Evidence of the double β decay of zirconium-96 measured in 1.8×10^9 year-old zircons

Michael E. Wieser* and John R. De Laeter
Department of Applied Physics, Curtin University of Technology, G.P.O. Box U 1987, Perth 6845, Western Australia

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Molybdenum extracted from geologically old zircons shows evidence for enhanced levels of ^{96}Mo, resulting from the double β decay of ^{96}Zr. Evidence of nuclear fission in ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo extracted from the old zircons accompanies the double β decay of ^{96}Zr, and is comparable in magnitude to the excess ^{96}Mo. Zircons are excellent minerals for an experiment of this nature, since zircon U-Pb geochronology demonstrates that zircons have remained as closed isotopic systems over eons of time. The experimental data indicate that the half-life of ^{96}Zr double β decay is $(9.4\pm3.2)\times10^{18}$ yr and is in good agreement with the theoretically predicted half-life for the ^{96}Zr decay to ^{96}Mo occurring as a two neutrino decay.

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I. INTRODUCTION

Double β decay is the rarest nuclear phenomenon in nature. In double β decay, a nucleus undergoes a transmutation from one element to another such that two electrons are emitted rather than the single electron emitted in the more commonly observed single β decay. All the parent and daughter isotopes involved in double β decay are even-even nuclei. The pairing force acting between like nucleons is responsible for the increase in the binding energy of these nuclei relative to the odd-odd isotopes, thus preventing single β decay. The basic instability of certain *r*-only process nuclides (as determined by atomic mass data), contrasts with their present abundance distribution which can only be explained if double β decay rates have an extremely small probability. For example, in the Zr-Ru mass region, Fig. 1 shows the *s*-process neutron capture path from ^{90}Zr to ^{102}Ru as well as the major nucleosynthetic processes for each of the stable isotopes. Molybdenum has two *p*-process nuclides (^{92}Mo and ^{94}Mo), one *s*-process nuclide (^{96}Mo), three nuclides which are produced by a mixture of *s* and *r* processes (^{95}Mo, ^{97}Mo, and ^{98}Mo) and one *r*-only process only nuclide (^{100}Mo). This latter isotope double β decays to ^{100}Ru whereas ^{96}Zr double β decays to ^{96}Mo.

There are two approaches to measuring the half-life of a double β decay reaction. In the direct detection method, coincidence counting is used to measure the radioactivity at the energy value predicted from precise atomic mass measurements [1]. The disadvantage of the radioactive counting method is that intrinsically faster radioactivities, such as those associated with uranium or thorium decay, produce significant backgrounds that may mask the β decay product. Instrumental experiments are designed to detect the electrons as they are emitted and are thus capable of not only measuring the lifetime of the double β decay, but also the electron energy spectrum.

The second approach to measuring the half-life of double β decay reaction is based on the cumulative effects of double β decay over geological time. This geochemical method depends on the mass spectrometric determination of stable double β decay products that have accumulated in geologically old minerals. The geochemical method does not directly determine the decay mode as is possible in the direct determination method. It indicates only the total decay probability of the decay channels.

The geochemical method is most likely to succeed if little of the daughter element was incorporated when the mineral of the parent element formed. The likelihood of this separation occurring in nature is enhanced if the geochemical nature of the double β decay product is radically different from that of the parent element. Success also depends on the mineral being geologically old and having survived intact over a long period of time so that detectable quantities of the daughter have accumulated in the mineral. Hard, high temperature minerals have a favored chance of surviving temperature/pressure variations to which the minerals may have been exposed during their geological history.

Geochemical measurements of double β decay have, until recently, been confined to the measurement of gaseous daughter products (by gas source mass spectrometry), which have accumulated in old tellurium and selenium minerals. The double β decay of ^{130}Te to ^{130}Xe is a favorable experimental situation because ^{130}Te is the most abundant nuclide of Te, old telluride minerals of high concentration are available, and the mass spectrometry of Xe can be carried out with high sensitivity. Inghram and Reynolds [2] first estimated the half-life of ^{130}Te for double β decay to be 1.4×10^{21} yr. Since that time, many ^{130}Te decay experiments have been carried out and a summary is given by Manuel [3]. Similar mass spectrometric determinations have been made for ^{128}Te and ^{82}Se [3].

