

# NEUTRON ACTIVATION APPLIED TO GEOCHEMISTRY

W. HERR

*Max-Planck-Institut für Chemie, Mainz, Institut für Kernchemie der Universität,  
Köln, Germany*

Au cours des dernières années, on a constaté que l'analyse par radioactivation est un moyen très efficace d'étudier les problèmes fondamentaux qui se posent en géochimie et en cosmochimie. L'auteur décrit les travaux récents accomplis dans ce domaine, et les remarquables possibilités qu'offre cette méthode. L'un des grands avantages de l'analyse par radioactivation est qu'elle permet souvent d'obtenir simultanément des renseignements sur la quantité des éléments présents à l'état de traces et sur leur composition isotopique. Une attention particulière sera accordée aux techniques nouvelles de traitement des gaz et des substances volatiles. Les recherches sur la répartition et l'abondance des éléments à l'état de traces, notamment les problèmes concernant la détermination de l'âge géologique des minéraux et des météorites présentent un intérêt croissant. La mesure du rapport K/Ar donne des résultats excellents lorsqu'elle est fondée sur la radioactivité induite de  $^{41}\text{Ar}$  et de  $^{37}\text{Ar}$ . On peut également appliquer l'activation neutronique aux méthodes classiques de détermination du rapport Rb/Sr et du rapport U/Pb. On peut recueillir des données utiles sur les radioactivités naturelles d'éléments tels que le  $^{176}\text{Lu}$  et le  $^{187}\text{Re}$  et sur leurs possibilités d'application aux problèmes géologiques. Dans les recherches sur les météorites, "l'activation neutronique" sert surtout de moyen d'analyse. Dans ce cas, des éléments à l'état de traces qui présentent un intérêt ont une concentration comprise entre  $10^{-7}$  et  $10^{-10}$  g/g; on peut aussi déceler les produits stables de spallation tels que  $^3\text{He}$ ,  $^6\text{Li}$ , K,  $^{45}\text{Sc}$ , etc. formés par l'action des rayons cosmiques. Ces données analytiques permettent de mieux connaître le spectre énergétique et la constance du rayonnement cosmique dans le temps. On peut en déduire l'âge "radiologique" et l'âge-matière des météorites.

The discovery of radioactivity has stimulated research in the natural sciences and especially in geology. Radioactive atoms have helped to solve two independent but related problems, the establishment of the geological time scale and the determination of the heat balance and geological and cosmological abundance of elements.

Only sixty years ago an English geologist, W. J. Sollas, remarked in his book entitled *The Age of the Earth*: "How enormous would be the progress in our science if it were possible to relate the important events of our earth-history to a time-scale" . . . and he continues: "Until now, this has often been tried but in every case the hope sublimed away. Nevertheless I do trust that one day a talisman will be found to enable geological dating."

By this time the still "unknown" talisman had already been discovered in the existence of the radioactive elements. Nature had built her own clock.

Here it may be of interest to remember that William Thomson, later Lord Kelvin, was the first to make an attempt to help the geologists with physical methods. Kelvin was convinced that the sun and also the earth were subject to the same physical laws of cooling. He calculated that at one time the earth had cooled according to these laws and that life could

exist no earlier than some 20 million years ago. Concerning the future he pointed out that the cooling of our earth is continuing, and therefore life is limited in time, and very cautiously he added: "in case there is not a new source of energy in nature still unknown to us." It is surprising that this argument was never seriously considered and the controversy about the possible age of the earth continued for many years.

It was in 1903 that Pierre Curie and Laborde made their famous experiment measuring the heat developed directly by radium. Shortly after this Strutt showed that radium is distributed in all minerals of the earth's crust, the amounts being large enough to balance the cooling.

Consequently all earlier calculations about the cooling time of the earth were incorrect.

Table 1. Primary natural radionuclides

<i>Nuclide</i>	<i>Isotope abundance (%)</i>	<i>Type of disintegration</i>	<i>Half-life (years)</i>	<i>Stable end-products</i>
<sup>235</sup> U	0.715	$\alpha$	$7.1 \times 10^8$	<sup>207</sup> Pb, <sup>4</sup> He
<sup>40</sup> K	0.012	$\beta$ (88%), $\epsilon$ (11%)	$1.3 \times 10^9$	<sup>40</sup> Ca, <sup>40</sup> Ar
<sup>238</sup> U	99.28	$\alpha$	$4.5 \times 10^9$	<sup>206</sup> Pb, <sup>4</sup> He
<sup>232</sup> Th	100	$\alpha$	$1.4 \times 10^{10}$	<sup>208</sup> Pb, <sup>4</sup> He
<sup>176</sup> Lu	2.60	$\beta$	$2.2 \times 10^{10}$	<sup>176</sup> Hf
<sup>87</sup> Rb	27.8	$\beta$	$5.0 \times 10^{10}$	<sup>87</sup> Sr
<sup>187</sup> Re	62.9	$\beta$	$6.3 \times 10^{10}$	<sup>187</sup> Os
<sup>147</sup> Sm	15.1	$\alpha$	$1.3 \times 10^{11}$	<sup>143</sup> Nd, <sup>4</sup> He
<sup>138</sup> La	0.089	$\epsilon$ (90%), $\beta$ (10%)	$2 \times 10^{11}$	<sup>138</sup> Ba, <sup>138</sup> Ce
<sup>190</sup> Pt	0.012	$\alpha$	$5 \times 10^{11}$	<sup>186</sup> Os, <sup>4</sup> He
<sup>115</sup> In	95.8	$\beta$	$6 \times 10^{14}$	<sup>115</sup> Sn
<sup>144</sup> Nd	23.9	$\alpha$	$3 \times 10^{15}$	<sup>140</sup> Ce, <sup>4</sup> He

I mention these historical events to underline the importance of an exact analysis of the natural radioelements and to show that the problem is still of current interest. For this subtle analytical work new sensitive methods had to be developed. The recent enormous progress in this field is directly related to the progress in nuclear energy. In particular neutron activation techniques have found wide use in geochemistry.

The principle of a radioactive age determination is well known. Using the decay law in the form  $N_d = N_m (e^{\lambda t} - 1)$  we have to determine in the same mineral sample the amount of the mother element  $N_m$  and the amount of its stable daughter product  $N_d$ . From the rate of decay we know the amount of the decay product which is produced in one year. It should then be easy to calculate how many years have passed since the mineral was formed.

Although the principle of the method seems to be quite simple, in practice many difficulties are encountered so that there are only a limited number of age determinations which are absolutely reliable. To explain this we should have a look at Table 1 where twelve primary natural radionuclides of major interest are given in order of increasing half-lives. These nuclides are not all suitable for age determination. If the half-life is very large, the amount of decay product is too small and the analytical difficulties increase considerably. Also if a gas is produced in the radioactive series,

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or is the end product, serious diffusion losses can occur. The rarer elements are applicable only in special cases to dating work. By far the most widely applicable method for a geologist is the potassium-argon dating method. Potassium minerals are most common, and their application is of growing importance in geochemistry. Therefore the work on this nuclide should be mentioned first in demonstrating the usefulness of the neutron activation technique.

