The Distribution and Redistribution of Heat-Producing Elements in the Continents [and Discussion]

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The distribution and redistribution of heat-producing elements in the continents

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Many geological data indicate that most sialic crust is of Archaean ($\geqslant$ 2.5 Ga) age. Evidence also seems to agree for an early formation of a 'protocrust' concentrating the heat-producing elements. On the other hand if present day production of oceanic tholeiites can be assumed to have been constant through geologic time, and if their radioactive element content is gradually added to the continents, one could argue that the formation of continents has taken place at a reasonably constant rate. After presenting the relevant data the author discusses how the two apparently opposed views may be reconciled, and how secondary processes regulate the distribution of heat-producing elements in the continents.

Introduction

It is only the elements K, U and Th which contribute significantly to the heat budget of the Earth through radioactive decay. Concerning the problem as formulated in the title of this paper, there are four fundamental questions to be answered:

(1) What caused the enrichment of the heat-producing elements in the crust, and are these elements uniformly distributed throughout the continents?

(2) Is the enrichment a continuous or an episodic process?

(3) In what type of continental rocks are the radioactive elements concentrated?

(4) To what extent and through which process(es) does redistribution of elements take place within the continents?

Primary introduction of Th, U and K into the continental crust

Plate tectonics theory provides a feasible model for present day continent formation. In this scheme of events the heat-producing elements, which are 'incompatible' elements in mantle mineralogy, are considered to be brought up from the Earth's interior along the mid-oceanic ridges, carried along with the oceanic plate, concentrated in the early melts formed from the subducted slab and because of their incompatibility with early fractionating mineral associations, they are concentrated in residual melts which crystallize into the highest levels of the continental crust. For these elements the process of their concentration in the continents is probably irreversible, although a recycling and separation of the elements certainly takes place in smaller cycles within the crust.

Although this is probably the way in which these elements have been incorporated in crust forming in the relatively younger geological periods, its validity as far back in time as the Archaean may be seriously queried. Further we may question whether the process really is the controlling factor for the concentration of the bulk of the Earth's content of these elements in the continents.

Archaean rocks have become recognized increasingly in all continents and their chemistries have not been observed to be radically different from those of younger eras. Gill & Bridgwater (1976) studied the pre-3100 Ma old Ameralik dykes from West Greenland and showed that they exhibit a range in primary composition from primitive low K, low Ti tholeiites virtually identical in composition to ridge basalts of modern oceanic crust, to more differentiated rocks similar to some present-day continental tholeiites. Goodwin (1976) pointed out that available Precambrian data indicate that most sialic crust is of Archaean (> 2.5 Ga) age.

The question of an early formation of a crust, or protocrust, with an upward concentration of the volatile and lithophile elements in the Earth, is probably closely linked to the problem of core formation. It appears that present opinion favours a relatively short time interval of the order of 10^8 a between accretion of the Earth and formation of the core (see, for example, Oversby & Ringwood 1971; Murthy 1976; Shaw 1976). Because of the large mass of the Earth's core relative to that of the planet as a whole, the process of core formation should have resulted in a global differentiation, and presumably in the formation of a protocrust on the Earth (Murthy 1976). This was already recognized by Patterson (1956) from considerations of the evolution of Pb isotopes in the Earth and later expanded on by Shimazu (1965) and Ringwood (1960). Murthy (1976) uses further evidence to argue that the protocrustal material formed under these conditions will nearly resemble the then mantle compositions for the major oxides MgO, FeO, SiO_2. The strongly incompatible elements such as Ba, U, Th, r.e.e., etc., will be only moderately enriched. For example, if the overall behaviour of these elements can be generalized by a distribution coefficient range of $D^{l/s} = 50\text{–}100$, then the liquid produced in large scale partial melting of the mantle, say 40–50 %, will only show incompatible element enrichment to twice or three times that of the original source.