The major analytical shortcoming of the Te/Xe and Se/Kr decay systems is that their daughters are gaseous, and therefore may have suffered some leakage from the ore sample over the long time period since the minerals were formed. Minerals of tellurium and selenium are particularly susceptible to gas loss because they are soft, low temperature minerals that may have recrystallized and lost radiogenic Xe or Kr during any deformation event or high temperature phase subsequent to mineralisation. Richardson *et al.* [4] have shown that gas retention ages are significantly less than min-

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*Permanent address: Department of Physics and Astronomy, University of Calgary, Alberta, Canada.

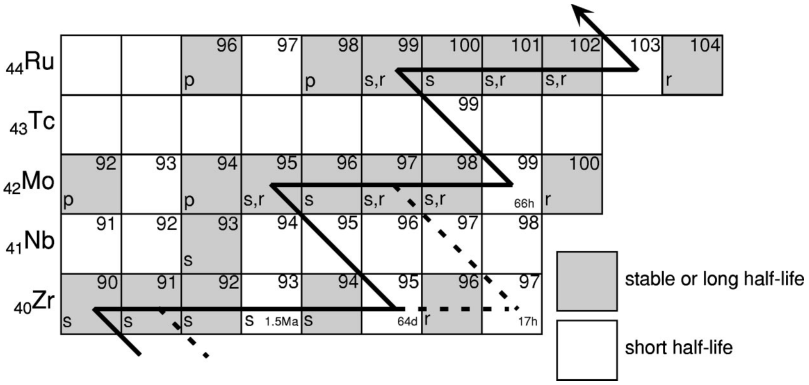

FIG. 1. Chart of the nuclides in the region of Zr and Mo. The *s*-process neutron capture path and the *r*-process produced isotopes are indicated.

eralization ages. Bernatowicz *et al.* [5], in a high precision Te/Xe experiment, determined the ratio of half-lives for the double β decays of ^{130}Te/^{128}Te to be $(3.52\pm0.11)\times10^{-4}$ using techniques to reduce interference due to trapped Xe. Half-lives of the ^{130}Te and ^{128}Te double β decays are $(2.7\pm0.1)\times10^{21}$ yr and $(7.7\pm0.4)\times10^{24}$ yr, respectively.

Doi *et al.* [6] list the various double β decay schemes in terms of the available disintegration energies calculated from their atomic masses [7]. The magnitude of the half-life is strongly dependent on the magnitude of the disintegration energy. The ^{96}Zr/^{96}Mo double β decay scheme is a favorable experimental situation in that the disintegration energy available for the reaction is 3350 ± 3 keV, old zirconium-rich minerals (e.g., zircon and baddeleyite) are available, and common Mo is not incorporated in the lattice of these minerals to any great extent.

Twenty years were to elapse from the time Pauli suggested the existence of a neutrino to the time when Inghram and Reynolds [2] determined the half-life of ^{130}Te double β decay using gas source mass spectrometry, and a further seven years before neutrinos were discovered [8]. However, it was not until 1993 that the half-life of double β decay was measured by thermal ionization mass spectrometry (TIMS). A thermal ionization mass spectrometer procedure was developed to improve the sensitivity for Mo isotope analysis by the use of ion-enhancing media. This enabled Kawashima *et al.* [9] to report a value of $(3.9\pm0.9)\times10^{19}$ yr for the double β decay of ^{96}Zr by measuring excess ^{96}Mo in old zircon samples. The measured half-life for ^{96}Zr is approximately 70 times shorter than the half-life of ^{130}Te [5]. However, it should be noted that theoretically predicted ^{130}Te decay rates are generally 1 to 2 orders of magnitude faster than the geochemically determined rates [5] and there is at least the possibility that geochemically determined half-lives for ^{130}Te are in error [5].

Zircons have a particularly tight lattice structure and this property has been successfully exploited in U-Pb geochronology because the radiogenic Pb has remained *in situ* over extensive geological periods. It would therefore be expected that the solid daughter ^{96}Mo generated by double β decay from ^{96}Zr would also be retained in the zircon lattice, in contrast to gaseous daughter products such as ^{130}Xe and ^{82}Kr in tellurium and selenium minerals. However, the presence of U in zircons generates fission products that make the mass spectrum of Mo extracted from zircons more complex than that of Xe extracted from telluride ores because of the almost complete absence of U in tellurides. Kawashima *et al.* [9] reported anomalous Mo at ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo, which they assumed was due to nuclear fission. Since the spontaneous fission yields of ^{238}U for Mo have not been measured, Kawashima *et al.* [9] assumed that they approximated to that of the thermal neutron fission of ^{239}Pu. These authors also reported a “strange excess” in ^{98}Mo, which they were unable to explain. An additional challenge is the existence of isobaric interference of Zr at mass numbers 92, 94, and 96 that overlap with the Mo isotopes being measured. In practice, it is extremely difficult to remove Zr contamination completely from Mo extracted from zircon crystals. Since one of the isobaric interferences occurs at ^{96}Mo, which is the key isotope in the determination of the double β decay half-life of ^{96}Zr, this places stringent requirements on the chemical separation procedure.