The isotope  $^{40}\text{K}$  decays in two ways, partly into  $^{40}\text{Ar}$ , but mainly (88%) into  $^{40}\text{Ca}$ . In potassium minerals practically pure  $^{40}\text{Ar}$  occurs. As the neutron capture cross-section for the production of  $^{41}\text{Ar}$  ( $t_{1/2} = 1.8 \text{ h}$ ) is relatively high, the limit of detection will be in the range of  $10^{-10} \text{ g}$  of  $^{40}\text{Ar}$ . The competing reaction  $^{41}\text{K}(n,p)^{41}\text{Ar}$  has a comparatively low cross-section

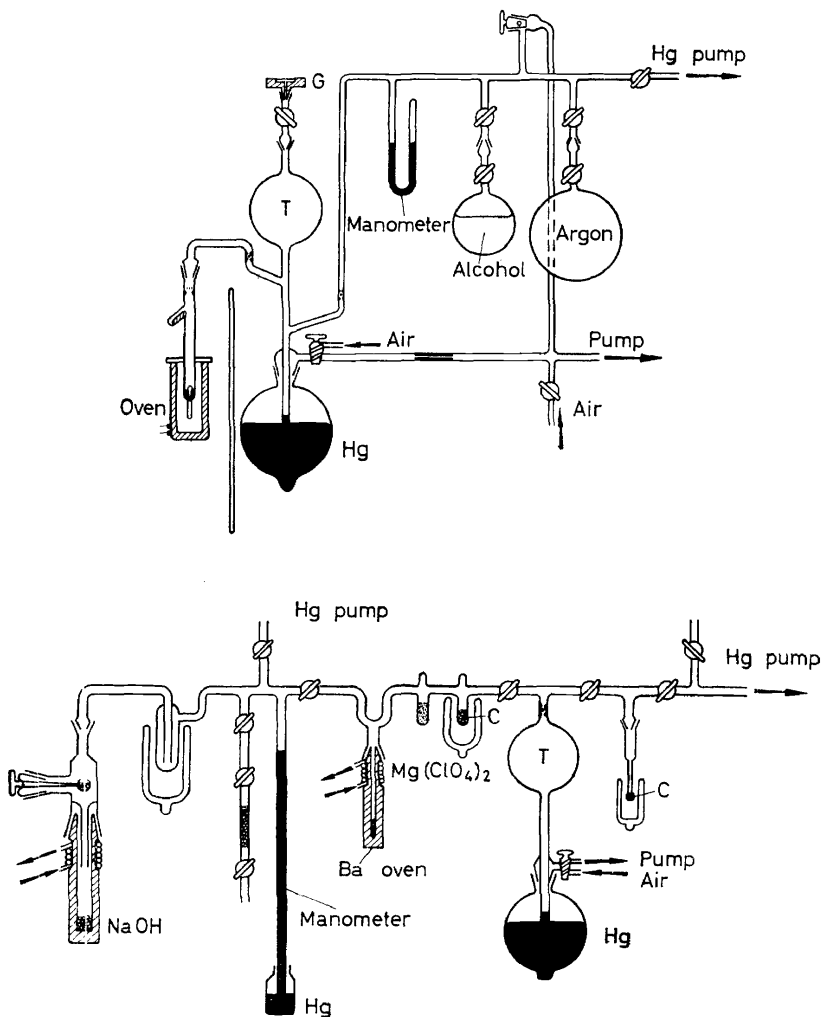


Figure 1. Apparatus for extraction and purification of argon from minerals

and depends largely on the presence of energetic neutrons. Therefore it might be preferable first to isolate quantitatively the argon from the mineral, so making the activation independent of the mineral composition. This would also make possible the investigation of minerals which contain boron, lithium, rare earth elements or other neutron poisons.

The separation of argon from a mineral sample is relatively easy and the procedure is well known. Using neutron activation we have the choice either of isolating the  $^{40}\text{Ar}$  quantitatively or of using one of the principles of this technique to measure the yield of recovery after mixing with a known amount of carrier argon gas.

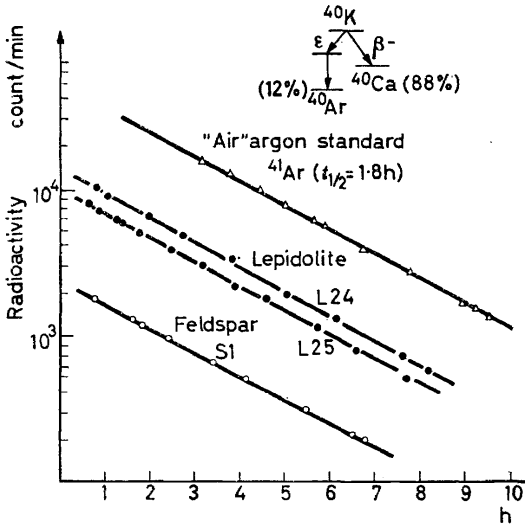


Figure 2. Decay curves of  $^{41}\text{Ar}$

As far as we know the first publication on this subject was by Moljk and co-workers<sup>1</sup> several years ago. We too in Mainz studied the applicability of the activation method to our geochemical work. In Figure 1 our apparatus for the extraction and measurement of small amounts of argon is shown.

The finely ground mineral (*ca* 2 g) is opened up in a melt of sodium hydroxide, the evolved gas is purified by traps and a barium oven, *etc.*, and finally the gas is condensed onto charcoal (C) in a little quartz ampoule only a few millimetres in diameter and 4 cm in length. Here the extraction must be quantitative. We checked the experimental conditions with a carrier-free tracer,  $^{37}\text{Ar}$  (a  $K$ -emitter), which can be measured only in a gas counter, whereas  $^{41}\text{Ar}$  and also  $^{39}\text{Ar}$  (in long irradiations) are energetic  $\beta$ -emitters and do not require internal gas counting. In the upper part of the apparatus the irradiated argon ampoule is broken and the argon brought by means of a Toepler pump (T) to a little counting chamber (G), a metal dish only *ca* 15 mm in diameter, which is closed by a thin foil. The dish with the enclosed gas is brought beneath an ordinary end-window counter and its  $\beta$ -activity is measured, Figure 2.

