Geochronology: Recent Development in the Lutetium-176/Hafnium-176 Dating Method

Abstract. *The application of the lutetium-176/hafnium-176 method to gram quantities of minerals containing rare earths is made possible by the development of analytical and isotope dilution techniques for microgram amounts of lutetium and hafnium. The geological redetermination of the half-life of lutetium-176 ($3.3 \pm 0.5 \times 10^{10}$ years) is in agreement with recent physical measurements.*

Among the possible radioactive methods of rock dating, the Lu-Hf method has not been fully exploited, mainly owing to analytical difficulties.

A single case of ^{176}Hf enrichment due to β decay of ^{176}Lu has been described on hafnium extracted from a 4-kg sample of gadolinite (*1*). To develop the potential of the Lu-Hf method, determination on a microgram scale of these two elements, as well as confirmation of the half-life of ^{176}Lu, appeared to be necessary (*2*, *3*).

Measurements with Lu and Hf on the microgram scale were made possible by stable isotope dilution techniques. The spikes were enriched in ^{176}Lu and ^{179}Hf, respectively. The mass spectrometer used for the study was a Nier-type 60° deflection instrument equipped with a thermal ionization source and a 17-stage electron multiplier.

The smallest amount of sample that may be isotopically analyzed is of the order of 0.1 μg for Lu [as lutetium chloride ($LuCl_3$) on a single-filament source; ionic form, Lu^+] and 20 μg for Hf [as hafnium oxydichloride ($HfOCl_2$) in a double-filament source, side filament (Re) for vaporization and central filament (Re) for ionization; ionic form, Hf^+ and sometimes HfO^+].

Good separation of Lu and Hf from all the rare earths (but not from Zr) is essential for analysis by mass spectrometry in order to eliminate the isobaric overlap of ^{176}Lu and ^{176}Yb and of ^{176}Hf and $^{176}Yb + {}^{176}Lu$.

Two minerals containing rare earths, previously dated by the Pb/U method, were analyzed for Lu and Hf. [For descriptions of chemical separations, see (*4*).]

There was no loss of these elements during dissolution of the sample, as was shown by identical concentration values obtained from spiked aliquots before and after borax fusion. Purification of the reagents and use of quartz and Teflon vessels brought down the contamination level to the order of 0.3 μg of Hf and 0.02 μg of Lu for a 1-g sample. The measurements are given in Table 1.

For Lu concentration, the precision is 3.5 percent (2 σ). The accuracy of the Lu determination on the gadolinite was checked by neutron activation (*5*), which yielded a value (2020 ± 30 parts per million) in good agreement with our isotope dilution value.

The precision of Hf measurement is no better than 10 percent (2 σ) for several reasons, including the instability of the ion current, the isobaric interference of the rare earths, the poor enrichment of the Hf spike, and the low content of radiogenic ^{176}Hf in the gadolinite. For the common hafnium correction, the measured isotopic composition of shelf hafnium was adopted because, in an environment containing Lu and Hf in the average crustal abundances, the isotopic composition of hafnium is not expected to vary significantly with time.

The two minerals show significant enrichment in radiogenic ^{176}Hf.

The values for the ^{176}Lu half-life calculated from the Pb/U ages and the Lu-Hf measurements are given in Table 1.

The apparent Pb/U ages obtained on the gadolinite [following the procedure described in (*6*)] are given in Table 2, where values for another sample of gadolinite from the same pegmatite are also reported. The three apparent ages are nearly concordant within the limits

Table 1. Lutetium and hafnium measurements on two minerals. The error on the half-life (last column) includes the uncertainty as to the age of the mineral and the errors (to the 95 percent confidence level on spectrometry and calibration) of Lu and Hf concentrations; m.y., million years; ppm, parts per million.