Despite these difficulties, the work of Kawashima *et al.* [9] has shown that isotopic systems, other than those with gaseous daughters, can be used to measure the half-life for double β decay. The measured value of the half-life of ^{96}Zr, reported by Kawashima *et al.* [9], is an exciting advance in double β decay measurements because of the implications of the lower half-life to particle physics. However, Moe and Vogel [10], in a review of double β decay experiments, concluded that the half-life of ^{96}Zr is not as firmly established as half-lives obtained from the noble gases, and recommended that another independent experiment should be performed on this double β decay scheme. This paper reports the result of such an experiment.

II. EXPERIMENTAL PROCEDURE

Reagents used for the dissolution of the zircons and separation of molybdenum by ion exchange were prepared by sub-boiling distillation and, in the case of HCl, by bubbling HCl gas through ultra high purity water. The ultra high purity water was prepared from tap water pretreated by reverse osmosis prior to filtration by a Milli-Q water filtration system (Millipore, MA). PFA Teflon beakers were refluxed with aqua regia, followed by 4M HCl and Milli-Q water prior to use. All separations were performed in a clean room under HEPA-filtered air.

Separated zircon samples from the Yoganup Strand Line were obtained from mineral sand mining operations at Capel,

TABLE I. Mo isotope abundance ratios measured from a Mo metal laboratory standard. The ratios are corrected for Zr isobaric interference ($^{90}\mathrm{Zr}/^{95}\mathrm{Mo}=0.0064\pm0.0053$). The data are not fractionation corrected. Uncertainties in parentheses are at the 95% confidence interval.

94/92	95/92	96/92	97/92	98/92	100/92
0.6174 (17)	1.0592 (25)	1.1026 (34)	0.6307 (22)	1.5865 (57)	0.6273 (28)

Western Australia. The average age of the zircons was $(1.822\pm0.003)\times10^{9}$ yr as measured by U-Pb dating techniques. In order to reduce the amount of molybdenum in the form of molybdenum mineral inclusions (such as MoS_2), the sands were washed overnight in a 3:1 solution of HCl:HNO_3 and rinsed the following morning five times in Milli-Q H_2O. The cleaned sands were crushed to a fine powder in an acid-cleaned zirconia ring mill. A carefully weighed amount of crushed sand was loaded into a Teflon lined acid digestion bomb along with 5 g HF and 1 g HNO_3 and placed into an oven at 180 °C for one week. After digestion, the acid was evaporated to dryness under an infrared heat lamp, the residue redissolved in 12M HCl, and again evaporated to dryness. This residue was redissolved in 0.7 g of 4M HCl and transferred to acid-cleaned 1.5 mL polypropylene centrifuge tubes. The samples were centrifuged to separate any remaining silica particles. The supernatant was loaded directly on anion ion exchange resin, which had been equilibrated with 4M HCl. Molybdenum and Fe were retained by the resin while it was washed with five column volumes of 4M HCl. Zirconium was eluted at this stage. Molybdenum and Fe were eluted from the anion column by washing the resin with two column volumes of 0.5M HCl. The eluate was collected in acid-washed Teflon beakers and slowly evaporated to dryness. The residue was taken up in 0.3 g of 0.5M HCl and loaded on a cation ion exchange column that was previously equilibrated with 0.5 M HCl. Molybdenum was eluted from the resin with two column volumes of 0.5M HCl and taken to dryness, ready for mass spectrometric analysis. The extraction efficiency of the entire separation process was approximately 70%. The procedural blank, including ion exchange chemistry, was measured to be 10±2 ng Mo by isotope dilution mass spectrometry [11].