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The decay curve of the  $^{41}\text{Ar}$  ( $t_{1/2} = 1.8$  h) has practically no tail. As a standard or reference source we use a certain quantity of "air" argon which is treated in the same way. Often in minerals and in the glass apparatus a small amount of "air" argon is absorbed which may affect the results, but this is not serious. "Air" argon contains a small percentage of stable  $^{36}\text{Ar}$  so  $^{37}\text{Ar}$  ( $t_{1/2} = 35$  d) is produced by the reaction  $^{36}\text{Ar}(n,\gamma)^{37}\text{Ar}$ . As the  $^{37}\text{Ar}$   $K$ -radiation cannot be observed under the window counter, the gas is transferred to an internal gas counter and the result used as a correction for the amount of the "air" argon impurity present. (The correction is mostly small,  $\sim 1-3$  per cent.)  $^{37}\text{Ar}$  is also produced by the  $^{40}\text{Ca}(n,\alpha)^{37}\text{Ar}$  reaction. We used the same apparatus for the determination of small amounts of calcium in minerals. This method of calcium determination is more sensitive and rapid than that using the  $^{44}\text{Ca}(n,\gamma)^{45}\text{Ca}$  ( $t_{1/2} = 225$  d) reaction.

The possibility of loss of the argon in minerals by diffusion during the ages is an important question. This calls for a more detailed study of the diffusion process. As neutron activation is not limited to analytical problems I should like to mention briefly this application. Little is known about the  $^{37}\text{Ar}$  diffusion constants in specific minerals such as feldspars, lepidolites and stone meteorites, but the results will probably contribute to an understanding of the observed variations due to diffusion losses in estimates of age.

Table 2. Potassium-argon ages by neutron activation  
(from A. Rassoul<sup>2</sup>)

Mineral	Weight (g)	$^{40}\text{Ar}$ ( $\mu\text{g/g}$ )	K (%)	$^{40}\text{Ar}/^{40}\text{K}$	$10^{-9} \times \text{Mineral age}$ (years)
Lepidolite L24					
S. Rhodesia	2.4185	2.931		0.373	$2.51 \pm 0.24$
Nolan mine	2.4600	2.921	6.6	0.372	
Alkyat, Bikita	2.4000	2.856		0.364	
Lepidolite L25					
S. Rhodesia	2.4236	2.511		0.329	$2.42 \pm 0.20$
Bikita mine,	2.4152	2.523	6.4	0.331	
E. Victoria F.					
Feldspar 1					
Swaziland, Mba-	2.4205	1.232		0.187	$1.86 \pm 0.16$
bane, S. Africa	2.3960	1.219	5.53	0.185	
Red granite H3	2.4316	0.384	6.64	0.048	
Torset, N. Norway	2.4238	0.385		0.049	$0.64 \pm 0.05$

Table 3. Comparison of rubidium-strontium and potassium-argon ages  
(from A. Rassoul<sup>2</sup>)

Mineral	Locality	$^{87}\text{Rb}$ (%)	$^{87}\text{Sr}$ (%)	$(t_{1/2} = 4.8 \times 10^9 \text{y})$ $10^{-9} \times \text{Rb/Sr age}$ (years)	$(t_{1/2} = 1.30 \times 10^9 \text{y})$ $10^{-9} \times \text{K/Ar age}$ (years)
Lepidolite 24	S. Rhodesia, Nolan mine, Alkyat, Bikita	0.574	0.0235 0.0232	$2.62 \pm 0.19$	$2.51 \pm 0.24$
Lepidolite 25	S. Rhodesia, Bikita mine, E. Victoria F.	0.436	0.0170 0.0168	$2.51 \pm 0.17$	$2.42 \pm 0.20$

Some of our results<sup>2</sup> in potassium-argon age determinations are shown in *Tables 2 and 3*. These include data for lepidolites and feldspars from South Africa and Norway. The age is found to be in the range of  $0.5\text{--}2.6 \times 10^9$  years. The neutron activations were all made in the B.E.P.O. reactor at Harwell and the samples were sent by air to Mainz. The earliest  $^{41}\text{Ar}$  measurements could only be done about 10 hours after dispatch from Harwell. The potassium-argon ages and the rubidium-strontium ages are slightly different in the same mineral. These differences might be due to diffusion losses. However, there is also a small uncertainty in the branching ratio and in the decay constants. Further investigation will serve to fix the values of the constants. (The long controversy on the "true" half-life of  $^{87}\text{Rb}$  will be recalled.)

The lepidolites attract our attention as they are relatively high in rubidium content and it was possible to compare the rubidium-strontium age with the measured potassium-argon age. Rubidium is easily detected by its 18-day activity. As lepidolites should not be irradiated directly in a pile (there might be shielding effects due to their high lithium content) the potassium together with rubidium and caesium were separated and bombarded with neutrons.

*Table 4.* Potassium-argon ages of stone meteorites  
(from H. Wänke and H. König<sup>3</sup>)

<i>Meteorite</i>	$10^6 \times \text{Ar content}$ ( $\text{cm}^3/\text{g}$ )	$10^3 \times \text{K content}$ ( $\text{g/g}$ )	$10^{-9} \times \text{K/Ar age}$ (years)
<i>Chondrite</i>			
Akaba	$45.0 \pm 2.7$	$1.00 \pm 0.04$	$3.58 \pm \begin{matrix} 0.10 \\ 0.12 \end{matrix}$
Beddgelert	$20.2 \pm 5.7$	$0.77 \pm 0.04$	$2.77 \pm \begin{matrix} 0.37 \\ 0.45 \end{matrix}$
Breitscheid	$33.1 \pm 2.2$	$0.82 \pm 0.03$	$3.39 \pm \begin{matrix} 0.12 \\ 0.12 \end{matrix}$
„	$32.0 \pm 3.0$	$0.82 \pm 0.03$	$3.34 \pm \begin{matrix} 0.20 \\ 0.21 \end{matrix}$
Modoc	$52.8 \pm 2.9$	$0.83 \pm 0.05$	$4.12 \pm \begin{matrix} 0.13 \\ 0.14 \end{matrix}$
„	$57.3 \pm 6.3$	$0.83 \pm 0.02$	$4.25 \pm \begin{matrix} 0.19 \\ 0.21 \end{matrix}$
Pultusk	$38.2 \pm 7.6$	$0.79 \pm 0.05$	$3.68 \pm \begin{matrix} 0.30 \\ 0.36 \end{matrix}$
„	$41.0 \pm 7.6$	$0.75 \pm 0.03$	$3.87 \pm \begin{matrix} 0.28 \\ 0.33 \end{matrix}$
<i>Achondrite</i>			
Pasamonte	$23.6 \pm 4.7$	$0.34 \pm 0.05$	$4.27 \pm \begin{matrix} 0.37 \\ 0.47 \end{matrix}$
Johnstown	0.4	0.01	

It is well known that radiogenic  $^{87}\text{Sr}$  is often nearly 100 per cent pure in these minerals. We isolated some milligrams of strontium element by processes which involved ion-exchange techniques and the removal of calcium and barium (using  $^{45}\text{Ca}$  and carrier-free  $^{89}\text{Sr}$  as a tracer). The isotopic composition of this strontium was determined by induced activities of  $^{89}\text{Sr}$  ( $t_{\frac{1}{2}} = 30$  d) and  $^{87\text{m}}\text{Sr}$  ( $t_{\frac{1}{2}} = 2.8$  h) which were compared with that of "normal" strontium samples. These activities served as indicators for

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the presence of "normal" strontium element in the radiogenic product. A high state of chemical purity is necessary.

