusion that more uranium (and potassium and thorium) is subducted than is produced in primary volcanic rocks which form the new ocean floor crust. This conclusion depends critically on the mass of subducted sediment. Sediment subduction over a period of 1 Ga could supply much of the radioactive elements of the present mantle. We are left with the critical question of how sedimentation rates have varied with time.

Return flow above subduction zones

Some subducted materials must return above subduction zones. Water nicely illustrates the general problem. The upper layers of the ocean floor contain the typical metamorphic minerals of zeolite, greenschist and amphibolite facies. The depth of fluid attack may be through the entire ocean floor crust and Lewis & Syndsman (1977) even suggest an hydrated low velocity layer at the crust–Moho interface. Water in mineral phases will not be lost until the descending material reaches temperatures of the order of 300 °C (30–40 km) and even then only if there is no non-hydrated basalt. At greater depth, water may be trapped in the overlying anhydrous mantle wedge (Fyfe & McBirney 1975). At a subduction rate of basalt of 3×10^{13} kg a^{-1}, and with 5% H_2O in minerals, the water subduction rate would be 1.5×10^{12} kg a^{-1} or enough to subduct the ocean mass (1.4×10^{21} kg) in 1 Ga. Most must return. But if the Earth is cooling, one might expect that incremental amounts would be left locked in the upper mantle in phases like amphibole, phlogopite, talc, The two sites of massive return flow must involve the blueschist environment and the environment of partial fusion. The laws of conservation of crust, would require that if sediments are subducted, they must be returned, presumably in the andesites.

Of uranium in the blueschist environment we know little. Even if there was return flow, we would hardly expect to see ore deposits as the gradients for precipitation are so low. Any such return path would lead to diffuse precipitation. Data on ecologites of basaltic composition (Wedepohl 1974) show little departure from basaltic values. In fact values are more like those for enriched spilites. While there is good evidence for extensive metasomatism in blue schists (Fyfe & Zardini 1967) we have no information on uranium behaviour in this process.

As discussed by Heier (1979, this volume) there is little evidence on uranium mobility except at the highest grades of metamorphism. In fact it seems that the two environments for mobility involve (*a*) the oxygenated surface environment and (*b*) the environment of partial fusion. Uranium dioxide is a most insoluble compound. The solubility product is given as 10^{-52} and unless complexing species are present, one would not expect much mobility. Further, Ku (1969) reports very low levels (0.6 part/10^9) in Red Sea brines showing that chloride complexes are not very stable. It thus appears that in a low temperature, reduced environment, uranium is, and should be, rather immobile (cf. lead, which is quite mobile in chloride solutions).

Further, data for metamorphic minerals show that uranium can be held at quite high levels in minerals such as garnet, epidote and sphene, which are common in low T, high P metamorphism.

The second major return flux must involve the andesites and the reactions between descending slab and overlying lithosphere. Overall balance in this process is critical to our understanding of the evolution of the mantle. Recent work of Armstrong *et al.* (1977) has clearly shown that we must be cautious in discussing the geochemistry of deep mantle products that invade crust. The work of Brooks, James & Hart (1976) is highly suggestive that the melting process in andesite formation is dominated more by mantle than by descending slab. Similarly, the discussion of andesite generation in Carmichael *et al.* (1974) clearly shows that obvious links between descending spilite or sediment are difficult to find. It appears to this writer that volatile fluxing of overlying mantle may provide the best general approach. But volatiles evolved from a slab at depths of 100 km or more would be a very concentrated solution of species such as silica, potassium and sodium, and could well be responsible for some of the chemical characteristics which separate andesite from basalt.

What is the typical uranium content of andesite near its source of origin? This poses a most difficult problem. The density of an andesite magma is similar to that of continental crust so such magmas may be ponded in and beneath continental crust. Here the magma may assimilate and exchange with crust. If one selects andesites well away from massive continental masses, do these give reasonable values? Data in Carmichael *et al.* (1974) show values of 0.2–0.4 part/10^6 for andesites from situations such as the Tonga and Kermadec systems. Higher values are associated with continental systems. It thus appears that some andesites have comparable uranium contents to basalts but those erupted through continental masses may have values in the range 0.5–1.0 part/10^6. Will this balance the input from subduction?