The sample was loaded on a single Re filament with silica gel and ascorbic acid to enhance ion production. The Re filaments were outgassed thoroughly prior to sample deposition to ensure that a minimum of Mo background came from the filament material. The Re metal was attached to the filament posts using Mo-free welding equipment. The mass spectrometric procedure realized stable ion currents of 10^{-14} A from 100 ng of Mo measured with the Daly collector in a VG354 thermal ionization mass spectrometer. Reproducible operating conditions including filament heating, filament temperature, and time-dependent mass fractionation, resulted in precise isotope abundance data from nanograms of molybdenum. Details of the mass spectrometric procedure are described elsewhere [11]. The procedures employed in this investigation for Mo isotope abundance measurements have been successfully applied to the measurement of Mo in meteorites [12] and geochemical reference materials [13].

III. RESULTS

In order to measure molybdenum isotope abundance anomalies resulting from nuclear decay processes, a terrestrial baseline was established that represents the average molybdenum isotope abundances found in common molybdenum-containing minerals and compounds. Recent high precision isotope abundance measurements of a number of molybdenum minerals and reagents have demonstrated that there are no significant terrestrial molybdenum isotope abundance variations [11,14]. Therefore a sample from a 99.993% pure molybdenum metal rod from Johnson Matthey Chemicals Limited was chosen as the laboratory standard (JMC 726 Laboratory No. S-8555). The molybdenum isotope composition of the metal rod can be taken as representative of the terrestrial values and all isotope abundance data are reported relative to this laboratory standard.

Trace amounts of ^{92}Zr, ^{94}Zr, and ^{96}Zr can constitute significant isobaric interference to ^{92}Mo, ^{94}Mo, and ^{96}Mo. Therefore the ^{90}Zr ion current was monitored throughout the data acquisition process to enable a correction for zirconium present in the standard and, more importantly, with the molybdenum extracted from the zircon minerals. Zirconium corrections, appropriate for this study, were based on zirconium isotope abundances measured for a zirconium nitrate laboratory standard. The zirconium isotope abundances were measured under identical analytical conditions as were present during Mo isotope abundance analyses. The molybdenum isotope abundance ratios measured for the Mo metal rod given in Table I were corrected for zirconium isobaric interference based on the average $^{90}\mathrm{Zr}/^{95}\mathrm{Mo}$ ratio of 0.0064 ±0.0053 and the Zr isotope abundances listed in Table II. This ratio was used to correct for the presence of Zr in the measured sample because only Zr appears at mass 90 and only Mo appears at mass 95.

Three separate digestions of zircons from Capel, Western Australia were analyzed and the isotope abundance ratios are presented in Table III. These data were corrected for zirconium isobaric interference and the measured $^{90}\mathrm{Zr}/^{95}\mathrm{Mo}$ isotopic ion current ratio was $\leqslant 0.08$ for each of the samples. Therefore the zirconium contribution to the measured $^{96}\mathrm{Mo}/^{92}\mathrm{Mo}$ ratio was $\leqslant 0.5\%$ for the three digested zircons. This low level of zirconium in the extracted samples is criti-

TABLE II. Zr isotope abundance ratios measured from a zirconium nitrate laboratory standard. The data are not fractionation corrected. Uncertainties in parentheses are at the 1s level.

$^{91}\mathrm{Zr}/^{90}\mathrm{Zr}$	$^{92}\mathrm{Zr}/^{90}\mathrm{Zr}$	$^{94}\mathrm{Zr}/^{90}\mathrm{Zr}$	$^{96}\mathrm{Zr}/^{90}\mathrm{Zr}$
0.2170 (18)	0.3298 (15)	0.3298 (26)	0.0528 (8)

TABLE III. Fractionation corrected Mo isotope abundance ratios measured for Capel zircons. The ratios are corrected for Zr isobaric interferences.

Sample	94/92	95/92	96/92	97/92	98/92	100/92
13/06B1	0.6174	1.0609	1.1091	0.6330	1.5906	0.6287
07/07S1	0.6174	1.0630	1.1097	0.6342	1.5972	0.6315
13/06B2	0.6174	1.0598	1.1075	0.6318	1.5880	0.6269

cal for an accurate determination of the ^{96}Mo present from the double β decay of ^{96}Zr and represents a significant improvement over the previous work of Kawashima *et al.* [9]. The data in Table III have also been corrected for in-run mass fractionation using the average measured ^{94}Mo/^{92}Mo ratio for the laboratory standard of 0.6174 (see Table I).

