# Geochemical evidence of the double $\beta$ decay of $^{100}$Mo

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Enrichment of the $^{100}$Ru isotope, resulting from the double beta ($\beta\beta$) decay of $^{100}$Mo, has been found in old molybdenites from Australia. Using Re–Os ages determined here together with the amount of excess $^{100}$Ru determined via isotope dilution mass spectrometry, consistent half-lives were obtained from two different molybdenite samples of varying ages (2.90 billion and 1.05 billion years old) with an average half-life of $(2.1\pm0.3)\times10^{18}$ years. This half-life is highly consistent with the theoretical model for a two-neutrino $\beta\beta$ decay.

## I. INTRODUCTION

Many previous studies aimed at determining $\beta\beta$ decay half-lives [1] have concentrated on the direct detection of emitted particles. This method involves the detection and measurement of the number and energies of emitted particles ($\gamma$,e$^-$) from $\beta\beta$ decay. This method can directly determine the number of neutrinos released from the decay event as well as the mode of decay, as the energies of the emitted particles are also measured. However, this technique is highly sensitive to background noise, due to the long half-lives of these decays [1].

Another method for determining $\beta\beta$ decay half-lives, which can circumvent the difficulties caused by the long half-life of these decays and the weakly interactive nature of neutrinos, is through the geochemical analysis of isotopic excesses in geological materials caused by the accumulation of the $\beta\beta$ decay daughter isotope. This takes advantage of geological time for the accumulation of a detectable amount of the daughter isotope in the mineral. However, this method does not provide direct information on the mode of decay, and is instead a sum of all decay modes. For the successful use of this method the mineral sample should incorporate little of the daughter isotope during formation, be geologically resistant so as to retain any daughter isotopes produced, and be geologically old so that detectable amounts of the daughter isotope have accumulated. The $^{130}$Te-$^{130}$Xe decay has been studied previously as $^{130}$Te is the most abundant Te isotope and precise measurements of Xe isotopes can be performed, results of which have confirmed the presence of $\beta\beta$ decay $^{130}$Xe [2,3]. Work has also been done on the $^{128}$Te-$^{128}$Xe and $^{82}$Se-$^{82}$Kr decay systems [2,4,5]. However, the main limitation with using noble gas daughters is the possible leakage of the daughter from the mineral lattice over the long time periods required for the accumulation of detectable amounts of daughter product. To avoid leakage, use of a nongaseous daughter is preferable. Recent work on the $^{96}$Zr-$^{96}$Mo $\beta\beta$ decay in old zircons has shown that it is pos-

sible to detect $\beta\beta$ decay via solid phase daughters [6,7]. These results also indicated that previous measurements of the $^{128}$Te-$^{128}$Xe, $^{130}$Te-$^{130}$Xe, and $^{82}$Se-$^{82}$Kr decays may have suffered from leakage of the daughter isotope. However, the authors suggested that further work on other solid phase daughters of $\beta\beta$ decay would be advantageous to support such a conclusion.

Several theoretical, as well as experimental, studies of the $^{100}$Mo-$^{100}$Ru $\beta\beta$ decay have provide a range of half-lives from $6.75^{+1.05}_{-1.10}\times10^{18}$ yr [8] to $11.6^{+3.4}_{-0.8}\times10^{18}$ yr [9]. Because $^{100}$Mo is one of the fastest $\beta\beta$ decay nuclides, evidence of this decay is expected, even through geochemical methods. However, there has only been one previous geochemical determination of the $^{100}$Mo-$^{100}$Ru half-life, and this was only able to provide a lower limit of $>1\times10^{18}$ [10]. In this paper the $^{100}$Mo $\beta\beta$ decay half-life is determined from Ru isotopic analyses of old molybdenite samples from Australia.

## II. EXPERIMENT

Molybdentie samples, as whole rocks, were crushed and molybdenite flankes handpicked and finely powdered in an agate mortar. Sample processing for Re-Os chemistry was undertaken using previously established analytical procedures, a detailed description of which is found elsewhere [11–13].

