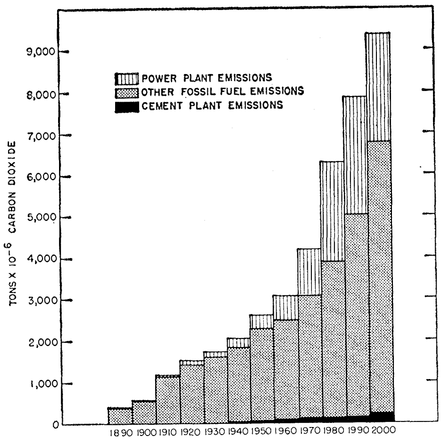

Fig. 1. Carbon dioxide emissions from power plant and other industrial operations.

Carbon dioxide emissions from industrial sources should project to approximately eighteenfold from 1890 to 2000. The greatest average increases in rates of carbon dioxide emissions will be about 4 percent per year and will occur between 1965 and 1985. This is the period when increased demands on fossil fuels for power generation will be the greatest and when nuclear power generation will be proved.

In the absence of more precise and definitive data from other countries one can only speculate on the increases in worldwide emission rate of carbon dioxide. It seems reasonable that emission rates in many other presently industrialized areas will be similar to those in the United States, and that in a large share of the world, particularly the underdeveloped regions, emissions will increase at even greater rates because these regions possess the latent urge and potential for greater industrialization and progress.

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6 February 1967; 3 April 1967

Ionium Dating of Igneous Rocks

Abstract. *Local fractionation of uranium and thorium, between minerals within a sample of igneous rock at the time of crystallization, makes it possible to date its solidification by use of ionium and uranium. Results on samples of granite, pumice, and lava suggest that this method of dating is reliable.*

Much chronological information on Quaternary events has derived from use, in dating, of the radioactive disequilibrium between ionium and uranium in pelagic sediments (*1*) and marine biologic carbonates (*2*). From carbonates, ionium was essentially excluded at the time of formation, and the observed approach to equilibrium makes it possible to date the time of formation. I now extend the application of ionium dating to igneous rocks, which almost always have had amounts of ionium in equilibrium with uranium since the time of their solidification.

In a rock that is not very old in comparison with the half-life of ionium, some of the ionium has been contained since the time of solidification; the remainder has grown *in situ* from U^{234} after the solidification. The ratio of these two amounts of ionium from different genetic origins varies in each mineral according to its uranium and thorium contents. The amount of accumulated ionium must be proportional to the amount of U^{234} or Th^{234} in each mineral, and the amount of original ionium that has survived since the time of solidification must be proportional to the amount of Th^{232}. With this expected regularity in the distribution of thorium isotopes in different parts or minerals of an igneous rock, we can determine the amounts of the two kinds of ionium, from which we can date solidification of the rock.

If thorium isotopes are completely mixed in a rock at the time it crystallizes, and if a phase or a mineral of the rock sample has been kept as a closed system for *t* years after solidification, the total amount of Th^{230} in this part is given by

$$A_{0i} = aA_{2i}\exp(-\lambda t) + A_{4i}[1-\exp(-\lambda t)] \quad (1)$$

where A_{0i}, A_{2i}, and A_{4i} are the disintegration rates of Th^{230}, Th^{232}, and Th^{234}, respectively, in a phase indicated by subscript *i*; *a* is an activity ratio $A_{0i} : A_{2i}$, at $t = 0$, which must be constant in all phases of a rock sample; and λ is the decay constant of Th^{230}. The first term of Eq. 1 indicates a decrease of the ionium that has been included, with Th^{232}, in the *i*-th phase of the rock sample since the time of solidification; the second term indicates increase of the ionium from U^{234}. By use of the ratios $R_{0i} = A_{0i} : A_{2i}$ and $R_{4i} = A_{4i} : A_{2i}$ for two different parts (*i* and *j*) of a rock sample, Eq. 1 gives an age of solidification (*t*) as

$$t = \frac{1}{\lambda}\ln\left[1/\left(1 - \frac{R_{0i} - R_{0j}}{R_{4i} - R_{4j}}\right)\right] \quad (2)$$

The precision of this method of dating depends mainly on the magnitude of the difference ($R_{4i} - R_{4j}$) arising from the fractionation of uranium and thorium in the phases *i* and *j*.