As we are working in Mainz in two groups on similar problems it is of interest to mention that Dr Wänke<sup>3</sup> recently developed a potassium-argon method for stone meteorites. These meteorites are fairly old and their potassium content is about 0.1 per cent. Therefore the amount of radiogenic <sup>40</sup>Ar is relatively high and is scarcely affected by cosmic ray production of argon.

The <sup>41</sup>Ar activity can easily be measured after a short (slow) neutron activation of the stone meteorite itself. There will not be severe interference by competing (n,p) nuclear reactions. Now Wänke observed a relatively strong <sup>39</sup>Ar activity ( $t_{1/2} = 260$  y) resulting from the <sup>39</sup>K(n,p)<sup>39</sup>Ar reaction when irradiating the same stone meteorite for a longer time (2 weeks).

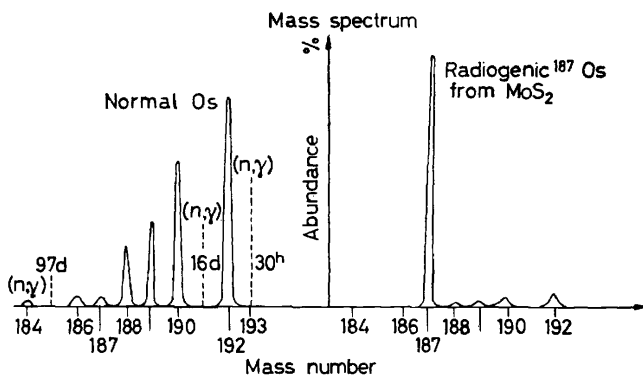


Figure 3. Mass spectrum of osmium

This activity is unaffected by other nuclear reactions and will give directly the amount of potassium present in the sample. Consequently the <sup>39</sup>Ar/<sup>41</sup>Ar ratio of activities corresponds to the age of the meteorite. The results are summarized in Table 4. They are in good agreement with other facts. Most probably the differences in the age result from diffusion losses in the individual meteorites. The age of the meteorites is found to be in the range of  $2.8-4.25 \times 10^9$  years.

It is worth mentioning that this simple method is similar to the Nier method where lead ages are estimated from the ratio <sup>207</sup>Pb/<sup>206</sup>Pb, without the necessity of knowing the true lead and uranium contents of the sample. In old minerals this method is by far the most reliable.

Several years ago we started a search<sup>4,5</sup> for decay products of <sup>187</sup>Re the natural  $\beta$ -radioactivity of which was discovered by Libby and Nalderett<sup>6</sup>. In geologically old rhenium-containing molybdenites we found osmium, which from a geochemical point of view should not be in this type of mineral. The results of the mass spectrometric investigation of the isotope abundance of this osmium are shown in Figure 3. It clearly shows that one isotope, namely the rare isotope <sup>187</sup>Os is the only one present. From this result it seemed clear that the half-life of <sup>187</sup>Re had to be corrected considerably.

We tried to evaluate the  $^{187}\text{Re}$  half-life by analytical methods<sup>7,8</sup> in order to determine the traces of rhenium and  $^{187}\text{Os}$  and to evaluate the age of the minerals by conventional means. Considerable difficulties were encountered because the molybdenites concerned were not found together with other natural radioelements. We had to establish a "relative" age scale, and tried to relate this to the known geological facts in the history of the deposits.

The trace elements rhenium and osmium were always present in concentrations of  $10^{-4}$  to  $10^{-7}$  g/g of mineral. In the case of rhenium this was determined by neutron activation, but for the radiogenic osmium we had to combine the conventional chemical analysis with neutron activation

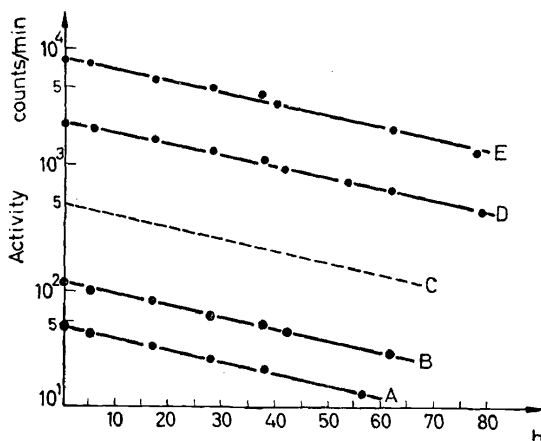


Figure 4. Rate of disintegration of different osmium samples after neutron activation: A, 1.08  $\mu\text{g}$  of Os from Stavanger  $\text{MoS}_2$ , containing 0.0150  $\mu\text{g}$  (= 1.4%) of normal Os; B, 1.12  $\mu\text{g}$  of Os from "Lofoten"  $\text{MoS}_2$ , containing 0.034  $\mu\text{g}$  (= 3.0%) of normal Os; C, theoretical 1.33-day disintegration of  $^{188}\text{Os}$ ; D, 0.8  $\mu\text{g}$  of "normal" Os; E, 4.13  $\mu\text{g}$  of Os containing 2.8  $\mu\text{g}$  (= 68%) of "normal" Os

techniques. The reason was that the isotope  $^{187}\text{Os}$  after neutron capture produces  $^{188}\text{Os}$  which is stable. However, there was a way to determine the  $^{187}\text{Os}$  concentration indirectly. The chemical amount of osmium element present in the sample having been established, the  $^{187}\text{Os}$  abundance was deduced from the reduction in the specific radioactivity of the induced radioisotopes  $^{191}\text{Os}$ ,  $^{193}\text{Os}$  and  $^{185}\text{Os}$ . The activation method has the advantage that the amounts of osmium required are very small, only in the order of micrograms. (For the first mass spectrometric investigation some hundreds of micrograms were needed.)

Figure 4 shows the results obtained from the activation analysis for radiogenic  $^{187}\text{Os}$  in osmium. The limit of detection of normal osmium is of the order of  $10^{-3}$   $\mu\text{g}$ , therefore in highly enriched  $^{187}\text{Os}$  an impurity of "normal" osmium is easily detected.