In his model, Murthy operates with two stages of primitive crust formation. The first stage, which is associated with core formation yields a crust of mafic to ultramafic composition which shows about 2–3 times enrichment for the incompatible lithophile trace elements and a strong depletion of the alkali elements. A basis for the assumption is that the core contains FeS simply because of the dominance of Mg, Fe, Si and O in the Earth and the large thermal energy release during core formation that must result in a global differentiation. The second stage begins with the accretion of Ca, Al and refractory lithophile-enriched material and some Fe–Ni planetesimals. According to Murthy this process will result in the outer regions of the Earth being enriched in siderophile and refractory lithophile elements such as Ca, Al, Ba, U, r.e.e. and others, and further 'subsequent magmatism in these regions will generate melts that are grossly different in their trace element characteristics and to some extent in the major oxides, particularly CaO and Al_2O_3.'

Shaw (1976) concluded that 'gravitational energy of accretion and core separation must have produced near total melting of the outer Earth, in order to (*a*) expel most of the primordial rare gasses, (*b*) transfer U, Th, r.e.e. from early condensates to the surface zone.'

The evidence quoted so far thus all seems to point to an early formation of a 'protocrust' concentrating the elements which we are discussing here. This, of course, is not synonymous with a concentration in what we today recognize as a 'continental crust'. Furthermore, potassium may exhibit a different concentration pattern compared with that of the two other heat producing elements, U and Th. The discovery by Fuchs (1966) of the mineral 'djerfisherite' with the formula K_2 (Na, Cu) (Fe, Ni)$_{12}$ S_{14} in two enstatite chondrites and an enstatite achondrite has prompted renewed interest in the possibility of considerable amounts of the

Earth's potassium being contained in the core (see later). It is possible that the chalcophilic properties of K (and presumably Rb as well) become significant under high pressure, reducing conditions such as may have existed in the primitive mantle of the Earth, and that rather than having been lost by volatilization, these elements are present in appreciable amounts in the lower mantle, and perhaps in the core. This, of course, would provide an explanation for the apparent difference in the K/U ratios in meteorites and in the Earth. Based mainly on Sr-isotopic evidence originally presented by Faure & Hurley (1963), a number of authors have argued for a continuous accretion of the continents through geological time. To my knowledge the latest discussion of this topic is given by Jahn & Nyquist (1976). They state that 'most of the old crustal segments on the Earth have an imprint of a world-wide thermal event about 2.7 b.y. ago' and 'the crustal evolution on the Earth probably involved extensive recycling processes in the crust–upper mantle system and transport of crustal material from the lower to the upper mantle'.

The Sr-isotope geochemists seem to agree that the available data on crystal–liquid distribution coefficients of Rb and Sr during partial melting favours accumulation of crustal material by partial melting of mantle materials and by subsequent differentiation processes. Initial Sr isotopic ratios in magmatic rocks of different ages have frequently been taken as evidence for a continuous formation of the continental crust. Fig. 1 of Jahn & Nyquist (1976) indicates, however, that the evolutionary paths may follow a number of different patterns. Present day oceanic tholeiites are reported to contain U, Th and K in the ranges 0.18/10^6 Th, 0.10/10^6 U and 0.17 % K (Rogers & Adams 1969). Present day production of oceanic tholeiites along the mid-oceanic ridges is estimated as 8.3 $\mathrm{km^3\,a^{-1}}$ (or 24.9×10^9 t), (relative density = 3) based on an average spreading rate of 2.6 cm $\mathrm{a^{-1}}$, a total length of the median ridges of 64000 km and oceanic crustal thickness of about 5 km (Shaw 1976). If all the Th, U and K originally present in this material is ultimately concentrated in the continents, the maximum average annual input of these elements into the crust is approximately 4.5×10^3 t Th, 2.5×10^3 t U and 4.1×10^7 t K. The continental surface is 14.7×10^7 $\mathrm{km^2}$ (29.3 % of the total surface of the Earth). Of this, 10.5×10^7 $\mathrm{km^2}$ (71.4 %) is covered by old shields and 4.2×10^7 $\mathrm{km^2}$ (28.6 %) by regions of young folded mountains (Wedepohl 1971). If we assume an average density of 2.8 t $\mathrm{m^{-3}}$ and thickness of 40 km the mass of the continents is approximately 1.6×10^{19} t. Adopting a set of assumptions, Lambert & Heier (1968) argued for a concentration in the Archaean shield crust of 4.5/10^6 Th, 0.7 (or 1.1)/10^6 U and 1.5 % K, and for a Palaeozoic crust (possibly comparable to Wedepohl's 'regions of young folded mountains') with 7/10^6 Th, 1.3 (or 1.7)/10^6 U and 1.7 % K. All of these estimates are, of course, conjectural and open to criticism. Nevertheless the order of magnitude is most probably correct. Using the data available (taking the lowest U content in both cases), the average concentration (shield and young crust) will be 5.2/10^6 Th, 0.9/10^6 U and 1.6 % K. This corresponds to 8.3×10^{13} t Th, 1.4×10^{13} t U and 2.6×10^{17} t K. Assuming that the present-day maximum annual input of these elements into the crust as indicated above (based on production of oceanic tholeiites) has been constant over the entire Earth history of 4.5×10^9 a, this would have produced a crust containing 2.0×10^{13} t Th, 1.1×10^{13} t U and 1.8×10^{17} t K.