The relative differences in the Mo isotope composition of the Capel zircon samples and Mo metal rod are given in Table IV and plotted in Fig. 2 as deviations in parts per thousand ($^{o}/_{oo}$). Because all zircon samples and standards were measured under identical analytical conditions and only relative isotope enrichments were required to quantify isotope abundance anomalies, it was not necessary to normalize measured Mo isotope abundance ratios to IUPAC isotope abundance data.

All three detrital zircon samples revealed significant ^{96}Mo enrichments of $+5.9^{o}/_{oo}$, $+6.4^{o}/_{oo}$, and $+4.4^{o}/_{oo}$, yielding an average of $+5.6\pm1.0^{o}/_{oo}$. Varying enrichments in ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo were observed in these samples giving average values of $+1.9^{o}/_{oo}$, $+3.7^{o}/_{oo}$, $+3.4^{o}/_{oo}$, and $+2.9^{o}/_{oo}$, respectively. This variability in the cumulative fission yields of the molybdenum isotopes is not unexpected since the zircons are detrital in nature, with a wide range of uranium content and age [15]. On the other hand, the zirconium content of these detrital zircons is remarkably constant, although the ages of the zircons in the various samples are somewhat variable.

Younger zircons from India and Vietnam, of approximate ages 500×10^{6} yr and 600×10^{6} yr, respectively, were also analyzed for evidence of ^{96}Zr double β decay and U fission products. However, no significant isotope abundance anomalies were detected since the samples were too young for any appreciable amount of daughter and fission products to have accumulated.

There are a several sources of Mo isotopes in zircon minerals, including mineral inclusions and products from the spontaneous fission of ^{238}U. An accurate determination of the amount of ^{96}Mo from the double β decay of ^{96}Zr must take into account the possible contributions of these other sources:

Mineral inclusions. Common molybdenum present in the form of molybdenum minerals can mask the relatively minute amount of daughter and fission products trapped in the zirconium silicate lattice. Therefore the mineral sand samples were washed with aqua regia prior to crushing and digesting the silicate matrix. Although it was not possible to completely remove all traces of nonradiogenic Mo, the small amount of Mo remaining served as a baseline for the measurement and identification of the radiogenic components.

The spontaneous fission of ^{238}U. The spontaneous fission of ^{238}U is a significant source of molybdenum because the zircon samples from Capel, Western Australia contained 178 ± 18 ppm U and Mo isotopes are near the peak of the lower mass hump of the mass yield curve for the spontaneous fission of ^{238}U. In addition, the average age of the detrital zircons used for the analysis was $(1.822\pm0.003)\times10^{9}$ yr allowing sufficient time for measurable amounts of ^{238}U fission products to have accumulated, despite the long half-life of ^{238}U spontaneous fission of 8.3×10^{15} yr [16]. Therefore the isotopes of ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo should show some enrichment relative to the nonradiogenic, terrestrial average (Table I). It should be noted that ^{96}Mo is not produced by the spontaneous fission of ^{238}U because ^{96}Mo is shielded by the ^{96}Zr nucleus. Although the absolute cumulative fission yields for Mo from ^{238}U spontaneous fission are poorly known, Rao [17] has measured the mass 97 fission yields using the radioactive decay of ^{97}Zr to give a value of $6.1\pm0.4\%$. Because of this paucity of measured fission yields for ^{238}U spontaneous fission for the Mo isotopes, Kawashima *et al.* [9] opted to use the cumulative yields for the thermal neutron-induced fission of ^{239}Pu, which was judged to potentially resemble the ^{238}U spontaneous fission. Crouch [18] gives a yield of 5.54% for ^{97}Mo from ^{239}Pu thermal neutron-induced fission. We have adopted an absolute fission yield of $6.0\pm0.4\%$ for ^{97}Mo in this paper since ^{97}Mo is adjacent to the double β decay product ^{96}Mo and the fission

TABLE IV. Fractionation corrected Mo isotope abundance data measured for Capel zircons expressed in permil deviations ($^{o}/_{oo}$) from the laboratory standard. The ratios are corrected for Zr isobaric interferences. Uncertainties in parentheses are at the $1s$ level.

