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Geochemical estimation of the half-life for the double beta decay of ^{96}Zr

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An excess amount of ^{96}Mo found in a 1.7×10^{9} yr zircon sample from Cable Sands' Western Australia, yielded a half-life of $(3.9\pm0.9)\times10^{19}$ yr for the double beta decay of ^{96}Zr to ^{96}Mo.

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The precise determination of the decay constant of double beta decay has put a constraint on, and is expected to verify, the mass of the neutrino [1]. The half-life for this type of decay is estimated to be of the order of $10^{18}-10^{21}$ yr, as shown in the half-lives of 1×10^{20} yr for ^{82}Se and 8×10^{20} yr for ^{130}Te [2]. Accordingly, it is difficult to directly detect the radioactivity accompanying double beta decays using counting methods. An alternative approach to counting methods is the detection of the decay product accumulated in very old natural minerals. In the present work, we have attempted to estimate the half-life of double beta decay of ^{96}Zr from the amount of radiogenic ^{96}Mo found in the Zr mineral. It is noted, however, that the concentration of molybdenum in natural zircon ($ZrSiO_4$) appears to be in the ppm range, which is too high a background to enable us to detect the ^{96}Mo "anomaly." Furthermore, the sensitivity of molybdenum in thermal ionization mass spectrometry (TIMS) is relatively low because of the high ionization potential of Mo. These difficulties hampered the success of a previous attempt [3]. Therefore, it was necessary to develop sophisticated empirical techniques in order to detect the positive anomaly of ^{96}Mo in the Zr mineral.

We analyzed 5.39 g of placer zircon found in a region south of Bunbury, Western Australia, which was provided from Cable Sands Pty. Ltd. The geological age was determined based on a measurement of the isotopic composition of lead and on the method by Kroth [4], and found to be 1.67×10^{9} yr. The samples contained over 99% of zircon. This was confirmed by an analysis of zirconium with an ICP-MS after chemical dissolution of zircon (see below).

Natural zircon ($ZrSiO_4$) usually contains a few ppm of molybdenum. Molybdenum, however, is believed to be present as a mineral inclusion (perhaps molybdenite, MoS_2) and the proportion of Mo substituting for Zr ions in the crystal lattice is anticipated to be low. Thus it is expected that radiogenic ^{96}Mo is not present in molybdenite inclusions but can be detectable in intrinsic portions of zircon. In order to reduce the Mo background and to find out the isotopic effect on Mo due to double beta decay of ^{96}Zr, molybdenite inclusions must be removed from the zircon mineral. For this purpose, the crystals of zircon were crushed to a fine powder and treated with aqua regia to remove the molybdenite inclusions. Zircon is not eroded by this treatment, and the molybdenum produced by the decay of zirconium is considered to be maintained in the pure zircon crystal grains.

Zircon, which had been treated with aqua regia, was then dissolved by hydrofluoric acid (ten times the weight of the zircon sample) and a few drops of nitric acid in acid digestion bombs. (Prior to treatment with aqua regia, the sample had been heated overnight with HF + $HClO_4$ to remove silicate impurities.) After concentrating the sample solution, hydrochloric acid was added. Molybdenum was extracted by 4-methyl 2-pentanone (methyl isobutyl ketone) and back-extracted by water [5]. The solution was evaporated to dryness, followed by the addition of dilute hydrochloric acid. An anion exchange resin column was employed to separate the molybdenum from the zirconium [6]. The eluate containing the molybdenum was evaporated to dryness again, and the second separation of Mo from Zr and other impurities was performed using another anion exchange resin column following the procedure as described above. Finally, a cation exchange resin column was used to complete the removal of Mo from Zr.

After the resulting solution containing the purified Mo was evaporated to dryness, 4 μl of a reducing solution with the composition of 15 mg ascorbic acid and 40 mg ammonium iodide per gram of HCl (6*M*) solution was added to the residue. The oxidation state or valency of molybdenum in the sample solution was thus reduced from +6 to +3 to depress the volatility of the molybdenum during the mass spectrometer measurement. The sample solution was then loaded on a rhenium single filament of the ion source of the TIMS. Small amounts of a mixed powder of rhenium and platinum Re:Pt = 1:2 were added to enhance the ionization efficiency of molybdenum. (Pt was mixed because of its relative high work function, and Re powder was added to increase the surface area of the ionizing filament.)