Instead of mechanical or dynamic separation of minerals, partial dissolution or extraction may be used to separate the portions having different ratios of uranium:thorium. I now report some results of analyses of portions separated by heavy liquids or acid treatment. The following acid treatments yield two portions: (i) boiling 20- to 200-gram samples of powdered rock in 2*N* HCl for 40 hours, and (ii) solution in 9*N* HF of most nonmafic minerals in the residues remaining from the treatment with HCl. In Table 1, G-1 and O-1 correspond to the HCl-extracted solutions, and G-2 and O-2 correspond to HF-dissolved portions. A-1 is a portion obtained by partial dissolution of the powdered rock by 9*N* HF without any pretreatment, and A-2 is a residue from the HF treatment that mainly consisted of mafic minerals. Separation of heavy liquid (Toulet solution) gave two portions: O-4, consisting mainly of glass, and O-3, consisting of mafic minerals.

The thorium in these separated portions was purified by mesityl oxide extraction, fluoride precipitation, and ex-

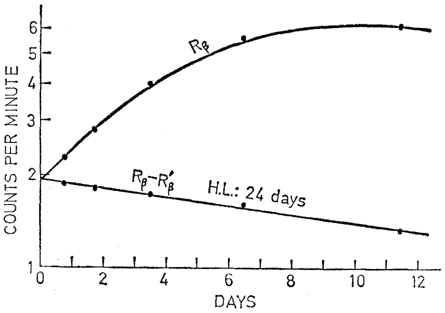

Fig. 1. Semilog plot illustrating the increase in observed beta activity (R_β) and decay in Th^{234} activity that were obtained from $R_\beta - R_\beta'$. *H.L.*, half-life.

traction with 2-thenoyltrifluoroacetone (*3*). Finally, thorium was back-extracted with 1*N* HNO_3 from solution in 2-thenoyltrifluoroacetone and electroplated on stainless steel disks from weakly acidic solution.

The energy spectrum of alpha rays from the thorium on a stainless steel disk was measured with a surface-barrier detector using a 100-channel pulse-height analyzer; the ratio of the areas of the peaks corresponding to Th^{230} and Th^{232} gives the activity ratio R_{0i}. On the same disk the beta activity was measured with a low-background proportional counter; the surface of the disk was covered with polyethylene film having a thickness of 39 mg/cm². The beta activity increases with time (Fig. 1) because of the increase of daughter nuclides of Th^{228}. The tight covering with polyethylene film, to prevent the escape and spread of radon from the surface of the disk, gives a regular increase of beta activity that is expressed by the formula

$$R_\beta' = kA_{8i}\left\{1 - \frac{1}{\lambda_{12} - \lambda_{24}}\right.$$
$$\left.[\lambda_{12}\exp(-\lambda_{24}t') - \lambda_{24}\exp(-\lambda_{12}t')]\right\} \quad (3)$$

where R_β' is the counting rate of beta rays from the daughter nuclides of Th^{228}, A_{8i} is the disintegration rate of Th^{228}, λ_{12} and λ_{24} are the decay constants of Pb^{212} and Ra^{224}, respectively, t' is the time after the separation of thorium from its daughter nuclides, and k is a constant that depends on the counting efficiency of the beta activities.

Subtraction of R_β' from the total beta-rays counting rate R_β gives the counting rate of the Th^{234} beta activity, which decays with 24.1-day half-life (Fig. 1). The activity ratio $R_{4i} = A_{4i}:A_{2i}$ was computed, with the Th^{232} alpha activity and this Th^{234} beta activity, at a time of separation of uranium from thorium during the process of chemical purification of the thorium.

The calculation of ages based on Eq. 2 gave results in good agreement with the expected ages (Table 1, last two columns). The errors indicated in Table 1 derive solely from the standard deviations of statistical errors in counting.

The sample of granite (Table 1) (*4*) is Cretaceous and should have an infinite age by ionium dating. In Fig. 2, the plotted points of G-1 and G-2 lie on a straight line through the origin, showing that there is no surviving Th^{230}. The extrapolated value of R_{0i}, for $R_{4i} = 0$ in the plot of R_{0i} versus R_{4i}, indicates the amount of Th^{230} present in the rock at the time of solidification that has survived to the present day.

The lava (*5*), which erupted in A.D. 1783, should have almost-zero age by this dating method. The plotted points A-1 and A-2 (Fig. 2) lie on a straight line parallel to the abscissa, indicating that the content of Th^{230} in each portion is independent of the content of Th^{234}, or that there are almost no Th^{230} atoms that have grown from U^{234} *in situ*.

Table 1. The ages of rock samples, and observed disintegration ratios of thorium nuclides in the separated portions.