Sample	94/92	95/92	96/92	97/92	98/92	100/92
13/06B1	0.0	+1.6	+5.9	+3.7	+2.6	+2.4
07/07S1	0.0	+3.5	+6.4	+5.6	+6.7	+6.7
13/06B2	0.0	+0.6	+4.4	+1.9	+0.9	−0.5
Average	0.0	+1.9 (1.5)	+5.6 (1.0)	+3.7 (1.9)	+3.4 (3.0)	+2.9 (3.6)

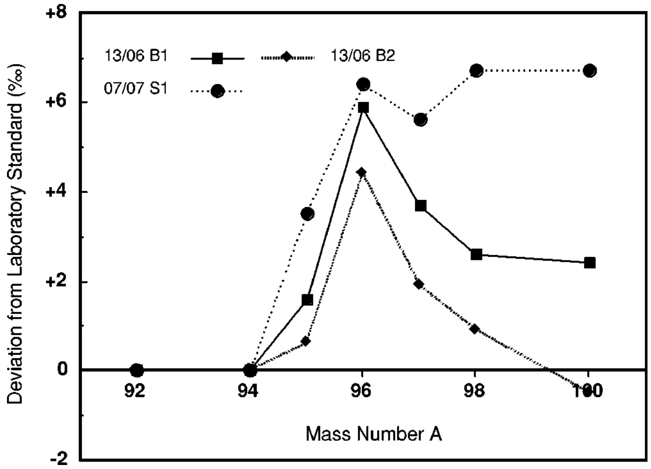

FIG. 2. Plot of Mo isotope abundance anomalies in zircon relative to a Mo metal laboratory standard, expressed in deviations in parts per thousand ($^o/_{oo}$) as a function of mass number $92 \leqslant A \leqslant 100$.

yield of ^{97}Mo has been measured for ^{238}U spontaneous fission, albeit with poor accuracy.

Thermal neutron capture. Thermal neutron capture by ^{95}Mo may also contribute to the observed enrichment in the isotope abundance of ^{96}Mo in the zircon samples. This is especially true for zircons that contain trace amounts of U that has undergone fission over 1.822×10^9 yr. The radiative capture cross section of ^{95}Mo is 23 times greater than that of ^{96}Mo (14 b vs 0.6 b). Therefore given a source of thermal neutrons (<0.025 eV) over a long period of time, ^{96}Mo would accumulate. In order for thermal neutron capture to occur, the fast neutrons emitted in the spontaneous fission of ^{238}U would have to be thermalized in the zircons. This would be a most inefficient process since no moderating-type elements make up the elemental composition of the zircon. The crystal structure of zircons is such that the rare earth elements (REE) can substitute for Zr^{4+} and REE concentrations increase rapidly for Sm to Lu. Two of the REE, Sm and Gd, have thermal neutron capture cross sections which are exceptionally high (^{149}Sm, ^{155}Gd, and ^{157}Gd have cross sections of 40 140 b, 60 900 b, and 254 000 b, respectively). Cadmium also has a high thermal neutron capture cross section of 20 600 b. Hinton and Upton [19] have shown that the REE concentrations in zircons from typical granite terrain are on the order of 2000 ppm, and that of Sm and Gd of the order of 20 and 70 ppm, respectively. It is therefore unlikely that sufficient thermal neutrons would be captured by ^{95}Mo to have any effect on the enhancement of ^{96}Mo by thermal neutron capture on ^{95}Mo.

Electron capture of Tc isotopes. In addition to the ^{96}Mo enrichment due to the double β decay of ^{96}Zr, Kawashima and co-workers [9] also observed an anomaly in the isotope abundance of ^{98}Mo. While the exact source of this enrichment was not determined, the authors did rule out electron capture of ^{98}Tc because of this isotope's relatively short half-life of 4.2×10^6 yr [9]. Similarly, the production of ^{96}Mo from the electron capture by ^{96}Tc is not a significant process as the half-life of ^{96}Tc is too short to have survived nucleosynthesis.

Cosmic ray effects. The detrital zircons used in this experiment were originally minerals in the whole rock matrix of granite rocks from the Yilgarn Craton and the Leeuwin-Naturaliste Complex in Western Australia. During Mesozoic times (60 to 200 million years ago), weathering processes released the zircons from these rocks into low-lying country between the Dunsborough and Darling faults [20]. More recently, in the Pleistocene period, rises in sea level have allowed these sandy sediments to be reworked and the zircons concentrated in the heavy mineral deposits in beach sands along the southwest coastline of Western Australia. Thus, for most of their existence, the zircons have been embedded in granite rocks or under beach sands. The flux of most cosmic rays is rapidly attenuated at the Earth's surface so that it is most unlikely that spallation reactions would have occurred in amounts that would have affected the production of ^{96}Mo. On the other hand, muons can penetrate the surface, but there are few spallation targets in zircons which have an abundance sufficient to cause significant amounts of cosmic-ray induced ^{96}Mo. The only elements in zircons with an abundance greater than 1% are Zr, Hf, and Si.