Age (m.y.)	Sample weight (g)	Lu (ppm)	Hf (ppm)	^{176}Hf (rad)* (ppm)	$\frac{^{176}Hf\ (rad)^*}{^{176}Hf\ (total)}$ (%)	^{176}Lu half-life (10^{10} yr)
		Gadolinite of Frikstad (Iveland)				
900 ± 20	1.0				38.0 ± 2.8	
	0.0435	2124				
	0.511	2178†	29.7			
	0.718	2105†	30.6			
	0.644		29.7†	0.92 ± 0.26	37.6 ± 10	3.64 ± 1.0
	1.206		31.2	1.07 ± 0.4	40.0 ± 16	3.14 ± 1.2
Adopted value		2134 ± 60	30.2 ± 3	0.96 ± 0.15	38.0 ± 2.8	3.5 ± 0.7
		Priorite of Mitwaba (Katanga)				
1080 ± 50‡	1.322	1089 ± 30†	3.04 ± 0.34	0.65 ± 0.06	81.0 ± 7	3.2 ± 0.5

* Radiogenic ^{176}Hf. † Spiked after the borax fusion; other entries were spiked before the borax fusion. ‡ Pb/U age measurements (*8*) on sample RGM from the Musée Royal de l'Afrique Centrale.

Table 2. Lead and uranium measurements on two samples of gadolinite from Frikstad, Iveland (Norway). The abbreviation "rad" stands for radiogenic; m.y., million years; ppm, parts per million.

Sample weight (g)	Composition of				Composition (rad) of			Pb (rad) (%)	Pb (rad) (ppm)	U (ppm)	Age* (m.y.)		
	^{204}Pb (%)	^{206}Pb (%)	^{207}Pb (%)	^{208}Pb (%)	^{206}Pb (%)	^{207}Pb (%)	^{208}Pb (%)				$\frac{^{207}Pb}{^{206}Pb}$	$\frac{^{207}Pb}{^{235}U}$	$\frac{^{206}Pb}{^{238}U}$
					Data of Boudin and Deutsch								
0.1030	0.089	39.38	3.97	56.56	40.41	2.77	56.80†	93.6	272.3	906.7	901 ± 20	863 ± 18	857 ± 18
0.1066									270.7	904.3		861 ± 18	854 ± 18
					Data of Herr et al. (*1*)								
	0.073	68.09	5.55	26.30	70.51	4.66	24.83‡				820 ± 30		755 ± 65

*Constants: $\lambda\ ^{238}U = 1.53_5 \times 10^{-10}\ yr^{-1}$; $\lambda\ ^{235}U = 9.72_2 \times 10^{-10}\ yr^{-1}$; $^{238}U/^{235}U = 137.7$. † Corrected Pb composition (*18*): 1/17.28/15.44/37.69 (feldspath of Birkremite, Laksevelefjeld, Egersund; model age, 900 ± 100 m.y. ‡Corrected Pb composition (*1*): 1/18.30/15.59/38.33.

Table 3. Half-life determinations of ^{176}Lu.

Half-life (10^{10} yr)	Method	References
4	β counting, gas counter	(*12*)
7.3 ± 2	β counting with absorbent, gas counter	(*13*)
2.4	β counting, gas counter	(*14*)
2.15 ± 0.1	γ counting, NaI crystal	(*15*)
2.1 ± 0.2	γ counting, NaI crystal	(*16*)
2.8	Proportional β counting, gas counter	(*16*)
2.17 ± 0.35	$^{176}Lu/^{176}Hf$ determination on a dated mineral	(*1*)
3.6 ± 0.1	$\gamma\gamma$ coincidence, NaI crystal	(*9*)
3.2	Proportional β counting with absorbent, gas counter	(*9*)
2.18 ± 0.06	β counting, liquid scintillator	(*17*)
3.5 ± 0.14	γ counting, NaI crystal	(*10*)
3.68 ± 0.06	$\gamma\gamma$ coincidence, NaI crystal	(*10*)
3.56 ± 0.05	β-γ coincidence	(*10*)
5.0 ± 0.3	γ-γ coincidence, NaI crystal	(*11*)
3.3 ± 0.5	$^{176}Lu/^{176}Hf$ determination on two dated minerals	This report

of error; they indicate an age of crystallization of 900 ± 20 million years, in good agreement with ages (880 to 930 million years) of other pegmatitic minerals in the same region (*7*).