No.	Method of separation	$Th^{230}:Th^{232}$ ($=R_{0i}$)	$Th^{234}:Th^{232}$ (R_{4i})	$Th^{228}:Th^{232}$	Age (yr) Known	Age (yr) Calc. from Eq. 2
			Granite (*4*)			
G-1	HCl on −200-mesh powder	0.284±0.005	0.285±0.005	1.01±0.02	(Cretaceous)	>310,000
G-2	HF on residue of G-1	.422± .004	.420± .005	1.00± .01		
			Lava (*5*)			
A-1	HF on +200-mesh powder	0.897±0.011	0.960±0.017	0.995±0.012	(A.D. 1783)	<6700
A-2	Residue of A-1	.905± .012	1.243± .025	1.018± .014		
			Pumice (*6*)			
O-1	HCl on +200-mesh powder	0.451±0.009	0.304±0.017	1.40±0.02	35,700± 1400	37,600± 5500 (*9*)
O-2	HF on residue of O-1	.565± .017	.662± .031	1.08± .014	(GaK-1047)	
O-3	Heavy liquid (*d* > 2.9	.583± .015	.786± .020	1.01± .02	(*8*)	
O-4	Heavy liquid (*d* > 2.7)	.555± .010	.566± .008	1.02± .02		

Radiocarbon dating of the pumice (*6*) gave 35,700 ± 1400 years ago (GaK-1047) on the basis of a wood sample associated with this pumice in layer

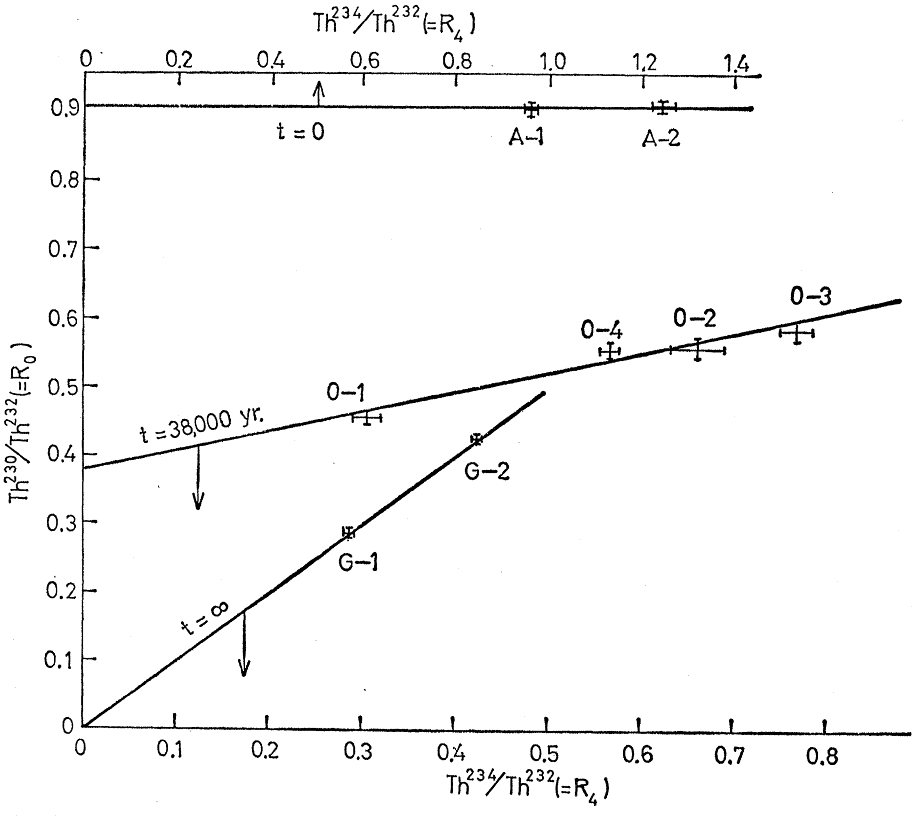

Fig. 2. Relation between uranium and ionium contents in the different parts of a rock sample. The plotted data are from Table 1; straight lines are the lines calculated from Eq. 1.

P-III and taken from the Ono Menyanthes bed (*7*).

The counting rate of the alpha rays from Th^{228}, which is required to compute R_{β}' by Eq. 3, was not always equal to that from the Th^{232}, even when the contribution from Ra^{224} to the 5.4-Mev peak of the Th^{228} spectrum was eliminated. The radioactive disequilibrium between Th^{228} and Th^{232} may result from difference in chemical behavior between these nuclides. A prominent excess amount of Th^{228} in O-1 (Table 1) seems to indicate that Th^{228} atoms were selectively extracted from the minerals during the acid treatment. The disequilibrium may support the view that recoil atoms produced by alpha decay in the solid are more soluble in the chemical treatment than are the atoms that have remained intact in the rock.