^{96}Mo from the double β decay of ^{96}Zr. The amount of ^{96}Mo produced by the double β decay of ^{96}Zr was calculated based on the amount of ^{97}Mo excess measured; the result of the spontaneous fission of ^{238}U ($T_{1/2} = 8.3 \times 10^{15}$ yr). The amount of U in the sample was determined to be 178 ± 18 ppm by isotope dilution mass spectrometry and the average age of the zircons was measured as $(1.822 \pm 0.003) \times 10^9$ yr by U-Pb dating techniques. Based on the average ^{97}Mo enrichment measured for the zircon samples ($+3.7 \pm 1.9\,^o/_{oo}$), the amount of Mo in the zircon produced by nuclear decay processes was calculated. Since the molybdenum decay products of both the spontaneous fission of ^{238}U and the double β decay of ^{96}Zr have accumulated in the zircon mineral lattice over the same period of time, the amount of ^{96}Mo from double β decay can be determined based on the amount of ^{97}Mo. The average ^{96}Mo enrichment measured was $+5.6 \pm 1.0\,^o/_{oo}$. The half-life of the double β decay of ^{96}Zr was then calculated based on the number of ^{96}Mo daughter atoms in the zircon, the number of parent ^{96}Zr atoms present, and the age of the sample. The number of ^{96}Zr nuclei that has decayed to ^{96}Mo is small compared to the total number of ^{96}Zr atoms present. Therefore the number of ^{96}Zr parent atoms originally present was based on the measured abundance of ^{96}Zr (2.8%, calculated from the data in Table II) and the amount of Zr present in the Capel zircons (48 wt %). The ^{96}Zr double β decay half-life determined in this study was $(9.4 \pm 3.2) \times 10^{18}$ yr. This result compares favorably with the theoretical two neutrino double β decay half-life of 8.5×10^{18} yr reported by Moe and Vogel [10] and 5.2×10^{18} yr published by Doi *et al.* [6]. This is shorter than the $(3.9 \pm 0.9) \times 10^{19}$ yr half-life determined by Kawashima *et al.* [9] for a zircon sample.

Doi *et al.* [6] have listed the possible double β decay transitions for 35 naturally occurring nuclides as a function of the available energy between the initial and final nuclear

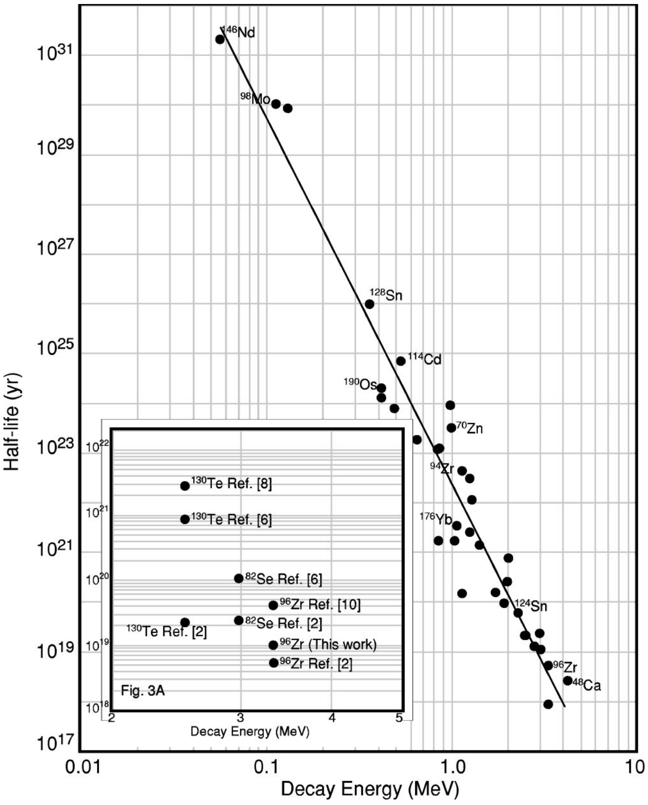

FIG. 3. Log-log plot of half-lives versus decay energies for several double β decay systems. The data are provided in full in Ref. [6]. Figure 3(a) is an expanded view of the plot comparing data that was obtained using geochemical techniques to theoretical values.

states. These energy differences have been calculated from the atomic mass data of Wapstra and Audi [21]. A more recent compilation by Audi and Wapstra [7] does not significantly alter the decay energies used by Doi *et al.* [6]. Doi *et al.* [6] list the corresponding theoretically determined double β decay half-lives for these nuclides.