Recently we continued this study in meteorites and it seems to be of interest. Previous attempts to determine the geological age of iron meteorites, for instance by Paneth and co-workers using the helium method, failed, because more recent investigations have shown that an appreciable



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amount of helium consists of helium-3 ( $\sim 25$  per cent) which is due to cosmic ray effects. Moreover, the uranium content of the iron meteorites was shown to be less than  $10^{-10}$  g/g. This latter information is due largely to Reed and Turkevich<sup>9</sup>. In consequence, it is now clear that an age determination based on the decay of uranium and thorium is not feasible. Another attempt made recently by Stoenner and Zähringer<sup>10</sup> with the potassium-argon method using the neutron activation technique gives results which are difficult to understand. The rhenium and osmium contents in some iron meteorites found by neutron activation are given in Table 5.

Table 5. Osmium and rhenium contents in iron meteorites  
(from W. Herr, W. Hoffmeister and L. Langhoff<sup>21</sup>)

Iron meteorite	$10^8 \times \text{Os content}$ (g/g)	$10^6 \times \text{Re content}$ (g/g)	$10^8 \times \text{Re content}^*$ (g/g)	$^{187}\text{Os}/^{186}\text{Os}$ ratio <sup>†</sup>
Tocopilla	1.29	0.25		$1.410 \pm 0.012$
Henbury	2.25	0.21	1.4	
Canon Diablo	2.07	0.25	0.28	$1.127 \pm 0.015$
Odessa (Fe)	2.61	0.25		
Sichote Alin	$< 0.02$	$\leq 0.01$		
Xiquipilco	2.54	0.22	0.25	$1.064 \pm 0.016$
Terrestr. Os-Ir (Ural)	—	—	—	$1.025 \pm 0.009$

\* Comparable results from E. D. Goldberg and H. Brown<sup>20</sup>.

† Results from J. Geiss, B. Hirt, W. Herr, E. Merz and F. Houtermans<sup>11</sup>.

In the last column is the observed  $^{187}\text{Os}/^{186}\text{Os}$  ratio obtained from mass spectrometric measurements by J. Geiss, B. Hirt, *et al.*<sup>11</sup> in Bern. These ratios show that "radiogenic"  $^{187}\text{Os}$  is present in the iron and it might be possible to calculate the age. In all probability we can exclude any interference from cosmic radiation effects. The primordial abundance of the  $^{187}\text{Os}$  in the meteorite osmium, however, is still an unknown factor.

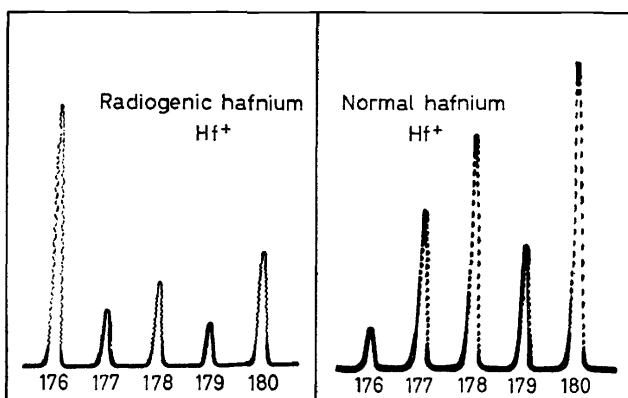
Another low natural radioactivity of possible geological interest is that of the  $^{176}\text{Lu}$  isotope. In our search for decay products we succeeded in isolating a small amount of pure hafnium oxide in a mineral containing lutetium<sup>12</sup>. After neutron bombardment of hafnium from a Norwegian gadolinite and comparison with an irradiated "normal" hafnium from a zircon mineral it was proved that in the gadolinite hafnium a large part of the  $^{176}\text{Hf}$  isotope is present. Normal hafnium is composed of six stable isotopes of which only the isotopes of mass numbers 174, 187 and 180 are suitable for the production of radioisotopes by neutron capture.

In irradiated pure "normal" hafnium we get a certain specific activity of  $^{181}\text{Hf}$ , whereas in the presence of a certain amount of stable radiogenic  $^{176}\text{Hf}$ , which produces stable  $^{177}\text{Hf}$ , the specific activity of  $^{181}\text{Hf}$  will decrease proportionally. As in the case of  $^{187}\text{Os}$ , here too the difference in specific activity can be used to deduce the amount of "radiogenic"  $^{176}\text{Hf}$  present in the sample. The hafnium was isolated in a very pure state from the lutetium mineral by means of ion-exchange techniques. Pile irradiation was carried out for three days with samples containing only 0.05 mg of  $\text{HfO}_2$  in a flux of  $10^{12}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$ . In order to eliminate interfering activities probably originating from traces of rare earth elements, the

neutron-irradiated  $\text{HfO}_2$  samples were dissolved in the presence of lanthanum as hold-back carrier and a relatively high amount of zirconium as carrier. The purification was repeated. Finally the activities were measured under identical conditions by ordinary Geiger-Müller counters or with a  $\gamma$ -spectrometer.

Mass spectrometry proved our results. This work was done by P. Eberhard and P. Signer of the University of Bern with another part of the isolated  $\text{HfO}_2$ . The results are illustrated in *Figure 5*. The  $^{176}\text{Hf}$  isotope is enriched to about 40 per cent in the gadolinite hafnium. It may be noted that the values show good agreement within experimental error.

The hafnium from the gadolinite mineral shows a decrease in the specific activity which is roughly half of the normal standard hafnium. The content in "normal" hafnium can be read directly from the ratio of the specific



*Figure 5.* Mass spectrum of hafnium

activities of the unknown sample to that of the hafnium standard. The constancy of the isotopic composition of the "normal" hafnium or standard hafnium can always be ascertained. It is worth mentioning that the radiometric abundance analysis of radiogenic hafnium was also done with the  $^{176\text{m}}\text{Hf}$  activity ( $t_{1/2} = 19$  sec) which has a high thermal neutron cross-section ( $\sim 100$  barns). But the gain in time brings a loss of accuracy owing to difficulties in fast handling.

Thus we succeeded in determining the half-life of  $^{176}\text{Lu}$  and proved the use of this isotope in geological dating work, especially in minerals containing rare earths and lutetium.