Brown (1977) has discussed the rate of crust production above descending lithosphere and has arrived at an average figure of 0.5 $\mathrm{km^3\ a^{-1}}$; Fyfe (1975) arrived at a rather lower figure for the Andean situation. It is obvious that we now encounter a major problem. If sediments with up to 3 parts U/10^6 are subducted at the rates noted above, then for andesites, even with high values (0.5–1.0 part/10^6) uranium, we would require 6–3 km of andesite per year to account for return flow. There is no evidence for this magma volume. If sediment subduction rates are reasonable, then the conclusion must be that: (*a*) uranium is being fed back to the mantle, and (*b*) the continental crust is not growing but shrinking. I do not believe that this problem can be resolved at present but it cannot be ignored. I would stress the fundamental fact that continental crust is not stable in a cooler but mixed Earth. If the lithosphere becomes cooler with time, virtually all hydrosphere and crustal components will form more stable species in the mantle (H_2O in hydrates, SiO_2 in pyroxenes, K in phlogopite, Na in jadeite, etc.). We require thermal energy to keep throwing these species back to the surface. It should also be noted that past sedimentation rates may be much less than the present (Hargraves 1976).

GRANITES

After several decades of intense debate and research, it seems to me that in a general way we are beginning to understand granites. Not all granites are the same but most form whenever we augment the background heat flow into the crust from a mantle source, or greatly overthicken the crust. The vast volume of more modern granitic types are associated with the subduction process, the west coast of the Americas being typical.

The present state of thinking is well summarized by Armstrong (1977), Brown (1977) and Brown & Hennessy (1978). The isotope and general geochemistry of rocks of the granite family requires that these are a product of a mixing process involving continental crust and magma produced above subduction zones. The andesite itself is a product of mantle contamination, in most cases the depleted continental tectosphere of Jordan (1978), by descending lithosphere which is itself contaminated by continental crust.

Rising subduction magmas carry heat and mass to the crust. Because basic magmas have a density comparable to crust, they may underplate, invade and extrude on continental crust. Via all the mechanisms of assimilation, fractionation, heat and mass transfer which in detail presumably are complex, a new range of granitic magmas are produced.

Uranium in most rocks of the granite family ranges from values of 2–5 parts/10^6, the lower range being most common. If we consider granite production of the Andean type, it appears that continental crust has been thickened by 30–40 km by over- and underplating by andesitic magmas. In the generation of the 'granitic' batholiths, some 5–10 km of continental crust may have been reworked. As discussed in this volume by Heier (1979), high grade rocks of an old basement may contribute little uranium to new granites. If we assume that the rising andesite has, say, 0.4 part U/10^6, and that most of this is fractionated into the later magma fractions which concentrate water and crustal assimilation products, then the ratio of andesites: granite of about 6 : 1 could account for most of the uranium. As a granite magma rises, it may assimilate rocks at higher crustal levels and become further enriched in uranium. In a general way, it thus seems that andesites could account for much of the uranium in granites (as with the strontium isotopes) but presumably the andesites themselves have gained most of their uranium via the weathering and eventual subduction of continental crust. Depleted mantle beneath continents does not seem a good source.

While most granitic rocks show strontium isotope abundances tending to mantle values, this is not true for all. Ancient examples of granites with a heavy crust imprint have been described by Moorbath, Wilson & Cotterill (1976) and very modern Himalayan granites by Hamet & Allègre (1976). The Himalayan granites presumably reflect a relaxation process after extreme thickening of continental crust following continental collision.

We have been intrigued by some of the peralkaline granites (500–600 Ma) which were produced as a result of the final stages of Pan-African events in Saudi Arabia. If our present ideas are possible, these granites may represent the final stage of collision of small continental masses (see Gass 1977), and they may represent the result of some degree of overthickening following continental collision and ocean closure. The granitic rocks formed at earlier stages in the cycle are perfectly normal types for a subduction process (Marzouki & Fyfe 1977). The late, typical circular plutonic masses show very high thorium and uranium values but at the same time have anomalous $\delta^{18}O$ values ranging up to $+20‰$. If there had been ocean closure there could also have been generation of evaporites and heavy formation brines.

Such waters interacting with rising plutons could lead to the peralkalinity via the reaction $2NaCl + SiO_2 + H_2O \longrightarrow Na_2SiO_3 + 2HCl$ and might cause late mobilization of elements in either alkaline or HF–HCl enriched vapour phases. Whatever the mechanisms involved in enrichment in this case, one might well expect that granitic rocks formed late in a continental collision process could be rich in uranium. A uranium-rich high level zone of one plate may underthrust an older depleted continental basement. A similar problem is discussed by Simpson *et al.* (1979, this volume).