For Ru separation, approximately 5 g of the powdered molybdenite samples were carefully weighted into Teflon bombs with 5 ml of 10 M HNO$_3$ and 15 ml of 8 M HCl. The bombs were then sealed and left on a hot plate at $\sim$180$^\circ$C overnight. Once dissolved, the samples were slowly evaporated to incipient dryness on a hot plate, in a clean air chamber, to reduce the aqua regia content. Samples were then redissolved in 4 M HCl and introduced into a glass distillation flask with 2 g of K$_2$Cr$_2$O$_7$ and 15 g of condensed phosphoric acid. The flask was sealed into a glass still and heated to 180$^\circ$C. In this environment Ru is readily oxidized into volatile RuO$_4$, which is guided into a trapping vessel containing 6 ml of a 1:1 mixture of HCl and ethanol. The trap solution was evaporated to incipient dryness and redissolved in 4 M HCl, to reduce the ethanol content in the sample. The sample volume was reduced to a small drop and microdis-

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TABLE I. Re-Os ages determined for molybdenite samples, using the $\lambda_{Re}$ value of $1.666\times10^{-11}$ Ref. [14].

| Name | Location | Re conc (ppm) | Os conc. (ppm) | Re-Os Age ($\times10^6$ yr) | Rb-Sr Age ($\times10^6$ yr) |
|---|---|---|---|---|---|
| Mt. Mulgine | West. Australia, Australia | $12\pm1$ | $0.63\pm0.03$ | $2903\pm4$ | $2684\pm94$ (Ref. [24]) |
| Osbourne | Queensland, Australia | $168\pm15$ | $2.9\pm0.1$ | $1051\pm1$ | Not available |

tilled, using a $K_2Cr_2O_7$-$HClO_4$ mixture as the oxidizing agent and HCl as the reducing agent, to further reduce the Mo concentration. The procedural blank, including sample dissolution and distillation, was determined to be $4\pm2$ pg via isotope dilution mass spectrometry (IDMS) [14].

Isotopic analyses of Re, Os, and Ru were performed on a Thermo Finnigan TRITON TI thermal ionization mass spectrometer (TIMS), in a negative ion mode, at JAMSTEC, Yokosuka. Measurements of Re, Os, and Ru were undertaken as $^{xx}Re^{16}O_4$, $^{xx}Os^{16}O_3$ and $^{xx}Ru^{16}O_3$, respectively. Oxygen was corrected using the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ values of Nier [15]. Re and Os contents were determined via IDMS, assuming a terrestrial value for the $^{185}Re/^{187}Re$ ratio, while the Os content was determined by direct comparison to the spike as only radiogenic $^{187}Os$ is present in the samples.

For Ru isotopic analysis, samples were loaded onto in-house single Pt filaments with 1 $\mu$l of a 10 000 ppm $Ba(NO_3)_2$ solution. Filament loading blanks were found to be $0.7\pm0.2$ pg. During the measurements, as well as the $^{xx}Ru^{16}O_3$ isotopic species, mass numbers 143, 145, and 151 were always monitored to determine the levels of $^{95}Mo^{16}O_3$, $^{97}Mo^{16}O_3$, and $^{135}BaO$, respectively, to make corrections for Mo and Ba isobaric interferences onto the Ru mass spectra. For the determination of Ru content in the molybdenite samples, IDMS was used. Prior to chemical dissolution and separation, a known quantity of a $^{99}Ru$ enriched isotope solution was added to each sample (spiked sample). The abundance of $^{100}Ru$ in the molybdenite could then be determined by comparison of the measured $^{99}Ru$ and $^{100}Ru$ signals. In addition to corrections for Mo, Ba, and O isotopes, the results from measurements of the spike samples were also corrected for procedural and loading blanks.

## III. RESULTS AND DISCUSSION

Re and Os data for the two molybdenites are shown in Table I. Using a $\lambda_{Re}$ value of $1.666\times10^{-11}$ yr$^{-1}$ [16], an age of $(2.902\pm0.004)\times10^9$ yr was obtained for the Mt. Mulgine molybdenite and an age of $(1.051\pm0.001)\times10^9$ yr for the