In the introduction I mentioned the importance of reliable uranium determinations in terrestrial and in cosmic matter. Reed and Turkevich<sup>9</sup> have used neutron activation techniques to determine reliable data on the uranium content of meteorites. They had to correct the older iron figures by at least  $10^2$ . This work was started because of remaining discrepancies in the calculation of heat production and stability of planetary bodies. In this work the uranium-fission product  $^{140}\text{La}$  was separated from the irradiated samples and simultaneously the yield in  $^{239}\text{Np}$  (formed by

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*Table 6.* Uranium contents by neutron activation using  $^{133}\text{Xe}$  fission products  
(from H. König and H. Wänke<sup>13</sup>)

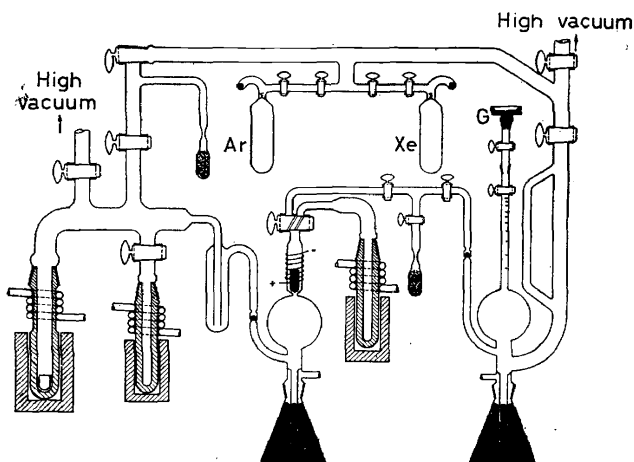
<i>Meteorite</i>	$10^8 \times \text{U content}$ (g/g)	<i>Meteorite</i>	$10^8 \times \text{U content}$ (g/g)
<i>Chondrite</i>		<i>Achondrite</i>	
Akaba	$0.82 \pm 0.05$	Johnstown	$0.19 \pm 0.06$
Beardsley	$1.13 \pm 0.11$	Nuevo Laredo	$12.6^*$
Beddgelert	$2.10 \pm 0.19$		
Breitscheid	$1.23 \pm 0.07$	Pasamonte	$5.40 \pm 0.50$
Forest City	$1.03^*$	Sioux County	$6.30 \pm 0.30$
Holbrook	$1.25^*$		
Modoc	$1.04 \pm 0.10$		
	$1.08^*$		
Pultusk	$1.23 \pm 0.10$		
Richardton	$1.22^*$		

\* Results from H. Hamaguchi, G. W. Reed and A. Turkevich using neutron fission:  
 $^{235}\text{U}(n,f)^{140}\text{Ba}$  and  $^{238}\text{U}(n,\gamma,\beta)^{239}\text{Np}$ .

$^{238}\text{U}(n,\gamma)^{239}\text{U} \xrightarrow{\beta} ^{239}\text{Np}$ ) was measured, proving that the isotope composition of uranium in meteorites is normal. The chemical procedure is rather tedious and somewhat time-consuming.

The glass apparatus used for the argon determination is also suitable, after slight modification, for uranium determination, as König and Wänke<sup>13</sup> showed recently. They used the  $^{133}\text{Xe}$  ( $t_{1/2} = 5.2$  d) fission activity with success. The method is reliable and has many advantages.

In *Table 6* their uranium results in stone meteorites are summarized. Some of the values marked with an asterisk can be compared with results from Reed and co-workers.  $^{133}\text{Xe}$  is unaffected by other nuclear reactions. The purification process, absorption on charcoal and desorption at  $140^\circ\text{C}$ ,



*Figure 6.* Modified Wänke apparatus

eliminates all other possible interfering gaseous activities. As most of the meteorites are rare and therefore valuable materials it is convenient to make age determinations, uranium analyses, *etc.*, on the same sample.

Figure 6 shows the modified apparatus of Wänke. It is only some years ago that Paneth and co-workers<sup>14</sup> discovered that helium in iron meteorites is a mixture of  $^3\text{He}$  and  $^4\text{He}$ . It is considered that helium is produced by cosmic radiation as a spallation product of iron. The  $^3\text{He}/^4\text{He}$  ratio is fairly constant at  $\sim 0.25$ . With regard to  $^3\text{He}$  a precursor,  $^3\text{H}$ , has to be expected. The first experimental approach made by Begemann, Geiss and Hess<sup>15</sup> proved the existence of tritium in the stone meteorite Norton County, and they calculated from the amount of  $^3\text{H}$  and  $^3\text{He}$  a so-called "radiation age" ( $t_r$ ), *i.e.*, the time needed to produce the  $^3\text{He}$  found:

$$t_r = \frac{\text{the number of } ^3\text{He atoms (corrected for direct production)}}{\text{the number of } ^3\text{H decays per second}}$$

The radiation age for "Norton County" was found to be in the range of 250 million years on the assumption that the cosmic-ray production was constant over that time. The potassium-argon method gives a greater age, of  $\sim 4 \times 10^9$  years.

Fireman and Schwarzer<sup>16</sup> reported on the determination of  $^3\text{He}$  in meteorites by neutron activation.  $^3\text{He}$  has a high neutron cross-section of  $\sim 6000$  barns and consequently it is detected with high sensitivity. On the other hand, the  $^3\text{H}$  in the freshly fallen meteorite can be measured only by low-level counting techniques. The two methods combined give valuable information about the earlier events in our planetary system. We may best understand the "radiation age" as the time in which smaller meteorites were circling in space, not shielded by big masses from interactions with cosmic radiation. In other words, collisions of bigger bodies took place at the beginning of this time.

It is worth mentioning that the same technique for the estimation of  $^3\text{He}$  by neutron activation is also applicable to the determination of lithium by the  $^6\text{Li}(n,\alpha)^3\text{H}$  reaction in meteorites. Lithium is (at least partially) of radiogenic origin. After driving out the  $^3\text{He}$  from the sample, in a following irradiation only the  $^6\text{Li}(n,\alpha)^3\text{H}$  reaction will contribute to the formation of tritium.

In connection with these investigations on cosmic matter, quite recently Wänke<sup>17, 18, 19</sup> discovered that  $^{45}\text{Sc}$  (the element consists of one stable isotope) is also produced by cosmic radiation in iron meteorites. The scandium concentration lies in the region of  $10^{-9}$  g/g of iron. Relative to the helium and neon contents he found that the scandium content is nearly proportional to the contents of these gases. These results are given in Table 7.

It is found that only a small part (*ca* 10 per cent) of scandium is not of cosmogenic origin. It is indeed remarkable that meteorites with very small amounts of helium also show a very small scandium concentration. From these figures the conclusion can be drawn that cosmogenic helium was never lost by a possible intermediate heating, a possibility which was discussed earlier by several scientists.