EROSION OF URANIUM

The general mobility of uranium in oxygenated waters is too well known to require discussion here. Solution in carbonate or biological (protein) complexes is also well established. The uranium content of surface waters is normally around 0.1 part/10^9 but is highly variable (Hawkes & Webb 1962). Deeper ground waters generally have a higher uranium content which may be correlated with more organic carbonate complexing species.

Present water flux off the continents of 3.6×10^{16} kg a^{-1} would carry in solution 3.6×10^6 kg of uranium to the oceans each year. The ocean mass of 1.4×10^{24} kg contains uranium at 1 part/10^9, giving a total ocean reservoir of 1.4×10^{12} kg and a resulting residence time for uranium in the order of half a million years.

Pelagic sediments average 2–3 parts/10^6 and at a sedimentation rate of 1 $km^3\, a^{-1}$ the 2×10^{12} kg of sediment would contain around $4\text{–}6 \times 10^6$ kg of uranium. There seems to be a good overall balance of uranium delivered in solution to that removed by pelagic sediments. The masses involved in this transport process again remind us of the importance of the hydrosphere linkage in the geochemical cycle.

Because of the ease of solution of uranium from grain boundary mineral phases, one might expect that uranium would be greatly depleted in laterites. But our data from heavily leached soils of the Amazon basin (Kronberg *et al.* 1978) show that this is not the case. Uranium varies commonly from 2–5 parts/10^6 and in extreme cases reaches 20 parts/10^6. Uranium : thorium ratios suggest that much of this uranium may be held in highly resistant minerals such as zircon and monazite. Similar observations are reported in Wedepohl (1974).

While there is a great deal of literature dealing with uranium in living organisms, the general biogeochemistry of uranium is not well understood. Recently, Blundell & Jenkins (1977) have reviewed work on heavy-metal – protein complexes with considerable emphasis on uranium complexes. As proteins, polysaccharides, etc., are present in most natural waters at levels around 1 part/10^6, they must be potentially important complexing species for uranium in hydrosphere systems (see Moore & Boström 1977).

While it is beyond the scope of this discussion to deal with the significance of such data, the recent findings of Degens, Khoo & Michaelis (1977) require mention. In their studies of Black Sea sediments, these authors have described extreme uranium enrichment in the upper sediment levels. They describe primary uranium fixation in the protein–polysaccharide complexes of coccoliths leading to a 10000-fold enrichment over the concentration in the waters of the Black Sea. The upper 90 cm of the sediment rich in biological debris contain 6.7×10^9 kg of U_3O_8 over an area of 3×10^5 km^2. The average concentration in the ash of this debris is about 100 parts/10^6. There is no doubt that such a sediment could provide an enormous future reserve of uranium.

The past

The distribution of the heat producing elements during evolution of the Earth is vital to any discussion of the general thermal evolution. At present, models of ancient tectonics and crustal evolution abound, but in a general way two of these illustrate the general features of the present debate. Largely on the basis of observations of lead and strontium isotope data, Moorbath (1977) has developed a model of gradual accumulation of the continental crust in a series of major periods of violent mantle activity. Vital to his argument is the proposition (cf. Gilluly 1971): 'The essential unsubductibility and indestructibility of continental crust, once it is formed. . . . Since the density of continental crust is relatively low, it would be impossible for such material to be pushed down and recycled through the mantle.'

Clearly such a model leads to continual continental growth and continual depletion of the mantle in heat producing elements.

A very different approach is that outlined by Hargraves (1976) who suggests very rapid formation of a globe-encircling sialic layer beneath a globe-encircling hydrosphere. Hargraves suggests a thin 'granitic' shell that has thickened with time, leading eventually to continental emergence. A corollary of this model would be that of rapid depletion of the mantle in heat producing elements.

I do not wish to enter this debate here (see Fyfe 1978). There are observations that can be taken to fit both models, some that are difficult for either. However, a key question in this discussion is the rôle of present and past subduction mechanisms.