Osbourne molybdenite. The Ru isotopic compositions measured for the two molybdenites are shown in Table II, including Ru isotope data from a standard Ru chemical reagent for comparison. The values shown in Table II have been corrected for Mo and Ba interferences before correcting for oxygen isotopes. An isotopic mass fractionation correction was completed for the Mt. Mulgine sample via the exponential law using $^{96}Ru/^{101}Ru=0.3237$ as the normalizing factor. The fractionation correction was not completed for the Osbourne sample because only a $^{100}Ru$ signal was detected for this sample and the other isotopes were below the detection limit. Although the analytical precision of the two molybdenite samples is poor, because of extremely low Ru contents, isotopic excesses of $^{100}Ru$ for the Mt. Mulgine and Osbourne molybdenites can be clearly identified from the $^{100}Ru/^{101}Ru$ ratio and from the lack of Ru isotopes other than $^{100}Ru$, respectively. Before this $^{100}Ru$ enrichment can be linked with the $\beta\beta$ decay of $^{100}Mo$, other possible sources of isotopic anomalies must be carefully considered.

### A. Spontaneous fission $^{238}U$ and neutron capture

Although it is known that Ru is a product of the spontaneous fission of $^{238}U$, this is not considered to be the source of the detected $^{100}Ru$ enrichment, as $^{100}Ru$ is shielded from direct contributions from the fission of $^{238}U$ by $^{100}Mo$. There is a possibility that the fast neutrons released during the spontaneous fission of $^{238}U$ will induce the capture reaction $^{99}Ru(n,\gamma)$ $^{100}Ru$. However, this is also highly unlikely, as there is an insufficient amount of $^{99}Ru$ and molybdenties contain relatively high concentrations of rare earth elements [17], two of which have exceptionally high capture cross-sections (i.e., Sm, Gd). Therefore, the spontaneous fission of $^{238}U$ and thermal neutron capture would not be a significant source of $^{100}Ru$.

### B. Decay of Tc isotopes

Tc has no naturally occurring stable isotopes, and only the $^{97}Tc$, $^{98}Tc$, and $^{99}Tc$ isotopes have half-lives of greater than a

TABLE II. Ru isotopic abundances measured for the AAS $RuCl_4$ standard solution and Ru extracted from the Mt. Mulgine and Osbourne molybdenite. All samples have been corrected for Mo and Ba interferences and oxygen isotopes. No fractionation correction was made for the AAS standard or Osbourne molybdenite. Data for Mt. Mulgine has been corrected for mass fractionation using the $^{96}Ru/^{101}Ru$ value of 0.3237.

| Sample name | $^{96}Ru/^{101}Ru$ | $^{99}Ru/^{101}Ru$ | $^{100}Ru/^{101}Ru$ | $^{102}Ru/^{101}Ru$ | $^{104}Ru/^{101}Ru$ |
|---|---|---|---|---|---|
| AAS Standard | $0.3237\pm0.0001$ | $0.7429\pm0.0001$ | $0.735\,38\pm0.000\,06$ | $1.8417\pm0.0002$ | $1.0919\pm0.0002$ |
| Mt. Mulgine | 0.3237 | $0.93\pm0.19$ | $1.40\pm0.17$ | $1.89\pm0.28$ | $1.09\pm0.24$ |
| Osbourne | | | Only $^{100}Ru$ isotope was detected. | | |

TABLE III. Parameters used to determine the $\beta\beta$ decay half-life of [100]Mo. Re-Os ages and Ru concentrations have been determined in this report, while the Mo concentration was calculated from the amount of Mo present in molybdenite (60 wt%).

| Name | Re-Os age ($\times 10^6$ yr) | Ru conc. (ppt) | Mo conc. (wt%) | $\beta\beta$ decay half-life (yr) |
|---|---|---|---|---|
| Mt. Mulgine | $2903\pm4$ | $50\pm11$ | $60\pm0.01$ | $(2.3\pm0.7)\times10^{18}$ |
| Osbourne | $1051\pm1$ | $22\pm5$ | $60\pm0.01$ | $(1.9\pm0.7)\times10^{18}$ |

few days. There is currently no evidence that any Tc isotopes survived early solar nebular processes, as demonstrated by recent Ru isotopic analyses of meteoritic samples [18]. Additionally, these isotopes do not directly decay to [100]Ru, and so the direct decay of a native Tc isotope would not cause the detected anomaly.