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Table 7. Scandium contents of iron meteorites compared with helium and neon contents

(from H. Wänke—to be published)

Meteorite	Weight (kg)	$10^8 \times \text{He content (cm}^3/\text{g)}$	$10^8 \times \text{Ne content (cm}^3/\text{g)}$	$10^9 \times \text{Sc content (g/g)}$	Ratio He/Ne	$\frac{\text{Ratio}}{\text{Sc} - 0.2 \times 10^{-9}}$
						Ne
Savik	66,000	<0.0002	—	0.14	—	—
Muonional Gibeon (Harvard)	7.5	<0.002	—	0.2	—	—
Odessa Gibeon (Amalia)	15,000 large	0.36	—	0.2	—	—
Bendego	5360	3.51	1.98	0.40	177	5
Carbo	450	7.62	4.70	1.1	162	9
Tamarugal	320	21.2	12.9	1.9	167	6.5
Treysa	63	23.1	14.7	2.2	157	6.6
Thunda	60	25.4	19.1	2.1	133	4.9
Mt Ayliff	14	27.1	18.7	2.6	145	6.4
Clark County	11.3	36.2	26.7	3.6	136	6.5
		44.0	33.6	4.7	131	6.6

Further, the following conclusion was made. If the energy of all primary cosmic ray particles lies above  $10^9$  eV, and the generally assumed energy spectrum for the range  $10^9$  eV to  $15 \times 10^9$  eV is correct, the ratio of Sc/Ne should be 1.4. However, even in small meteorites, where spallation reactions induced by low-energy secondary particles are of little influence, the ratio found was about 6.5. From this it is concluded that the primary component of the cosmic radiation contains a relatively high percentage of particles with energies below  $1.0 \times 10^9$  eV, so the "cut-off" in the range  $< 1 \times 10^9$  eV should not exist. The "cut-off" is only effected by the influence of the magnetic field of the earth and the flux of the primary radiation has to be two or three times higher than that measured by rocket and balloon experiments. To understand these conclusions it is necessary to mention that scandium is a special case insofar as its spallation cross-section in iron by protons energies higher than 350 MeV is fairly constant. This is not the case for neon where the cross-section rises sharply with the energy of the incident protons.

Many other applications in the wide field of geochemistry could have been mentioned. The results of radioactivation analysis should shed light on such problems as the cosmic abundance of elements, the distribution relationship of trace elements in different phases, the radioactive balance of mother and daughter substances, etc. An important problem still will remain the study of the course of nucleogenesis, especially of the higher elements.

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<sup>18</sup> H. Wänke. *Report of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*. A/CONF15/P/1962  
<sup>19</sup> H. Wänke. *Z. Naturforsch.* (In preparation). See also *Z. Naturforsch.* **13a**, 645 (1958)  
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## DISCUSSION

G. W. REED (U.S.A.): I should like to discuss some work performed at the Argonne National Laboratory and at the University of Chicago in which activation analysis has been used to determine isotopic compositions of elements present in amounts ranging from  $10^{-6}$  to  $10^{-9}$  g/g. The participants in this work other than myself and Professor Anthony Turkevich (University of Chicago) were Professors H. Hamaguchi and K. Kigoshi of Japan.

I should like to re-emphasize first the versatility of the method. Extremely small quantities, isotope ratios, a large number of elements in the same sample and irradiation, fast as well as slow neutron reactions, freedom from accidental contamination—no prior separations are necessary—are all factors which make this an attractive and, frequently, the only method for doing reliable analyses.

In reply to the physicists I should like to point out that frequently one is measuring a few counts in samples initially having curie levels of activity and it seems unlikely that the chemist can be dispensed with. The experimental results shown were really secondary, except for lead, to the purpose of the experiments which was to measure concentrations.

*Table 8* indicates the sensitivity of the method. As Dr Cook has already pointed out, the two really important factors are the half-life and cross-section. The sensitivities in the last column are based on these values and

Table 8. Nuclear data and sensitivity

Nuclide and reaction	Cross-section of isotope for thermal neutrons (barns)	Half-life of product nuclide	Approximate sensitivity ( $\mu\text{g}$ )
$^{238}\text{U}(n,\gamma,\beta^-)^{239}\text{Np}$	2.8	2.33 d	$10^{-6}$
$^{235}\text{U}(n,f)^{140}\text{Ba}$	4.2	12.8 d	$5 \times 10^{-5}$
$^{232}\text{Th}(n,\gamma,\beta^-)^{233}\text{Pa}$	7	27.4 d	$3 \times 10^{-6}$
$^{209}\text{Bi}(n,\gamma)^{210}\text{Bi}$	0.019	5.0 d	$3 \times 10^{-4}$
$^{208}\text{Pb}(n,\gamma)^{209}\text{Pb}$	0.00045	3.3 h	1
$^{204}\text{Pb}(n,2n)^{203}\text{Pb}$	(0.002) <sub>eff</sub>	52 h	1
$^{203}\text{Tl}(n,\gamma)^{204}\text{Tl}$	11	4.1 y	$2 \times 10^{-4}$
$^{202}\text{Hg}(n,\gamma)^{203}\text{Hg}$	3	46.9 d	$3 \times 10^{-5}$
$^{196}\text{Hg}(n,\gamma)^{197}\text{Hg}$	2500	65 h	$6 \times 10^{-7}$

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Table 9. Terrestrial rocks

Type		Heavy elements ( $\mu\text{g/g}$ )			
		Pb*	Bi	Tl†	U*
Perthite (Tory Hill)	Activation analysis	$6.7 \pm 0.2$	0.011	2.3	0.3
	Literature	9.5		3.1	0.34
Basalt (Snake River)	Activation analysis	$6.8 \pm 0.2$	0.0076	0.073	0.84
	Literature	6.5		0.124	0.8

\* From G. R. Tilton *et al.* *Bull. Geol. Soc. Am.*, **66**, 1131 (1955) and C. Patterson, G. R. Tilton and M. Inghram. *Science*, **121**, 69 (1955).

† Averages of several granites and four basalts from D. M. Shaw. *Geochim. et Cosmochim. Acta*, **2**, 118 (1952).

activity measurements made 18 h after a three-day irradiation at a flux of about  $10^{13}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$ .

Table 9 gives a comparison of our results with measurements made by other methods. The samples were not the same, hence the differences are not surprising. It is obvious that for the relatively large quantities measured the results are in good agreement.

All the results are based on comparison measurements, thus avoiding absolute flux, disintegration rate, half-life and cross-section determinations.

In the data that follow I should like to point out that we were dealing with about  $10^{-6}$  g of barium,  $10^{-9}$ – $10^{-5}$  g of mercury,  $10^{-6}$ – $10^{-5}$  g of lead, and  $10^{-8}$ – $10^{-7}$  g of uranium.

$^{130}\text{Ba}$  and  $^{134}\text{Ba}$  in meteorites have been determined and the results are given in Table 10. The barium measurements were made on electrons

Table 10. Isotopic composition of meteoritic barium

Meteorite	$\frac{(^{135}\text{Ba}/^{131}\text{Ba}) \text{ meteorite}}{(^{135}\text{Ba}/^{131}\text{Ba}) \text{ monitor}}$
Modoc	1.08
	1.00
Holbrook	1.02
Beardsley	0.98
Indarch	0.97
Nuevo Laredo	1.08
Average	$1.03 \pm 0.05$

arising, in the case of 29-hour  $^{135}\text{Ba}$ , from conversion of the gammas associated with the decay of the excited state and, in the case of  $^{131}\text{Ba}$ , from conversion of the gammas arising from 11.6-day orbital electron capture. The measurements were, of course, quite sensitive to sample thickness and the data quoted are from samples and monitors of nearly the same weight. Within 5 per cent the isotopic ratio of these two is the same as for terrestrial barium. The 5 per cent is the uncertainty in the average and could undoubtedly be improved upon in experiments in which such a measurement is the primary purpose. This holds for the results for uranium in Table 11 and also for mercury.