The decay energies (in MeV) are plotted against the theoretically determined half-lives listed in Ref. [6] in Fig. 3. There is an obvious correlation between the two parameters; the greater the energy, the shorter the half-life. Primakoff and Rosen [22] showed that, if all the nuclear matrix elements have the same value, the half-life of two neutrino double β decay is inversely proportional to the tenth power of the decay energy. In Fig. 3, the logarithm of the theoretically determined values of the half-lives are plotted against the logarithm of the known values of the decay energies to give an inverse correlation similar to that predicted by Primakoff and Rosen [22].

Also plotted in Fig. 3(a) are the geochemically determined values of the half-lives for ^{96}Zr, ^{82}Se, and ^{130}Te. The values for ^{96}Zr are $(9.4 \pm 3.2) \times 10^{18}$ yr (this work) and $(3.9 \pm 0.9) \times 10^{19}$ yr [9]; for ^{82}Se 1×10^{20} yr [3]; and for ^{130}Te 8×10^{20} yr [3] and $(2.7 \pm 0.1) \times 10^{21}$ yr [5]. It can be seen that in each case the geochemically determined half-lives are greater than the theoretically determined values of Doi *et al.* [6]. In the case of ^{130}Te, the experimental values are a factor of 38 times [3] and 130 times [5] greater than the theoretical value; for ^{82}Se some 43 times greater [3]; and for ^{96}Zr some 7.5 times greater [9], but only 1.8 times for the half-life determined in this work.

As discussed above, the daughter products of the ^{128}Te, ^{130}Te, and ^{82}Se parents are both rare gases and there is the attendant probability that ^{128}Xe, ^{130}Xe, and ^{82}Kr may have partially escaped from the parent telluride and selenide minerals over the geological time frame involved. In comparison, ^{96}Mo is a solid daughter product from the parent element Zr, the major constituent of zircon. Zircons are ideal minerals for this experiment in so far as the lattice structure has been shown, through U-Pb geochronology, to tightly contain any radioactive decay products.

The present value for the half-life of the double β decay of ^{96}Zr is in good agreement with the theoretically determined value of Doi *et al.* [6] and the discrepancy could well be explained in terms of the uncertainties in the experimental and theoretical values. This experiment therefore strongly supports the two-neutrino mode of double β decay.

It would be possible to reduce the uncertainties of the present experiment by using zircons extracted from a rock whose age has been dated at $> 3 \times 10^{9}$ yr, rather than the detrital zircons used in this experiment. If the absolute cumulative fission yields of ^{238}U spontaneous fission could be measured, this would also remove an element of doubt on the yield of $6.0 \pm 0.4\%$ used in this experiment. It would also be advantageous to the arguments used in this paper if the half-life of another double β system with a solid daughter product could be experimentally determined.

IV. CONCLUSIONS

Evidence for the double β decay of ^{96}Zr to ^{96}Mo was found in zircon minerals from Capel, Western Australia. Careful sample preparation and high sensitivity thermal ionization mass spectrometric techniques were employed to provide precise Mo isotope abundance data from three individual zircon samples. In all cases, the results showed an excess amount of ^{96}Mo and enrichments in the isotope abundances of ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo. The latter were likely the result of the spontaneous fission of ^{238}U. The presence of trace amounts of uranium in the zircon enabled the age of the zircon to be determined by U-Pb dating techniques. Based on the age of the sample, the relative enrichments of ^{97}Mo from the spontaneous fission of ^{238}U and the enrichment of ^{96}Mo from the double β decay of ^{96}Zr, the half-life for the double β decay of ^{96}Zr was calculated to be $(9.4 \pm 3.2) \times 10^{18}$ yr. This is significantly shorter than the value determined by Kawashima *et al.* [9] on samples from the same region. However, the value for half-life of the double β decay of ^{96}Zr reported in this paper as well as that from Ref. [9] show that the Te/Xe and Se/Kr results [5,3] do not give an accurate portrayal of double β decay half-lives because of gas loss from the mineral lattice. The present value for the half-life of the double β decay of ^{96}Zr to ^{96}Mo is in excellent agreement with the theoretical half-life predicted by Doi *et al.* [6] and supports a two-neutrino mode for double β decay.

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