The three Pb/U ages on the priorite are also concordant, around 1080 ± 50 million years (*8*).

The values for the half-life of ^{176}Lu deduced from the two minerals agree with each other within their limits of error; thus it may reasonably be admitted that both minerals have behaved as closed systems for Lu and Hf since their crystallization. The weighted average value is $3.3 \pm 0.5 \times 10^{10}$ years. The weight of each determination is inversely proportional to its precision.

The various determinations of the half-life of ^{176}Lu given in Table 3 range from 2 to 7×10^{10} years. The physical determinations of MacNair (*9*) and of Brinkman *et al.* (*10*) are in agreement and seem to be the most reliable. Brinkman *et al.* extracted the radioactive impurities from the Lu and found concordant values close to 3.6×10^{10} years by three counting methods.

Our determination agrees with this value within the limits of error. It definitely differs, however, from a recent value of 5.0×10^{10} years (*11*).

The geological determination of Herr *et al.* ($2.17 \pm 0.35 \times 10^{10}$ years) (*1*) is significantly lower. A possible explanation is that their sample did not behave as a closed system either for Lu and Hf or for U and Pb. Losses of lead may be inferred from the admitted age of 810 million years, which is lower than the age of pegmatitic minerals from the same region, and from the discordancy of the apparent Pb/U ages.

Additional Lu-Hf determinations on other dated minerals are necessary to obtain a more precise value for the half-life of ^{176}Lu and to obtain information about the geochemical behavior of these two elements. The analytical and the isotope dilution techniques already developed permit the application of the $^{176}Lu/^{176}Hf$ dating method to 10 g of minerals that are 1000 million years old and that contain 100 parts per million of Lu.

ANDRÉ BOUDIN
SARAH DEUTSCH
Service de Géologie et Géochimie Nucléaires, Université Libre de Bruxelles, Brussels, Belgium

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19. We thank Professor E. Picciotto, who suggested this work. Supported by the Belgian Institut Interuniversitaire des Sciences Nucléaires. One of us (A.B.) received support from the Belgian Fonds National de la Recherche Scientifique.

15 December 1969; revised 7 February 1970 ■

Experimental Allergic Encephalomyelitis: Synthesis of Disease-Inducing Site of the Basic Protein

Abstract. *A highly encephalitogenic peptide whose structure resembles the sequence of amino acids surrounding the single tryptophan residue in the encephalitogenic A1 protein from bovine myelin was synthesized. This peptide is similar in the sequence to peptic peptide E and tryptic T27, derived directly from the A1 protein, and is as active on a molar basis as the A1 protein. The major disease-inducing site of the A1 protein resides in a linear sequence of nine amino acids: H-Phe-Ser-Trp-Gly-Ala-Glu-Gly-Gln-Lys-OH. This region of the A1 protein is apparently the major encephalitogenic determinant since specific modification of the tryptophan residue in the A1 protein with 2-hydroxy-5-nitrobenzyl bromide destroyed its encephalitogenic activity.*

The factor in the central nervous system responsible for experimental allergic encephalomyelitis (EAE) is a basic protein (A1 protein) present in myelin where it constitutes at least 30 percent of the total protein (*1*, *2*). At doses of 0.1 μg or greater, the A1 protein induces EAE (*1*) in guinea pigs. The pathogenesis of EAE appears to be associated with an immune response involving sensitized lymphocytes (*3*), presumably by a delayed-type hypersensitive mechanism. Thus, EAE provides a useful model for the study of autoimmune disease and may have relevance to some human demyelinating diseases such as multiple sclerosis.

The Al protein is a basic protein