Table 11. Uranium contents of meteorites\*

Meteorite	$10^8 \times \text{U content (g/g)}$	
	via $^{239}\text{Np}$	via Ba- $^{140}\text{La}$
<i>Chondrites:</i>		
Forest City	(1.30) 1.05 0.92	0.97 1.11 $\pm$ 0.18 1.15
Average	0.99	1.06
Modoc	1.08	1.08
Richardton	1.31 1.14 $\pm$ 0.33	1.15 $\pm$ 0.14 1.05 $\pm$ 0.26
Average	1.30	1.13
Holbrook	1.54 $\pm$ 0.25 1.36	1.17 $\pm$ 0.24 1.11 $\pm$ 0.18
Average	1.40	1.12
<i>Achondrite:</i>		
Nuevo Laredo	12.5 12.0 13.2	12.5 10.8 14.0
Average	12.6	12.6
<i>Minerals:</i>		
Hualalai Basalt	46.3	45.2
Twin Cities Dunite	0.10 0.10 $\pm$ 0.08	0.14 $\pm$ 0.07 0.11 $\pm$ 0.05
Average	0.10	0.12

\* H. Hamaguchi, G. W. Reed and A. Turkevich. *Geochim. et Cosmochim. Acta*, **12**, 337 (1957).

The  $^{235}\text{U}$  and  $^{238}\text{U}$  measurements involved preparing different samples in contrast to all the other measurements. One was for neptunium and the others were for barium and lanthanum. In spite of this the meteoritic and terrestrial uranium is shown to have the same isotopic composition to within 10 per cent. Neptunium was measured as a weightless sample from a fixed position in the counter to avoid the complications arising from the large number of low energy betas. Barium and lanthanum have sufficiently hard radiations so that their measurement is not difficult.

Data on the isotopic ratio  $^{196}\text{Hg}/^{202}\text{Hg}$  are shown in Table 12. Weak radiations also make the mercury measurements difficult. It was necessary here, as with all nuclides measured, to prepare scattering and absorption

Table 12. Isotopic composition of mercury in meteorites

Meteorite	$^{196}\text{Hg}/^{202}\text{Hg}$ in meteorite vs monitor
Canyon Diablo Troilite	1.02
Toluca Troilite	1.06
Nuevo Laredo	1.02
Orgueil	0.92
	1.01 $\pm$ 0.06



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vs sample weight curves.  $^{197}\text{Hg}$  decays by electron capture and is particularly sensitive to variations in sample thickness and counting position. The 0.92 value for the last sample arises from the fact that the sample was too "hot" to measure under our standard counting conditions and corrections had to be made.

D. MAPPER (*U.K.*): I think Dr Herr would agree that although he has dealt with the use of activation techniques in age determinations, the method of isotope dilution, *e.g.*, in rubidium-strontium age determination in stone meteorites, is, generally speaking, the best technique to employ. It is in regard to abundance determinations that neutron activation analysis is of the greatest importance. Results on meteorites and rocks illustrating both approaches have recently been published\*. The great advantage of activation analysis is that a large number of elements can be determined on small quantities of sample with complete freedom from the blank and contamination difficulties which are so common in other methods of trace analysis. Activation analysis is now playing a major role in geochemical abundance determinations.

W. W. MEINKE (*U.S.A.*): I should like to describe some work on the radioactivation analysis of meteorites and other materials carried out at the University of Michigan. The facilities of the reactor and hot laboratory of the Michigan Memorial Phoenix Project have been modified to allow measurements on radioisotopes of short half-life.

By means of pneumatic tubes it is possible to bring a sample from the core of the reactor directly into the hood in the neighbouring chemistry laboratory, while an auxiliary tube system carries a prepared counting sample down to the detector for rapid measurement†. A special 100-channel pulse-height analyser with two memories has been constructed for use with radioisotopes of short half-life. One memory is plotted while the other is stored and then, on a given signal, the two memories are switched. Samples can be taken from the reactor to the counting equipment in a total of five seconds plus transfer time and/or radiochemical separation.

The graph obtained when calculated sensitivity values‡ at a flux of  $10^{12}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  for a six-minute irradiation are plotted against the half-lives, and similar graphs for irradiation times of ten and one thousand hours have been published§. Some isotopes with a very high sensitivity, such as rhodium, silver, vanadium, *etc.*, are ideal for radioactivation analysis if a fast radiochemical procedure is developed.

Rhodium, silver and indium have been studied in amounts of 0.1 parts/million in meteorites||. The key to the work on meteorites is the technique, developed by Schindewolf and Wahlgren, of dissolving the finely divided meteorite sample in about  $1\frac{1}{2}$  min by fusion with sodium peroxide in a nickel crucible and then dissolving that solution in hydrochloric acid. Radiochemical procedures have been developed which require only nine minutes for the rhodium and five minutes for the silver determinations.

\* A. A. Smales *et al.* "Some geochemical determinations using radioactive and stable isotopes", *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958*, **2**, 242 (1958).

† These facilities are described in *Nucleonics*, **17**, No. 9, 86 (1959).

‡ U. Schindewolf, *Angew. Chem.*, **70**, 181 (1958).

§ *Anal. Chem.*, **31**, 792 (1959).

|| *Geochim. et Cosmochim. Acta*, **18**, 36 (1960).

The work on the determination of vanadium in samples of oil is similar to that reported by Dr Colard at the first meeting of this Symposium\*. J. Brownlee has worked on the determination of vanadium in samples of oil and cracking catalysts. The results have been reported at the Boston meeting of the American Chemical Society in April 1959 and will be published by *Analytical Chemistry*.

Difficulties are encountered if a cracking catalyst has to be analysed instead of a crude oil sample—a point of considerable importance in the oil industry. The best method of overcoming the difficulties is to treat the cracking catalyst by the same sort of procedure as that used for meteorites. A separation of the vanadium can be made in about ten minutes, and sensitivities in the order of 0.01  $\mu\text{g}$  can be obtained.

On the whole, analysis on vanadium can be made within two or three half-lives of the  $3\frac{1}{2}$ -minute vanadium.

L. GORSKI (*Poland*): It is possible to use the technique of radioactivation analysis in geological wells, but the problems involved are different from those which arise when using a reactor. The concentration of the elements sought is much greater, but the neutron sources are much weaker. We have employed several Po-Be sources or else special neutron generators operating on the T + D reaction. The advantages are considerable. Results are obtained very quickly, and are representative for a wider area than the actual diameter of the well. The method could be employed in prospecting for ores containing copper, vanadium, molybdenum and other metals.

\* See p. 30.