

Reports

Relative Contributions of Uranium, Thorium, and Potassium to Heat Production in the Earth

Abstract. *Data from a wide variety of igneous rock types show that the ratio of potassium to uranium is approximately 1×10^4 . This suggests that the value of $K/U \approx 1 \times 10^4$ is characteristic of terrestrial materials and is distinct from the value of 8×10^4 found in chondrites. In a model earth with $K/U \approx 10^4$, uranium and thorium are the dominant sources of radioactive heat at the present time. This will permit the average terrestrial concentrations of uranium and thorium to be 2 to 4.7 times higher than that observed in chondrites. The resulting models of the terrestrial heat production will be considerably different from those for chondritic heat production because of the longer half-life of U^{238} and Th^{232} compared with K^{40} .*

Recently, in considering the production of uranium and thorium during nucleosynthesis, Hoyle and Fowler (1) calculated that the abundances of uranium and thorium relative to silicon for solar-system material is about four times that which is found in chondritic meteorites. They pointed out that, if the earth contained such an enrichment in these elements and had the K/Si ratio of chondrites, the resulting heat production would far exceed that permitted by geophysical considerations. The purpose of this report is to examine the general consequences of an earth model with uranium and thorium concentrations that are higher than the values for chondritic meteorites.

It was first pointed out by Urey (2) that the present surface heat flow of the earth is approximately equal to the heat which would be produced in the interior if the earth had a chondritic composition. In addition, he pointed out that if the moon and Mars had similar compositions, no gross difficulties would obtain with regard to the temperatures of these objects. Birch (3) also noted the coincidence of the heat flow from the earth with the present heat generation in a chondritic earth model. In addition, Birch pointed out that this chondritic model would require almost all of the uranium to be concentrated in the continental crust while 80 percent of the potassium would remain buried below the continental crust.

The "chondritic coincidence" has been used as evidence in support of

the chondritic model for the earth. Clearly other concentrations of the radioactive elements could also account for terrestrial heat flow.

The assumption of a chondritic earth model has been made in a number of theoretical treatments. However, Gast (4) has questioned the applicability of this model on the basis that the observed crustal concentrations of potassium, rubidium, and cesium are anomalous when compared with uranium, strontium, and barium. Gast further showed that the observed isotopic abundances of Sr^{87} in crustal and presumed upper mantle material are inconsistent with the chondritic model. Possible explanations that are discussed by Gast include a loss of the alkali metals by the earth because of volatilization from material of chondritic composition, or a marked differentiation of the earth in which rubidium, potassium, and cesium remain buried in the lower mantle. The volatilization mechanism would require that initial heat compensate for the energy which was supplied by K^{40} in the chondritic model. The differentiation mechanism differs from that observed in crustal rocks and presumably would be due to the effects of high pressures on the chemical behavior of the alkalis.

The observed concentrations of uranium, thorium, and potassium in terrestrial materials range widely; however, the ratios of potassium to uranium and of thorium to uranium in a great variety of rock types exhibit

rather constant values (see Table 1). Within magmatic differentiation series in which the bulk chemical composition changes, the ratio of potassium to uranium remains relatively constant. Studies by Adams (5) on a series of volcanic rocks from the Lassen volcanic area show a remarkable constancy of the K/U ratio. Heier and Rogers (6) studied the K/U ratio in the various differentiates of the Duluth lopolith. These rocks ranged from anorthosites and gabbros to granophyres, but show a total range in the K/U ratio of from 0.5×10^4 to 4×10^4 , with only 1 sample in 22 having a ratio greater than 2×10^4 . The results of Heier and Rogers (6), Rogers and Ragland (7), and Witfield, Rogers, and Adams (8) on the rocks of the Southern California Batholith also show remarkable constancy in the K/U ratio, at about 10^4 , for rocks ranging from hornblende pyroxene gabbros to granites.

In addition to these studies of differentiation series, there are numerous analyses of various rock types. A number of results are reported by Nockolds (9), Senftle and Keevil (10), and Evans and Goodman (11). In a summary of the results on 755 granites, Heier and Rogers (6) report a mean K/U ratio of 0.77×10^4 . Of these samples only 7 percent had ratios greater than 2×10^4 . They also report a ratio of 1.7×10^4 for basalts. Tilton and Reed (12) and Heier (13) have analyzed eclogites from igneous and metamorphic environments. They did not find any samples with a K/U ratio greater than 2.5×10^4 and the average ratio calculated from their results is 1.0×10^4 . The only reliable measurements of uranium in ultramafic rock are those reported by Tilton and Reed (12). However, the uranium was undetectable on the one sample for which the potassium was measured. The result gives $K/U > 3 \times 10^4$. It is obvious that more measurements of the uranium, thorium, and potassium content of ultramafic rocks are necessary. Tilton and Reed (12) discuss possible mantle materials and note that the K/U ratio of eclogites is considerably different from that found in chondrites. These workers emphasized that the data on Hawaiian eclogites are a better guide to the composition of the upper mantle than the results on chondritic meteorites, and that the resulting heat production in eclogites would be more uniform over geologic time.