The occurrence of this chemical effect on recoil atoms is a disadvantage in a method based on separation, by acid extraction, of portions having different uranium:thorium ratios. When an extraction is used as a source of a portion from the total rock sample, the isotopic composition of thorium in the portion from which a part of thorium was extracted must be represented in the extracted solution. The chemical effect on the atoms, of disintegration products of uranium, possibly makes observed Th^{230}:Th^{232} or Th^{234}:Th^{232} ratios in the extracted solution different from the ratio in an analyzed portion of the rock sample. However, since in that portion Th^{234} and some Th^{230} are grown *in situ* by alpha decays of nearly equal energy, these nuclides may behave in about the same manner: that is, the ratio of extracted Th^{230} to Th^{230} grown *in situ* in that portion may be the same as the ratio of extracted Th^{234} to total Th^{234}. If these two ratios are the same, a plot of R_{4i} versus R_{0i} gives a point on a straight line given by Eq. 1.

In the cases of O-2, O-3, and O-4, there was no distinct difference between the counting rates of Th^{232} and Th^{228}. Although O-1 showed significant difference between the counting rates of Th^{232} and Th^{228}, all four points O-1, O-2, O-3, and O-4 (Fig. 2) lie on a straight line. Thus it is shown that, in the acid-extraction process for O-1, the chemical behavior of Th^{230} grown *in situ* was just the same as that of Th^{234}.

When this dating procedure is used with separated minerals, there should be no complex problem in regard to the basis of the dating. Separations by partial dissolution or extraction probably involve the recoiled-atom effects when the observed Th^{228} and Th^{232} activities are not equal. Fortunately in the case of this pumice (*6*) these effects appear to have been the same for Th^{234} and Th^{230}. Because of a great difference between the half-lives of Th^{234} and Th^{230}, it is also plausible that in the other rocks only a feeble effect is left on the recoiled Th^{230} atoms; further studies are necessary to establish a general conclusion.

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9. Calculated from the data on O-1 and O-3.

14 February 1967

Iodide Abundance in Oilfield Brines in Oklahoma

Abstract. *Samples of subsurface water, oil, and rock from strata of Mississippian and Pennsylvanian age in the Northern Oklahoma Platform area were analyzed. Several of the water samples contained iodide at more than 500 parts per million. Analyses of the brines and rock indicated that the iodide originated organically.*

Samples of water, oil, and rock were obtained from various strata in the marine-sedimentary Anadarko Basin, coming from primary production wells; they should represent connate data as closely as possible. Some of the water samples were analyzed at the wellhead for unstable properties and constituents; others were stored in plastic bottles and transported to the laboratory for analysis. Each sample was in duplicate; one half was acidified immediately to *p*H 1.5 with HCl. They were analyzed by reported methods (*2*). The oil samples were transported to the laboratory in metal containers and analyzed by reported methods (*3*), except for the iodide analysis which was done by a neutron-activation technique.

Concentrations of iodide exceeded 500 ppm in several samples of water from various oil wells; the highest were in brines taken from rocks of Mississippian and Pennsylvanian age in the Northern Oklahoma Platform area (Fig. 1). These brines contained some of the highest concentrations of iodide on record. Most oilfield brines contain less than 10 ppm of iodide; some approach 100 ppm, but few contain more.

The data indicate that the heaviest concentration of iodide is in the Oklahoma Platform area east of the Nemaha Ridge; here the top of the Mississippian sediments is about 1830 m deep. Table 1 gives the pertinent data for six brines high in iodide content and the iodide and bromide contents of some seaweeds and corals. All these brine samples were taken in Oklahoma from depths exceeding 1800 m, and the associated rocks were Mississippian or Pennsylvanian in age. Sample 5 (Table 1) is obviously a meteoric water containing relatively high concentrations of iodide and bromide; it cannot be relict sea water because of its low content of chloride.

The brines were depleted in magnesium and relatively rich in calcium (up to 16,000 ppm), indicating that they are very old and that diagenetic dolomitization could have occurred. Other constituents detected were lithium, up to 25 ppm; potassium, up to 2100 ppm; rubidium, up to 5 ppm; cesium, up to 2 ppm; strontium, up to 1500 ppm; barium, up to 15 ppm; boron, up to 220 ppm; and sulfate, up to 900 ppm.

Some of the brines were analyzed at the wellhead for ferrous iron, ferric iron, thiosulfate, sulfite, sulfide, dissolved carbon dioxide, bicarbonate, and ammonium. Thiosulfate, ammonium, dissolved carbon dioxide, bicarbonate, and traces of sulfite were present; hydrogen sulfide was absent.

High ratios of ferrous iron to ferric iron indicate a reducing environment. The Fe^{2+} : Fe^{3+} ratios varied from 5.0 to 40.0; *p*H, from 5.9 to 6.5. The measured *Eh* (*4*) ranged from 270 to 300 mv. A reducing environment is characteristic of a petroleum-bearing formation.

It is often assumed that, in brines in which the I:Cl and I:Br ratios are much greater than those of sea water, marine concentrators of iodine are