However, of more concern is the proton capture of [100]Mo(p,n)[100]Tc, and the subsequent decay of [100]Tc to [100]Ru. Possible sources of protons, required to induced the captrue reaction, could come from cosmic ray spallation and the reaction of S with alpha particles and neutrons emitted during the spontaneous fission of [238]U, i.e., S($\alpha$,p)C1 and S($n$,$p$)P. The exact depth of both the Mt. Mulgine and Osbourne is not known, however, both molybdenites were embedded in granite, rather than in a soil sample. As such, the samples must have originated at depths of least ∼10 m below the surface, and a majority of the cosmic rays would therefore, have been attenuated. Only muons are known to penetrate deeper into geological material.

Previous work by Cleveland *et al.* [19] determined the amount of [37]Ar produced by reactions from muon evaporation protons, in a tank filled with $C_2Cl_4$ at a depth of 1478 m. In an earlier work, Cowan and Haxton [20] estimated that at a depth of 1500 m, the amount of muon-induced Tc in a molybdenite ore body was reduced to 10%. Assuming that the production rate of [37]Ar is the same as the production rate of [100]Tc, and that it is a factor of 10 less than in near-surface samples, we have calculated that muon-induced [100]Tc, and therefore [100]Ru, would represent less than 90 pg for a 3000 Ma sample. This value is based on a large target, i.e., 6700 li of $C_2Cl_4$, whereas our samples of molybdenite only represent approximately 5 $cm^3$. Therefore, we would expect the calculated background to be an overestimate.

To estimate and account for Tc production from the two-stage reaction of fast neutrons released during the spontaneous fission of [238]U, with S nuclides and subsequent proton capture of the release proton, we again rely on measurements made by Cleveland *et al.* [19]. In this work they measured the production rate of [37]Ar due to fast neutrons from the wall rock. The short free mean path of alpha particles would make them an unlikely source of secondary protons. We assumed a similar production rate as that determined by Cleveland *et al.* [19], and have calculated that Tc produced from the two stage reaction from fast neutrons would represent less than 10 pg over $3.0\times10^6$ yr. Again, this estimate is based on a much larger target, and therefore, is likely to be an overestimate of the true background.

It should be noted that in either case, proton capture reactions on Mo would also involve the [98]Mo isotope. The production rates by proton capture can be generally deter-

mined by the term $\Psi\sigma N$; where $\Psi$ is the proton fluence derived from cosmic rays, $\sigma$ is the cross section for proton capture reactions, and $N$ is the number of target isotopes. Proton captured Mo isotopes turn to Tc, and the Tc then decays to Ru. From the values for integrated proton capture cross sections [21] and the isotopic abundances of [98]Mo and [100]Mo, the production rate of [98]Tc is estimated to be around 2.8 times higher than that of [100]Tc. The lack of excess of the [98]Ru isotope in both the Mt. Mulgine and Osbourne samples indicates that these samples have not been greatly influenced by proton capture reactions. However, the half-life of [98]Tc $(4.2\times10^6$ yr) is much longer than that of [100]Tc (15.8 s), and [98]Tc may have behaved differently from Ru over geologic time scales by the geochemical differentiation of Tc and Ru in the ore body. Therefore, we cannot completely exclude the possibility of background from proton capture of Mo.

## C. $\beta\beta$ decay of [100]Mo

Taking into account the above background estimates, scaled to the age of the two samples, the remaining [100]Ru detected in our molybdenite samples must have originated from the $\beta\beta$ decay of [100]Mo. We were thus able to determine the $\beta\beta$ decay half-life from the measured amount of excess [100]Ru, less the ∼100 pg background, using the Re-Os age and the initial amount of parent [100]Mo present in the molybdenite. The amount of [100]Mo initially present was calculated from the [100]Mo abundance of Wieser and De Laeter [22] and the amount of Mo present in molybdenites (60 wt%). The parameters used to calculate the half-life are given in Table III. Using these parameters and the standard equation for radioactive decay, the $\beta\beta$ decay half-life for [100]Mo was estimated to be $(2.3\pm0.7)\times10^{18}$ yr and $(1.9\pm0.7)\times10^{18}$ yr for the Mt. Mulgine and Osbourne molybdenites, respectively. The presence of a non-radiogenic Ru isotopic component in the Mt. Mulgine molybdenite may be due to contamination in this sample, which is not seen in the Osbourne sample. However, the consistency of the estimated half-lives from these two measurements indicates that the Mt. Mulgine data has been effectively corrected for this contaminating Ru, and that the two half-lives are from the same set. As such we can average the two half-lives to obtain an estimate for the $\beta\beta$ decay half-life of $(2.1\pm0.3)\times10^{18}$ yr, which is a significant improvement over the previous result [8]. The absence of a contaminating Ru signal in the Osbourne sample also leads us to conclude that the behaviour of Ru during the formation of molybdenite is similar to that of Os, which is readily excluded during crystallzation.