Tabulated values of the average

Table 1. Potassium, uranium, and thorium abundances and ratios in meteorites and terrestrial materials.

Source	Potassium (ppm)	Uranium (ppm)	Thorium (ppm)	10^4 K/U
Chondrites (14, 21, 22)*	845 [50] †	0.0127 [17] .011 [4]	0.0398 [8]	6.7 7.7
Achondrites (14, 21)				
High calcium	430 [5]	.081 [3]	.51 [5]	0.5
Low calcium	9 [1]	.0021	.0059 [1]	.4
Granites (6)	37,900 [755]	4.75 [755]	18.5 [755]	.8
Basalts (6)	8,400 [24]	0.6 [24]	2.7 [24]	1.4
Eclogites				
Low uranium (12, 23)	360 [2]	.048 [7]	.18 [6]	0.8
High uranium (13, 23)	2,600 [10]	.25 [12]	.45 [12]	1.2

* Numbers in parentheses indicate the reference. † Numbers in brackets indicate the number of samples used to compute the average.

potassium, uranium, and thorium content of chondrites, achondrites, and terrestrial rocks are shown in Table 1. The K/U ratio for terrestrial rocks is relatively constant for samples ranging in uranium concentration from 0.048 to 4.75 parts per million. The results on chondrites and achondrites represent the majority of published results. The uranium data is somewhat variable in quality and many replicate analyses show considerable spread so that the average is uncertain to about 20 percent. The average value of 0.011 parts per million on four samples by Hamaguchi, Reed, and Turkevich (14) is probably to be preferred. Some few results on the K/U ratio of achondrites show marked similarity to the terrestrial value. The average Th/U ratio is not tabulated since there are, unfortunately, only a few determinations of this relation in meteorites. More precise determinations of both thorium and uranium on the same sample are needed.

The ratio of radiogenic helium to radiogenic argon in natural gases provides another line of indirect evidence regarding the relative abundance of potassium, uranium, and thorium. Studies of natural gas accumulations, volcanic gases, and occluded gases in such minerals as beryl show that they exhibit a total range of values of the ratio of radiogenic He^4 to Ar^{40} from 0.5 to 213. Most of the samples have values between 6 and 25, and the most frequent ratio is about 10 (15). These investigations showed that the radiogenic $\text{He}^4/\text{Ar}^{40}$ ratios are in general compatible with present production rates in terrestrial igneous rocks, and that these rocks have a rather constant K/U ratio which is distinct from chondrites. Of the 100 samples reported, only one sample had values for radiogenic

$\text{He}^4/\text{Ar}^{40}$ that were compatible with the present production rates of chondrites. There was only one sample which had a ratio as low as that produced by chondrites when integrated over the past 3 aeons (3×10^9 yr).

The relative constancy of the K/U ratio obtained in a wide variety of chemically distinct igneous rocks, in magmatic differentiation series, and inferred from the composition of natural gases strongly suggests that surface materials provide a good estimate for the K/U ratio of the earth, and indicates that this value is distinctly lower than that for chondrites. This conclusion must be tempered by the fact that only crustal and possibly upper mantle materials have been sampled. In addition, there is no adequate explanation for the association of potassium with uranium and thorium and consequently the extrapolation of observations on crustal materials to depth has no theoretical basis. However, we conclude that there is ample justification for examining a terrestrial heat budget based on $\text{K/U} = 10^4$ g/g. In this discussion we will assume a Th/U ratio of 3.7. We wish to compare the above model with a chondritic model in which the concentrations are as follows: potassium = 8.45×10^{-4} g/g, uranium = 1.1×10^{-8} g/g, and thorium = 4.07×10^{-8} g/g. The concentrations chosen for uranium and thorium are somewhat arbitrary since these data are still not known with great certainty.

At present the average heat flow is 63.9 ergs/cm² sec (16). The rate of heat production per gram of chondritic material is 5.17×10^{-8} ergs/gm sec. If the earth's mantle and crust have the chondritic concentrations and there are no radioactive elements in the core, the present rate of heat pro-

duction per square centimeter of earth's surface is 41.6 ergs/cm² sec. If the total earth has chondritic concentrations, the production rate per square centimeter of earth's surface is 60.7 ergs/cm² sec (17). The first-mentioned model appears preferable on the grounds that an iron-nickel core would be free of potassium, uranium, and thorium (18). MacDonald (19) has studied the case where the total earth has the chondritic concentrations. His results do not indicate any serious difficulty with this higher heat production. However, such a rate does not permit the contribution of much initial heat to the present surface losses, and it would also indicate essentially no lag between production and loss even with the increase in the estimate of the average heat flow (16).