The TIMS method used in this work involved a VG Sector 54 mass spectrometer (54 cm ion beam radius) manufactured by VG Co. The ion beam was detected using a Daly detector system, a type of photomultiplier. An ion beam current of 3×10^{-15} A was maintained for 3 h. It is worthwhile to note that the rhenium ribbon, which is used as a filament for thermal ionization in the

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TABLE I. Measurement of isotope ratios of molybdenum in zircon.

	Raw data[a]	Corrected[b]	Relative std. error (%)	Standard	Apparent[c] deviation (%)
^{92}Mo/^{95}Mo	1.069 79	0.941 32	0.040	0.9322	0.978
^{94}Mo/^{95}Mo	0.709 21	0.579 63	0.033	0.5810	−0.235
^{96}Mo/^{95}Mo	1.064 59	1.042 91	0.035	1.0477	−0.457
^{97}Mo/^{95}Mo	0.597 85	0.597 85	0.033	0.5999	−0.342
^{98}Mo/^{95}Mo	1.500 57	1.500 57	0.045	1.5157	−0.998
^{100}Mo/^{95}Mo	0.596 15	0.596 15	0.042	0.6049	−1.447
^{90}Zr/^{95}Mo	0.384 43				

[a] Without correction for the isobaric effects from Zr$^+$.

[b] With correction for Zr$^+$ isobaric effects, based on the observed ^{90}Zr/^{95}Mo ratio, but without any correction for the isotope fractionation effect.

[c] Including the isotope fractionation effect, which will be corrected later by a normalization procedure.

ion source, contains a trace amount of Mo as an impurity, and the Mo ions originating from this impurity can be emitted at an elevated temperature of the ion source filament. It is therefore important to maintain the temperature of the rhenium filament within an optimum range, to avoid isotopic contamination from the rhenium ribbon.

The concentrations of lead and uranium in zircon were determined by using the ICP atomic emission spectrometer. The isotopic composition of lead in zircon was measured by TIMS after separation from the zirconium matrix.

Raw data on the molybdenum isotopic composition are presented in Table I. The reliability of our data is supported by the values of the relative standard error (0.033–0.045%). The apparent deviations between the data observed for our sample and IUPAC's data are shown in Fig. 1. As is well known, in any case of mass spectrometry using thermal ionization, a considerable amount of mass fractionation takes place, and a correction to the measured data is made usually by assuming a fixed value for a pair of isotopes which are independent of any nuclear reactions or decays.

The pattern of deviations in Fig. 1 reflects the common isotope fractionation effect plus additional nuclear effects. Molybdenum has seven stable isotopes, and the abundances of five isotopes can be affected by the effects of two nuclear processes: ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo are produced by spontaneous fission of uranium, and ^{96}Mo by double beta decay of ^{96}Zr. Therefore, ^{92}Mo and ^{94}Mo are the most appropriate to be chosen for the correction of the mass fractionation effect by means of normalization. According to IUPAC's data, $^{92}\mathrm{Mo}/^{94}\mathrm{Mo} = 1.6043$, but we have employed the normalizing value of 1.6051 on the basis of our experimental data. It will be confirmed later that the difference in normalization has little effect on the final result.

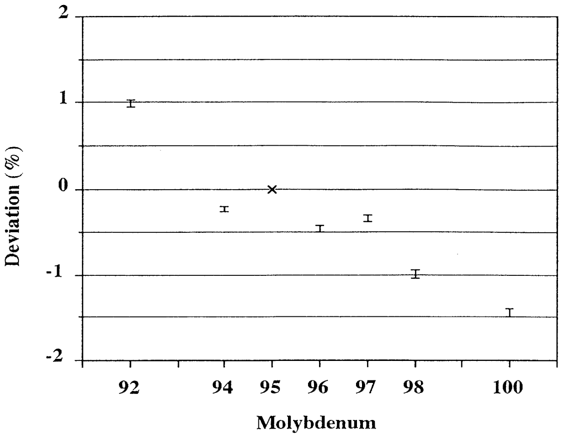

FIG. 1. Apparent unnormalized deviations (see Table I) of molybdenum isotopes in Cable Sands' zircon, relative to ^{95}Mo.