In spite of the admittedly large number of uncertainties on which all of the above assumptions and calculations are based, one cannot help being struck by the similarities between the present-day maximum oceanic tholeiite radioactive element contribution to the crust, taken over the whole age span of the Earth, and the total contents of these elements in the continental crust. In spite of the reservations made at the beginning of this paper the one reasonable conclusion which can be made from this would be that the formation of continents has taken place at a reasonably constant rate throughout the history of the Earth. Allowing for the formation of a protocrust in the first thousand million years or so of Earth history, with possibly more of a resemblance to the upper mantle in chemical composition than to present day oceanic and continental crust, a slight, but in view of the uncertainties involved possibly insignificant, decrease in upward flux of these elements with time might be deduced.

The distribution of the radioactive elements in the continents

As originally demonstrated by Lambert & Heier (1968) and Roy, Blackwell & Birch (1968), and later confirmed by a number of authors, the heat-producing elements must be contained in a fairly thin upper portion of the continental crust. Lambert & Heier based their calculations on an empirical model combining estimates of surface concentration of Th, U and K with heat-flow measurements and an assumed petrological zoning, or layering of the crust. On this basis they found that most of the heat-producing elements in the Australian shield crust were concentrated in the uppermost 4.5 km. Exactly the same value was given by Jaeger (1970) using the approach outlined by Roy *et al.* (1968). Lambert & Heier indicated a thicker top layer of younger continental crust (Palaeozoic).

The method of Roy *et al.* was to use an empirical relation between heat flow Q and heat production A, in different heat flow provinces, of the form $Q = a+bA$. This is solved graphically; a represents heat flow from the mantle and lower crust (Q_0) and b (the slope of the line) is the distance from surface to depth for which radioactivity measured at the surface is constant. The thickest upper crust (10.1 km) was indicated for the geologically young area of Sierra Nevada. The Basin and Range Province, which contains rocks ranging in age from Precambrian to Tertiary, but which is assumed to be a young heat flow province, indicates an upper crust of 9.4 km. The Eastern U.S. (Palaeozoic) gave the lowest value of 7.2 km for the upper crust.

It is interesting that the very old Australian shield has the minimum thickness for the upper crust while the maximum thickness is found in geologically young areas or young heat flow provinces.

From the available evidence presented so far we may not only conclude that most of the Earth's radioactivity is concentrated in the continents but also that repeated recycling of crustal material is gradually concentrating these elements in the uppermost layers.

The redistribution of Th, U and K in the continents

It is clearly established that a strong correlation between the three elements exists in primary magmatic differentiation series (Heier & Rogers 1963). The concentration of all three elements increases with increasing differentiation, and there is also a tendency towards an increase in Th:K, U:K and Th:U ratios with differentiation, as well as a greater spread in their values.