For rocks with terrestrial K/U ratio of 10^4 and the same present heat production as chondrites, the following concentrations are required: potassium = 2.255×10^{-4} g/g, uranium = 2.255×10^{-8} g/g, and thorium = 8.344×10^{-8} g/g. If the earth as a whole has the heat production of chondrites and if the radioactive elements are eliminated from the core and put into the mantle and crust, this would give an increase in the concentrations by a factor of 1.46 giving a uranium value of 3.29×10^{-8} g/g. Such concentrations of uranium, thorium, and potassium are not grossly incompatible with our knowledge of the terrestrial elemental abundances. Assuming that the mass of the crust is 2.4×10^{25} g and that the crustal abundances of potassium and uranium are 1.9 percent and 1.9 parts per million, respectively, we find that 33.8 percent of both the potassium and uranium are in the crust, compared to an earth model of chondritic composition which gives 9.0 percent of potassium and 69 percent of uranium in the crust. If only the mantle plus crust have the chondritic values this gives 13 percent of potassium and 100 percent of uranium in the crust.

If we consider an earth model with the potassium, uranium, and thorium concentrations of chondrites, then the average concentration of uranium in the mantle and crust will be 1.6×10^{-8} g/g. We assume that the radioactive elements do not remain in the core and are concentrated in the outer layers of the earth. As mentioned earlier, this amount of radioactive elements has a present rate of heat production equal to the heat flow. For a similar model with the same rate of heat pro-

duction, but with a terrestrial K/U ratio this corresponds to a uranium concentration of 3.3×10^{-8} g/g. If the integrated heat production for a chondritic earth is a limit in earth heat balance models, then a mantle and crust with a uranium concentration of 5.2×10^{-8} g/g and a terrestrial K/U ratio is permissible. This range in uranium concentration of from 3.3×10^{-8} g/g to 5.2×10^{-8} g/g is consistent with the values estimated by Hoyle and Fowler (1) for solar system nucleosynthetic material. This agreement of course cannot be taken as direct evidence that the earth is composed of unfractionated solar system material.

The relative contribution of K^{40} to the heat production is drastically different for chondritic material and for material with a terrestrial K/U ratio. At present, K^{40} produces 59 percent of the heat generated in chondrites while for material with the terrestrial K/U ratio, K^{40} produces only 15.8 percent of the heat. A material having a uranium concentration of 2.255×10^{-8} g/g and a terrestrial K/U ratio of 10^4 would have the same present production rate as chondrites, but over the past 4.5 aeons would produce only 63 percent as much heat as chondrites. This lower heat production is due to the relatively short half-life of K^{40} (1.3 aeons) as compared with the longer half-lives of U^{238} (4.5 aeons) and Th^{232} (13.7 aeons). The fundamental difference between models in which potassium is the principal heat source and ones in which uranium plus thorium dominate is that in the former case the potassium releases almost all its energy in the first 2 aeons (20). This early release of heat provides a longer time scale for escape, whereas in uranium- and thorium-dominated models, the heat production is distributed more uniformly over earth history. The ratio of the rates of heat production 4.5 aeons ago to the present rate for chondrites is 8.2, while for the terrestrial model the ratio is 4.5. In the past 3 aeons the production rates for the terrestrial ratio model have changed only by a factor of 2.2. Because of the more uniform heat production, the terrestrial ratio model may require early differentiation so that the heat sources are near the earth's surface (outer few hundred kilometers) during most of earth history. Such a near surface concentration of heat sources would permit a close approach to matching the rate of heat production with loss; this circumstance is of course not permitted

in a chondritic model where the largest part of the potassium is buried in the lower mantle, unless, of course, the conductivity is extremely high.

The detailed development of the model for the terrestrial ratio requires a consideration of the differentiation of the earth, the mechanism of heat transport, and the conditions prevailing during the early stages of development of the earth. Preliminary calculations have been carried out by MacDonald and will be published elsewhere.