For normalization of the isotopic abundance ratios, a power law [7] was used. This method can be expressed using the following equation:

$$\left[\frac{{}^{x}\mathrm{Mo}}{{}^{94}\mathrm{Mo}}\right]_t = \left[\frac{{}^{x}\mathrm{Mo}}{{}^{94}\mathrm{Mo}}\right]_r \left\{\frac{({}^{92}\mathrm{Mo}/{}^{94}\mathrm{Mo})_s}{({}^{92}\mathrm{Mo}/{}^{94}\mathrm{Mo})_r}\right\}^a ,$$

where $a = (94-x)/(94-92)$, ^{x}Mo refers to a molybdenum isotope with mass number x, t to a theoretical value, r to an observed value, and s to a standard value.

The isotope fractionation of the ^{92}Mo/^{94}Mo ratio presented in Table I is 1.2% in reference to the standard value. It is noted here that isotope fractionation often occurs to a similar extent in the measurement of the ^{88}Sr/^{86}Sr ratio using trace amounts of Sr. Normalized data are presented in Table II and the deviation pattern is shown in Fig. 2. The isotopic deviation pattern for molybdenum shown in Fig. 2 clearly exhibits the effect of the spontaneous fission of ^{238}U.

At present, there are no data of "directly" measured molybdenum isotope yields from spontaneous fission of ^{238}U. However, one can collect the relevant values from individually separate fragmentary sources [8–10], which are summarized in Table III. The relative errors of the yields radiochemically determined are not so small, with the value for ^{138}Cs and its mirror nuclide ^{98}Mo involving the largest uncertainty. The yield of ^{100}Mo which is estimated from the mirror nuclide relation [11] appears to be most precise. A scrutiny of the original data [10], however, discloses that the apparent high precision for ^{100}Mo refers to the empirical error only, and does not give an assurance that the sample used (Clinch Lake pitchblende) is free from any loss of fissiogenic xenon.

TABLE II. Isotope ratios of molybdenum in zircon.

	Unnorm.[a]	Norm.[b]	Std. error[c] (%)	Standard	Deviation[d] (%)
^{92}Mo/^{94}Mo	1.623 98	1.605 1	0	1.6051	0
^{95}Mo/^{94}Mo	1.725 23	1.735 343 3	0.053	1.7211	0.828
^{96}Mo/^{94}Mo	1.799 26	1.820 445 2	0.075	1.8032	0.956
^{97}Mo/^{94}Mo	1.031 43	1.049 704 5	0.093	1.0324	1.676
^{98}Mo/^{94}Mo	2.588 82	2.650 155 0	0.125	2.6086	1.593
^{100}Mo/^{94}Mo	1.028 49	1.065 269 5	0.165	1.0411	2.322

[a] Corrections have been made for zirconium isobaric effects on ^{92}Mo, ^{94}Mo, and ^{96}Mo based on the observed ^{90}Zr/^{95}Mo ratio (cf. Table I).

[b] Normalized against ^{92}Mo/^{94}Mo = 1.6051, taken from the standard.

[c] After IUPAC.

[d] After normalization based on ^{92}Mo/^{94}Mo ratio.

Thus the yield value, 6.3%, for ^{100}Mo should be taken as a minimum value. Accordingly, the use of the set (Table III) synthesized from scattered references would inevitably introduce rather large ambiguity into the results of the discussion about the nuclear effect pattern for molybdenum isotopes.

On the other hand, there exist mass spectrometric direct measurements pertaining to the yields of molybdenum isotopes in neutron-induced fission of ^{238}U or ^{239}Pu. These yields are listed in Table IV (Ref. [12]). A comparison of the data in Table IV with those in Table II shows that the numerical values of three sets of yield values in Table IV are much closer to each other than to those of the set presented in Table III. As evident from the foregoing consideration, the values in Table IV are considered to be more dependable than those in Table III. If any particular set of yield values in Table IV are employed, it would give rise to only a small difference in the results of calculations. However, since the thermal neutron fission of ^{239}Pu can be judged to potentially resemble the spontaneous fission of ^{238}U, taking into account its energy level, the thermal fission yields for molybdenum isotopes from ^{239}Pu are adopted here for the spontaneous fission of ^{238}U. The relative effects estimated for the spontaneous fission of ^{238}U are plotted in Fig. 2. It is observed that the resultant deviation effects are in good agreement with the fissiongenic effects for ^{95}Mo, ^{97}Mo, and ^{100}Mo.