The average Th:U ratio of stony meteorites is between 3 and 4. This has long been presumed to be the fundamental ratio for the solar system. This has been substantiated by the more recent studies of lunar samples. Calculations of the age of the Earth based on lead isotope data are generally based on the assumption of a primordial Th:U ratio of 3.5. Primitive tholeiitic basalts frequently exhibit lower Th:U ratios while granitic rocks are typically characterized by higher ratios. In some cases the ratios may be extremely high. It suffices to mention the international rock standards GSP-1 and G-1. Low Th:U ratios in granites are also observed but seem to be restricted to special types of granites (Heier & Brooks 1966). K:U ratios of crustal and upper mantle material seem to average around 10^4 (Heier & Rogers 1963; Wasserburg, MacDonald, Hoyle & Fowler 1964). The fractionation of the three elements and the scatter of their ratios in granites is interesting for a discussion of the problem of their redistribution in the continental crust. Granites may form in at least two ways: (i) by differentiation of a primitive mafic magma and (ii) directly by partial melting of pre-existing crustal rocks. In both cases the effect of a vapour phase must be considered and fractionation of Th and U is generally ascribed to the tendency for uranium to be oxidized to the comparatively soluable uranyl ion.

However, in order to understand the redistribution of Th, U and K and their fractionation in the continents it is necessary to understand their behaviour during processes of weathering and rock alteration.

Behaviour during weathering and rock alteration

Summaries with references have been given by Rogers & Adams (1969) for Th and U, and by Heier & Billings (1970) for K. Just a few comments will suffice for the purpose of this paper.

The above mentioned tendency for uranium to be oxidized to the uranyl ion permits it to be relatively easily mobilized in surficial alteration processes. This is assumed to be the primary reason for the wide variation in Th:U ratios observed in surficial material. The redistribution of uranium takes place through the action of surface water and ground water, and the element may be fixed to surface rocks by adsorption on mineral surfaces. It is interesting to note that both the average thorium and uranium contents of ordinary shales are very close to the values commonly cited for the average concentration in the continental crust. Black shales characteristically have a high uranium concentration and comparatively low Th content. Two reasons may account for the concentration of uranium in black shales: (i) adsorption of uranium by organic material, or (ii) reduction of the uranyl ion in sea water to the less soluble uranous form by the decay of organic matter and consequent precipitation of uranium oxide. Some black shale formations are economically important uranium deposits today, for instance that at Ranstad in Sweden.

Interesting information about the geochemistry of uranium may be gained by considering its most important types of ore deposits. According to Bowie (1975), well over 60 % of the uranium reserves valued at over $7/kg U_3O_8 occur in sandstones and conglomerates with the bulk of these occurring either in Precambrian rocks or in sediments immediately overlying a Precambrian basement, as in the case of the Colorado–Wyoming province in the U.S. and the Rum Jungle area in Australia. Adamek & Wilson (1975), demonstrated pitchblende mineralization associated with soda-metasomatism in Precambrian rocks (1940–1850 Ma) from Sweden. The same mode of occurrence is known in north Norway. In the United States most of the uranium production is from mineralized sandstones in the Colorado Plateau province. Canada has large reserves in the Blind River conglomerate, although most of its production comes from vein deposits in the Northwest Territories. Likewise, South African production is almost exclusively a byproduct of gold mining in the Witwatersrand area, where pitchblende mineralization has apparently accompanied gold deposition. The largest reserves are disseminated in sediments, usually sandstones. The Rum Jungle deposit in Australia is in low grade metasediments including arkoses and conglomerates derived from the surrounding granitic rocks. The majority of smaller deposits are pitchblende veins such as those of Great Bear Lake, Canada; Erzgebirge, Germany and Czechoslovakia; Katanga, Congo; and Portugal (Rogers & Adams 1969).

In conclusion, all of the available information about the geochemistry of uranium in igneous and surficial processes indicate its concentration in the very highest levels of the continental crust. Once brought to the surface, its geochemical cycling takes place at very shallow depths.

While the behaviour of thorium in magmatic processes is similar to that of uranium, its behaviour during rock alteration, weathering and sedimentation is very different. Thorium becomes concentrated in residual material such as soil and weathered rock. High thorium concentrations in bauxites were reported by Adams & Richardson (1960), while residual accumulations in clays have been noted by Adams & Weaver (1958). Pliler & Adams (1962) demonstrated the retention of thorium during weathering and alteration in a weathering profile in the Flagstaff Mountain granite, Colorado. The concentration of thorium minerals in beach sands is another example.