Table IV lists the half-life determined here, together with previously determined geochemical [2,4,6,7], direct counting

TABLE IV. List of selected $\beta\beta$ decay nuclides with their decay energy and theoretical, geochemical and direct counting estimates of their half-life. No uncertainty was provided for the theoretical estimates.

| Species | Decay energy | Half-life (yr) | Source |
|---|---|---|---|
| $^{82}$Se | 2.995 MeV | $(1.12\pm0.3)\times10^{20}$ | Geochemical (Ref. [4]) |
| | | $1.08^{+0.26}_{-0.06}\times10^{20}$ | Direct counting (Ref. [1]) |
| | | $2.30\times10^{19}$ | Theoretical (Ref. [23]) |
| $^{96}$Zr | 3.35 MeV | $5.19\times10^{18}$ | Theoretical (Ref. [23]) |
| | | $2.1^{+1.0}_{-0.6}\times10^{19}$ | Direct counting (Ref. [1]) |
| | | $(3.9\pm0.9)\times10^{18}$ | Geochemical (Ref. [6]) |
| | | $(9.4\pm3.2)\times10^{18}$ | Geochemical (Ref. [7]) |
| $^{100}$Mo | 3.034 MeV | $1.06\times10^{19}$ | Theoretical (Ref. [23]) |
| | | $(8.0\pm0.7)\times10^{18}$ | Direct counting (Ref. [1]) |
| | | $(2.1\pm0.3)\times10^{18}$ | This work |
| $^{128}$Te | 0.868 MeV | $1.18\times10^{23}$ | Theoretical (Ref. [23]) |
| | | $(2.2\pm0.3)\times10^{24}$ | Geochemical (Ref. [3]) |
| $^{130}$Te | 2.533 MeV | $(9.0\pm1.5)\times10^{20}$ | Geochemical (Ref. [1]) |
| | | $2.09\times10^{19}$ | Theoretical (Ref. [23]) |

[1] and theoretical half-lives [23] for $^{100}$Mo and other $\beta\beta$ decay species. Table IV shows that the experimentally obtained half-lives from both geochemical and direct counting methods are, in each case except $^{100}$Mo, much larger than theoretical estimates. In the case of $^{100}$Mo $\beta\beta$ decay [1,23], the half-life determined in this work, $(2.1\pm0.3)\times10^{18}$ yr, is a factor of 4 lower than current direct counting measurements, and a factor of 5 lower than the theoretical value.

However, if the $^{100}$Tc production rate has been underestimated in our work, the half-life might be considerably longer than that calculated here.

## IV. CONCLUSION

Evidence has been found for the $\beta\beta$ decay of $^{100}$Mo in old molybdenite samples. Mass spectrometric analyses of chemically purified Ru extracted from molybdenites obtained from Mt. Mulgine and Osbourne, Australia, indicate large enrichments in the $^{100}$Ru isotope. For the Osbourne molybdenite, measurements indicated that only $^{100}$Ru was present in the sample. After careful consideration of other possible sources and the subtraction of background signals, the remaining enrichment has been linked with the $\beta\beta$ decay of $^{100}$Mo. Large Re concentrations and low terrestrial Os concentrations enabled the age of these molybdenites to be determined precisely via the Re-Os geochronometer. From the age of the samples and the measured amount of excess $^{100}$Ru, the half-life for the $\beta\beta$ decay of $^{100}$Mo was calculated to be $(2.1\pm0.3)\times10^{18}$ years, which favors the two-neutrino decay model. However, because of the uncertainty in the $^{100}$Tc production rate from the interaction of cosmic rays, further work is needed to conclusively determine the half-life.

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