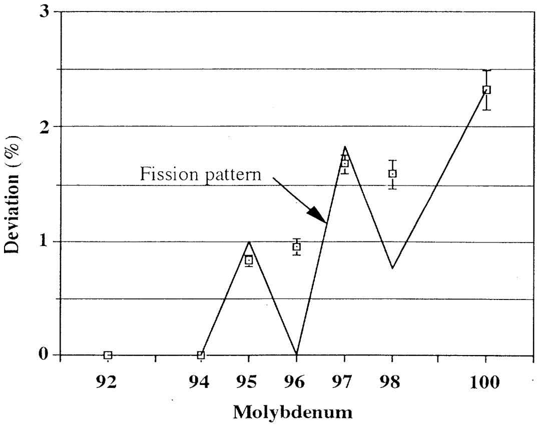

FIG. 2. Normalized relative deviations of molybdenum isotopes in Cable Sands' zircon. [The total amount of Mo for the sample (5.39 g) is estimated to be 1.46 ng.]

The positive anomaly of ^{96}Mo can be regarded as resulting from the double beta decay of ^{96}Zr. To begin with, the amount of radiogenic ^{100}Mo produced by spontaneous fission of ^{238}U is calculated from the concentration of uranium in zircon (130.5 ppm), half-life of spontaneous fission of ^{238}U (8.2×10^{15} yr) [13], half-life of alpha decay of ^{238}U (4.47×10^{9} yr), and fission yield of ^{100}Mo (7.1%) (cf. Table IV). Based on the amount of radiogenic ^{100}Mo calculated from these parameters and the age, the amount of radiogenic ^{96}Mo derived from ^{96}Zr has been evaluated to be 2.3 pg from the extent of deviation observed for ^{96}Mo relative to that for ^{100}Mo. Taking into account the formation age of zircon and the sample amount decomposed, the half-life of ^{96}Zr is evaluated to be 3.9×10^{19} yr. If the error is taken into account, the value turns out to be $(3.0-4.8)\times10^{19}$ yr (68% confidence level).

Our calculation is based on the normalization value of ^{92}Mo/^{94}Mo=1.6051. If the IUPAC value 1.6043 is adopted, one can obtain a result of 4.0×10^{19} yr. Meanwhile, if the yield of ^{100}Mo is taken to be 6.6% corresponding to the fast neutron-induced fission of ^{238}U (see Table IV), the half-life of the double beta decay of ^{96}Zr comes out 4.2×10^{19} yr.

Another sample was investigated using the same method. It was also a placer zircon provided by Westralian Sands Ltd., with a formation age of 1.8×10^{9} yr. The isotopic composition of molybdenum in this sample is shown in Fig. 3. From these data, the half-life of dou-

TABLE III. Yields of nuclides leading to, or closely associated with, molybdenum isotopes in spontaneous fission of ^{238}U.

Mass	Measured nuclide	Mirror nuclide[a]	Yield (%)	
95	^{95}Zr		5.3±1.3	Radiochemistry [8]
97	^{97}Zr		6.6±1.3	Radiochemistry [8]
98	^{138}Cs	^{98}Mo[a]	7.7±?	Radiochemistry [9]
100	^{136}Xe	^{100}Mo[a]	6.3±0.38[b]	Mass spectrom. [10]

[a] cf. Ref. [11]; if two neutrons are emitted, the mirror nuclide of ^{136}Xe is ^{100}Mo, but the emission of three neutrons yields the mirror nuclide ^{99}Ru.

[b] See discussion in text.

TABLE IV. Molybdenum isotope fission yields (%) by fast and thermal neutrons (Ref. [12]).