The relative immobility of thorium could indicate that (*a*) it is primarily contained in granites crystallizing at moderate depths in the crust, and that (*b*) the element is readily taken down in subducted crustal slabs whereupon it again becomes concentrated in anatectically derived granite magmas. Both processes would explain the high Th:U ratios frequently observed in granites. One would also expect that anatectically recycled granites would tend to show the maximum Th:U ratios. Whether the available data on initial Sr isotope ratios substantiate this or not is not known, but the hypothesis could certainly be tested. It follows from the above that the maximum concentration level of thorium in the crust extends to somewhat deeper levels than that of uranium.

The geochemistry of K is fairly well known and any detailed discussion here would be superfluous. Its concentration in granitic rocks would naturally lead to its upward concentration in the continents.

The discovery of the potassium sulphide 'djerfisherite' mentioned on p. 394 has led to some discussion about a possible concentration of K in the core. A concentration of potassium in the core could give an alternative explanation to the volatilization model of the different K:U ratios in the Earth and in meteorites. Arguments for a considerable concentration of potassium in the core and some geophysical and geochemical consequences have been given by Murthy & Hall (1970), Lewis (1971) and Goettel & Lewis (1973). On the other hand, Oversby & Ringwood (1972, 1973) argue from data on the distribution of potassium in meteorites, and experimental work on potassium distribution between silicate and metal sulphide phases, that the amount of potassium in the core is limited to between 1 and 2 % of the Earth's total potassium. Though the answer to the problem is of great geophysical and geochemical significance it hardly affects the topic of the paper and a further discussion will not be pursued.

PROVINCES WITH HIGH Th AND U CONTENTS

The problem of high-value thorium and uranium provinces has been discussed by Rogers & Adams (1969). There is some evidence for the view that high thorium and uranium concentrations within certain areas are characteristic of igneous rocks formed over considerable periods of time. This, as well as a possible relation between age and Th:U ratios, is a problem that requires further investigation. However, Dahlkamp (1975) demonstrated how statistical studies reveal that certain types of uranium deposits and uranium source rocks prevail in certain geological periods, especially in the Upper Archaean–Lower Proterozoic and Hercynian, and that numerous uranium deposits in sediments and metasediments show a distinct affinity to the uranium-rich source rocks, irrespective of age.

CONCLUSIONS

Present day production of oceanic tholeiites, if this has been constant throughout geological time, could account for all of the thorium, uranium and potassium in a continental crust formed through continuous growth at a constant rate. While this is in agreement with interpretation of the isotopic evidence, it is contrary to more recent geological observations which appear to indicate that most sialic crust is of Archaean (> 2.5 Ga) age.

Heat flow data combined with determinations of surface radioactivity indicate an upward concentration of radioactive elements in the continental crust.

The upward concentration of these elements appears to become more pronounced with the age of the crust.

Th, U and K constitute a set of geochemically very coherent elements during magmatic fractionation.

In general, the more fractionated rocks have the highest Th:U, Th:K and U:K ratios as well as the largest scatter in the ratios.

The geochemistries of Th, U and K in melting processes, crystallizing melts and surficial processes indicate that (*a*) uranium is most strongly concentrated in the very highest crustal levels and undergoes very shallow, later cycling; and (*b*) thorium and potassium may show secondary cycles extending down to the zone of anatexis.

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Discussion

G. C. Brown (*Department of Geophysics, Liverpool University*). All reasonable calculations of modern crustal accretion rates suggest the modern rate is $\frac{1}{2}$ to $\frac{1}{10}$ of the time-average over the Earth's history. So I find it interesting that the speaker suggests a constant rate of evolution. We must bear in mind that not all the K, U and Th will be efficiently partitioned into melts which reach the crust and some will be subducted. Surely it would be more consistent with both the Earth's thermal decay and Professor Heier's geochemical arguments if the modern crustal accretion rate is somewhere between $\frac{1}{2}$ and $\frac{1}{10}$ of the average.