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References and Notes

1. F. Hoyle and W. A. Fowler, in *Isotopic and Cosmic Chemistry*, H. Craig, S. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1963).
2. H. C. Urey, *Proc. Natl. Acad. Sci. U.S.A.* **42**, 889 (1956).
3. F. Birch, *Bull. Geol. Soc. Am.* **60**, 483 (1958).
4. P. W. Gast, *J. Geophys. Res.* **65**, 1287 (1960).
5. J. A. S. Adams, *Nuclear Geology*, H. Faul, Ed. (Wiley, New York, 1954).
6. S. Heier and J. J. Rogers, *Geochim. Cosmochim. Acta* **27**, 137 (1963).
7. J. J. Rogers and P. C. Ragland, *ibid.* **25**, 99 (1961).
8. J. M. Whitfield, J. J. Rogers, J. A. S. Adams, *ibid.* **17**, 248 (1959).
9. S. R. Nockolds, *Bull. Geol. Soc. Am.* **65**, 1007 (1954).
10. F. E. Senftle and N. B. Keevil, *Trans. Am. Geophys. Union* **28**, 732 (1947).
11. R. D. Evans and C. Goodman, *Bull. Geol. Soc. Am.* **52**, 459 (1941).
12. G. R. Tilton and G. W. Reed, in *Earth Science and Meteoritics*, J. Geiss and E. D. Goldberg, Eds. (Interscience, New York, 1963).
13. S. Heier, *Geochim. Cosmochim. Acta* **27**, 849 (1963).
14. H. Hamaguchi, G. W. Reed, A. Turkevich, *ibid.* **12**, 337 (1957).
15. P. E. Damon and J. L. Kulp, *Am. Mineralogist* **43**, 433 (1958); R. E. Zartman, G. J. Wasserburg, J. H. Reynolds, *J. Geophys. Res.* **66**, 277 (1961); G. J. Wasserburg, E. Mazor, R. E. Zartman, in *Earth Sciences and Meteoritics*, J. Geiss and E. D. Goldberg, Eds. (Interscience, New York, 1963).
16. W. H. K. Lee and G. J. F. MacDonald, *J. Geophys. Res.*, in press.
17. The chondritic values used in this calculation should on this basis be increased by a factor of about 1.16 to account for the metallic iron present in these objects; however, the uncertainty in the uranium and thorium contents does not at present warrant such a refinement.
18. H. C. Urey, *Proc. Natl. Acad. Sci. U.S.A.* **41**, 127 (1955); ———, *Nature* **175**, 321 (1955); G. W. Reed and A. Turkevich, *ibid.* **176**, 794 (1955).
19. G. J. F. MacDonald, *J. Geophys. Res.* **64**, 1967 (1959).
20. If the age of the earth were increased by 1 aeon (10^9 yr), the integrated heat production would be increased by about a factor of 1.7 in both models. In the case of heat production dominated by uranium and thorium, the heat production of U^{238} becomes very important in periods before 4.5 aeons ago.
21. G. L. Bate, J. R. Huizenga, H. A. Potratz, *Geochim. Cosmochim. Acta* **16**, 88 (1959); G. W. Reed, K. Kigoshi, A. Turkevich, *ibid.* **20**, 122 (1960); M. W. Rowe, M. A. Van Dilla, E. C. Anderson, *ibid.* **27**, 983 (1963); T. Kirsten, D. Krankowsky, J. Zahring, *ibid.* **27**, 13 (1963); H. Konig and H. Wanke, *Z. Naturforsch.* **14a**, 866 (1959).
22. G. G. Goles and E. Anders, *Geochim. Cosmochim. Acta* **26**, 723 (1962).
23. J. F. Lovering and J. W. Morgan, *Nature* **197**, 138 (1963).
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Negative Temperature Coefficient of Resistance in Bismuth I

Abstract. Measurements of the electrical resistance have been made on bismuth I between 15 and 35 kilobars at temperatures between 77.4° and 120°K. Above about 150°K, the temperature coefficient of resistance is positive, as in a metal; below 150°K, the coefficient becomes negative, as is characteristic of semiconductors. On the basis that bismuth is a semiconductor, the energy gap, calculated by the exponential resistance formula, is 0.006 ev at 15 kb with a steady rise to 0.018 ev at 35 kb. At higher pressures, bismuth I is transformed into a metallic modification with the normal temperature dependence of the resistance. The energy gap in bismuth I is not visible at room temperature because thermal excitation populates the conduction band and metallic behavior is the result. From available evidence the observed behavior is due to an energy gap rather than to a decrease in carrier mobility.

Bismuth I, the form found under normal conditions, has long been considered a semi-metal. The resistivity, 123.2×10^{-6} ohm-cm (1), is very high for a metal. From a study of bismuth-III alloys, Jones (2) suggested that all five of bismuth's valence electrons lie in a single energy zone (valence band).

A slight overlap into a higher zone (conduction band) gives the metallic conduction found in pure bismuth. Since Jones introduced this hypothesis, many experiments—the deHaas-van Alphen effect, cyclotron resonance, galvanometric effects, and the anomalous skin effect (3)—have verified the