	^{238}U (fast)	^{239}Pu (fast)	^{239} Pu (thermal)
^{92}Mo	0	0	0
^{94}Mo	0	0	0
^{95}Mo	5.28	4.71	4.98
^{96}Mo	0	0	0
^{97}Mo	5.55	5.21	5.54
^{98}Mo	5.79	5.64	5.87
^{100}Mo	6.60	6.59	7.08

ble beta decay of ^{96}Zr was calculated to be $(7.2\pm2.4)\times10^{19}$ yr, and this value is consistent with that of Cable Sands' zircon. Also note that the deviation pattern for the Westralian Sands' sample is very similar to that for Cable Sands' although the empirical uncertainties are larger for Westralian Sands' zircon in our measurements. Because of a higher precision for Cable Sands' zircon, our attention is directed to this sample.

There exists a clear "positive anomaly" of ^{98}Mo compared with the value expected from fission. There is a possibility that this unexpected anomaly is an artifact caused by a molecular ion. However, this can be refuted for two reasons. First, we could recognize the reproducibility of this anomaly in the same sample. Second, this anomaly was constant during a measurement for three hours. (The "strange excess" of ^{98}Mo corresponds to 3.0 pg in 5.39 g of zircon.)

There can be two other possible explanations of the anomaly in question. First, the disparity is interpreted to suggest that the spontaneous fission yield of ^{98}Mo may be strikingly different from that of the neutron-induced fission. But in view of the good fittings to ^{95}Mo and ^{97}Mo on the basis of ^{100}Mo, this interpretation is not definitely plausible.

The second possibility is that the ^{98}Mo excess in question may reflect the electron-capture product of ^{98}Tc. However, the half-life of ^{98}Tc is 4.2×10^{6} yr [13] and is too short to survive from nuclear synthesis in a supernova. Another question is that ^{98}Tc is reported to encounter beta decay, not electron-capture decay. Accordingly, so far as the currently available information on ^{98}Tc is concerned, the second possibility would be too speculative to be accepted at present. But it would be worth mentioning that some doubt might be cast on the soundness of current nuclear knowledge about ^{98}Tc, and that the valency of technetium can be $+4$ and its geochemical behavior can be similar to that of zirconium and/or uranium (IV). (According to nuclear physics [13], the Q values of beta decay and electron capture for ^{98}Tc are found to be 1.792 MeV and 1.682 MeV, respectively. Therefore, one cannot rule out the possibility that ^{98}Tc can be subjected to a branching disintegration of beta decay and electron capture.)

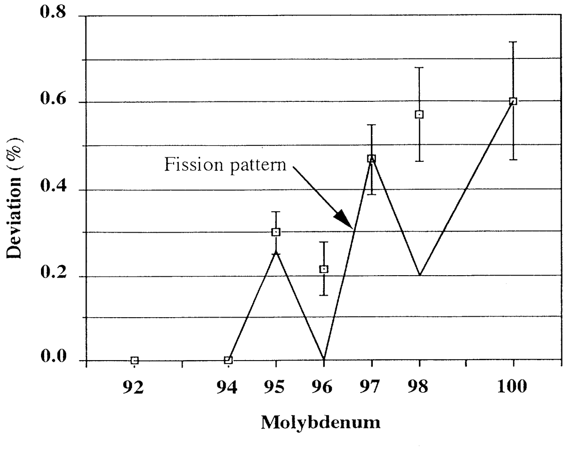

FIG. 3. Normalized relative deviations of molybdenum isotopes in Westralian Sands' zircon. [The total amount of Mo for the sample (3.52 g) is estimated to be 2.50 ng.]

Previously, the geochemical approach aiming at estimating the half-life of double beta decay has been successfully applied to only two nuclides, ^{130}Te and ^{82}Se. In contrast with these two cases resulting in a production of rare gases, the decay product of ^{96}Zr geochemically studied here is a solid element. Consideration will be given here to the half-life of ^{96}Zr (3.9×10^{19} yr, $Q=3.353$ MeV) in comparison with the half-lives of other double beta decay nuclides [2] which were geochemically investigated:

$$^{130}\mathrm{Te}\ \text{to}\ ^{130}\mathrm{Xe},\ T_{1/2}=8.0\times10^{20}\ \text{yr},\ Q=2.534(\mathrm{MeV})\ ,$$

$$^{82}\mathrm{Se}\ \text{to}\ ^{82}\mathrm{Kr},\ T_{1/2}=1.0\times10^{20}\ \text{yr},\ Q=3.00\ (\mathrm{MeV})\ .$$