I do not think we fully understand the present process and certainly not the past. But there is also no doubt that some crustal species are subducted now (e.g. K and U in spilites) and if sediment subduction is considered we come to a third model, that of rapid formation of continental crust followed by a trend to sediment subduction and fixation in a cooling mantle. It then becomes a short route to see how a widespread Jordan-type (1978) depleted continental tectosphere would become modified as modern ocean floor spreading processes, sedimentation and subduction began to dominate global tectonics. In this case, the U–Th–K content of the mantle would pass through an early minimum and now would be increasing. The reworking of continental crust via the 'erosion ⟶ (sediment + spilite) ⟶ subduction ⟶ andesite' path is a subtle process. If Moorbath is correct, and if for the early Earth only small areas of continental crust were present, there must have been an even greater dominance of ocean floor crust of the modern type. If this is so, where are the residual ophiolite complexes in our preserved sample of the Archaean crust?

It should also be noted that if Hargraves's model has merit, the preservation of ancient high-level crust presents no problem for most would be preserved in a submarine environment. Sediment subduction would only become large-scale as modern-type ocean floor crust was widespread and continental emergence significant.

Concluding remarks

In general, most parts of the present general geochemical cycle of uranium appear to be moderately rational. The greatest unknown, and an area of critical importance, involves the question of sediment subduction of the modern type and its rôle in the past.

As Clark (1979, this volume) has stressed, there appear to be problems with the possible uranium content of the deep Earth. There are also problems with the influence of fluid motions on the significance of heat flow measurements, particularly in the ocean floor environment and perhaps more than we appreciate on the continents as well as indicated by recent studies of O–H isotopes in altered crustal rocks (see, for example, Wenner & Taylor 1976). At the present rate of progress in our science, we should see the resolution of some of these problems in the next decade.

In putting together these remarks I must acknowledge the assistance of Professor R. Kerrich of this university and two of our students from Saudi Arabia, M. Radain and F. Marzouki. Discussions with my former research colleague, Dr G. C. Brown, continue to contribute to my education as do the many stimulating discussions with Dr Stephen Moorbath, F.R.S., who must consider me a most refractory student of isotopes.

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Discussion

G. C. BROWN (*Department of Earth Sciences, The Open University, Milton Keynes MK7 6AA, U.K.*). I should like to thank Professor Fyfe for a fascinating and stimulating lecture: I look forward to digesting the contents of the published paper. However, the concept of progressive uranium transfer from crust to mantle will take some time to digest. Indeed the concept is rather alien to those of us who like to think in terms of crustal growth, together with the extraction of heat-producing elements *from* the mantle, throughout geological history. I appreciate the arguments in favour of geosphere mixing, and the deposition of continental debris in ocean basins necessitates the ultimate marginal accretion or subduction of this material. However, to my knowledge there are few subduction zones at the present day accumulating sediment and I should be interested to know whether the author can suggest where the volume of new continental crust (*ca.* 0.5 km; a^{-1}) is matched by the erosion and subduction of a rather similar volume required to actually enrich the mantle in uranium.

A second point: I think that we are agreed that the new continental crust at destructive margins comprises a consanguineous suite of andesites and granites of upper mantle derivation above a subduction zone. I wonder, therefore, whether the proposed model of tectonic overthrusting is necessary for the production of the highly uraniferous Saudi Arabian Pan-African granites which otherwise have petrochemical and isotopic characters similar to those of modern destructive margins. We know the upper mantle beneath Saudi Arabia also to be uranium enriched (cf. harzburgite nodules with 50–60 parts U/10^6) and I wonder if the upper mantle is not a more plausible source region for these granites. Where granites are indeed the product of crustal overthrusting, as in the Himalayas, we find very mature initial $^{87}Sr/^{86}Sr$ ratios whereas mantle-type ratios characterize the Saudi plutons.

W. S. FYFE. On the first point I would suggest that it is perhaps already answered by Gilluly as mentioned in my manuscript. Further, it is quite clear that present erosion rates of about 10^{13} kg a^{-1} far exceed the andesite–granite creation rate of 1.5×10^{12} kg a^{-1} mentioned by Brown. Where are the required sediments (see Garrels & Lerman 1977)?

On Dr Brown's second point I think there is a little confusion. I am not discussing the major granite–andesite event in Saudi Arabia which is quite normal for any subduction environment like the Andes or Sierra Nevada. These granites are riddled with basic and acid dykes (see Marzouski & Fyfe 1977) showing that the entire magma suite was being produced at the same time. I am mainly concerned with the late peralkaline granites which seem to represent the final magma episode. They are not associated with complex dykes or more basic magmas and appear to be quite unique in their geochemical nature. To my knowledge, we do not know their Sr isotope systematics.