Based on classical theory, Primakoff and Rosen [15] derived the conclusion that, if all of the nuclear matrix elements have the same value, the half-life of two neutrino double beta decay would be inversely proportional to the tenth power of decay energy [14]. This is identical to the fact that the logarithm of the half-life is proportional to the logarithm of the decay energy, with a correlation coefficient of -10. In Fig. 4 are plotted the logarithms of the theoretical and experimental values of the half-lives against the logarithm of the decay energy. The slope of the line for the theoretical values is about -10, consistent with theory. The experimental values of three nuclides geochemically studied also appears to be about -10; the least squares method yields -10.8. If the half-life of ^{130}Te is taken to be 7×10^{20} yr (Ref. [16]), the coefficient under consideration becomes -10.4. In addition, if the half-life of ^{96}Zr is taken to be 4.2×10^{19} yr (see above), the coefficient turns out to be -10.2. The deviation of each experimental value from the theoretical line is considered due to uncertainty in nuclear matrix elements. (The absolute value geochemically obtained for ^{96}Zr is higher than the theoretically estimated one by a factor of 8.)

Anyway it can be seen that our data on ^{96}Zr are in line with the values geochemically determined for ^{82}Se and ^{130}Te. As mentioned above, in the case of these two nuclides, the daughter nuclides ^{82}Kr and ^{130}Xe are rare gases. As a result, there is a probability of the daughter nuclides escaping from the parental elemental minerals over the geochemical time frame. The apparent consistency observed here for three nuclides including ^{96}Zr would endorse the belief that the half-lives currently adopted for ^{82}Se and ^{130}Te are free from an effect of loss due to escape.

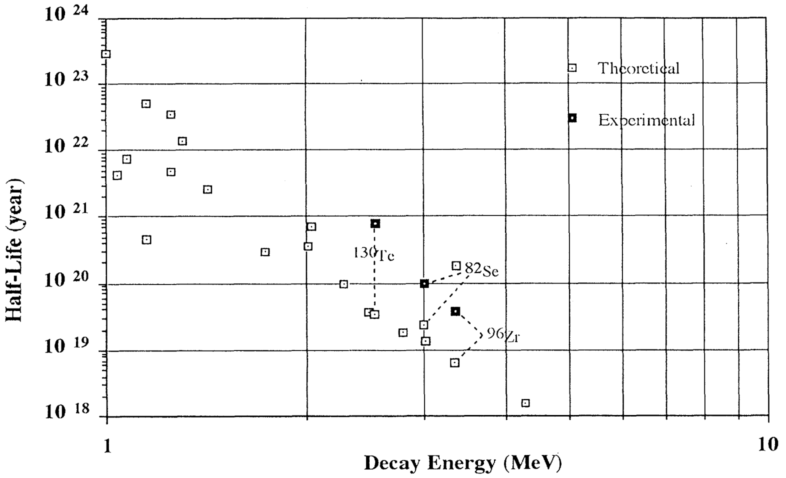

FIG. 4. Correlation between decay energy and half-life of double beta decay.

The very low concentrations of long-lived radioactive nuclides such as ^{40}K, ^{87}Rb, ^{147}Sm, and ^{238}U in minerals of Se and Te have often posed serious difficulties in the age determination of minerals. But zircon contains a sufficient amount of uranium to give the precise age based on uranium-lead dating.

Thus the system studied here is advantageous in five respects: (1) The "authentic" content of molybdenum in zircon is very low, (2) the geological formation age can be determined easily by U-Pb dating, (3) the fissiogenic molybdenum isotopes produced from spontaneous fission of ^{238}U can serve as an internal standard or spike in a quantitative estimation of radiogenic ^{96}Mo excess under consideration, (4) the deviation patterns of ^{95}Mo, ^{97}Mo, and ^{100}Mo are helpful in checking the appropriateness of the results, although there remains a question about ^{98}Mo, and (5) the nuclide produced by the decay can be retained well in the host mineral. It is expected that a more precise measurement of molybdenum isotopes in zircon will shed more light on double beta decay.

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