1 # No [182]W excess in the Ontong Java Plateau source

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A B S T R A C T

Small-scale W isotope variations in ancient and modern terrestrial rocks provide insights into Earth's accretion and early differentiation history as well as the long-term evolution of the Earth's mantle. Tungsten isotope studies on such rocks have exploited advances in mass spectrometry, both NTIMS and MC-ICPMS, which now permit the determination of W isotope ratios at unprecedented precision. While W isotope studies performed in different labs by MC-ICPMS and NTIMS generally exhibit excellent agreement, obtaining accurate W isotope data at this level of precision remains analytically challenging. For example, a recent NTIMS study reported a relatively large, +24 ppm excess in $^{182}W/^{184}W$ for a Phanerozoic sample from the Ontong Java Plateau (OJP), but no such $^{182}W/^{184}W$ anomaly was found in another study by MC-ICPMS. The present study aims to resolve the discrepancy between these two previous studies, and more generally to evaluate the agreement between different recent W isotope studies by NTIMS and MC-ICPMS. To this end, we report new W isotope data for OJP drill core samples obtained by MC-ICPMS. The OJP samples analyzed here exhibit no resolvable $^{182}W/^{184}W$ excess relative to the standards and most terrestrial rocks. Moreover, the OJP samples as well as the terrestrial rock standards analyzed here exhibit small but variable W isotope variations for ratios involving ^{183}W, producing coupled variations in both 'radiogenic' (*i.e.*, $^{182}W/^{183}W$) and 'non-radiogenic' (*i.e.*, $^{183}W/^{184}W$) ratios. These W isotope variations are analytical in origin, induced during sample preparation, and very likely caused by a nuclear field shift isotope fractionation affecting primarily the odd isotope (^{183}W). The recently reported ^{182}W excess for an OJP sample may result from this nuclear field shift effect, as the NTIMS analyses had to rely on a double normalization involving the $^{183}W/^{184}W$ ratio. More generally, these results demonstrate that using ^{183}W data from any MC-ICPMS or NTIMS study requires a careful quantification of any potential analytical ^{183}W effect. Nevertheless, once such effects are taken into account, then both $^{182}W/^{184}W$ and $^{183}W/^{184}W$ can accurately be determined to a very high level of precision.

Keywords: Archean rocks, Hf-W system, MC-ICPMS, NTIMS, mantle differentiation, late accretion

1. Introduction

The short-lived ^{182}Hf-^{182}W system (half-life: 8.9 Ma) has been widely used as a chronometer for dating early solar system processes including planetary core formation (see e.g., Jacobsen, 2005; Kleine et al., 2009; Kleine and Walker, 2017). Nevertheless, through recent advances in measurement techniques the Hf-W system is now also used to study the evolution of the Earth's mantle. In particular, analytical improvements in isotope ratio mass spectrometry have enabled the resolution of $^{182}W/^{184}W$ measurements on the order of ~5-10 ppm (2s.d.). Such precise W isotope measurements are performed either using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS; e.g., Kruijer et al., 2012; Willbold et al., 2011) or negative thermal ionization mass spectrometry (N-TIMS; Archer et al., 2017; Touboul and Walker, 2011). This improvement in measurement precision has provided new insights in the earliest history of the silicate Earth. For instance, Willbold et al. (2011) demonstrated that Archaean rocks from the ~3.8 Ga Isua Supracrustal Belt exhibit small ~10-15 ppm excesses in $\mu^{182}W$ relative to the present-day BSE (where $\mu^{182}W$ is the parts-per-million deviation of $^{182}W/^{184}W$ from the ratio of terrestrial standards). Moreover, Touboul et al. (2012) found W isotope anomalies of similar magnitude in ~2.8 Ga Kostomuskha komatiites.

73 Subsequent studies have identified similar small-scale $\mu^{182}W$ anomalies in several suites of Hadean to
74 Archean terrestrial rocks with a total range in $\mu^{182}W$ between *ca.* –8 and +20 (Dale et al., 2017; Liu et
75 al., 2016; Puchtel et al., 2016; Rizo et al., 2016b; Touboul et al., 2014, 2012, Willbold et al., 2015,
76 2011), although the data exhibit a preponderance of $\mu^{182}W$ values between +10 and +15 ppm. More
77 recently, ^{182}W heterogeneities have also been reported for some Phanerozoic rocks, including samples
78 from the Baffin Bay locale (60 Ma) and the Ontong Java Plateau (120 Ma) (Rizo et al., 2016a), as
79 well as ocean island basalts from Hawaii, Samoa, and Iceland (Mundl et al., 2017). The existence of
80 $\mu^{182}W$ anomalies in these young rocks implies that isotopically distinct mantle domains have survived
81 until the present-day, and this has therefore been taken as evidence that the mantle has not completely
82 mixed over geological history. The Ontong Java Plateau (OJP) in the western Pacific Ocean is the
83 largest known volcanic province on Earth (Neal et al., 1997) and has geochemical characteristics that
84 are consistent with a relatively primitive mantle source (Jackson et al., 2011), although this remains
85 debated (Day, 2017).

86   There is considerable debate regarding the origin of the $\mu^{182}W$ anomalies. They have been
87 interpreted to reflect (i) late accretion of on average chondritic (*i.e.*, ^{182}W-depleted) material following
88 core formation and extinction of ^{182}Hf (*e.g.,* Willbold et al., 2011, 2015; Dale et al., 2017), (ii) early
89 silicate mantle differentiation processes within the lifetime of ^{182}Hf (*e.g.,* Touboul et al., 2012; Rizo et
90 al., 2016b), and (iii) early (incomplete) metal-silicate separation within the mantle (*e.g.*, Touboul et
91 al., 2014; Rizo et al., 2016a; Mundl et al., 2017). Note that $\mu^{182}W$ anomalies due to early
92 differentiation would have to be generated within the lifetime of ^{182}Hf, *i.e.*, very likely prior to the
93 Moon forming impact. By contrast, $\mu^{182}W$ anomalies due to late accretion would have been produced
94 after the formation of the Moon (Touboul et al., 2007, 2015; Kruijer et al., 2015, 2017). Thus,
95 identifying the origin of $\mu^{182}W$ heterogeneities in Earth's mantle is essential for assessing whether
96 signatures of early differentiation processes predating the formation of the Moon have been preserved.

97   One problem with the identification of $\mu^{182}W$ anomalies in terrestrial samples is that these
98 anomalies are very small and are at the edge of the analytical resolution of current mass spectrometric
99 techniques. This issue becomes apparent when high-precision ^{182}W data for some of the same samples
100 analyzed in different laboratories and by different techniques are compared. For instance, for one OJP
101 drill core sample (192-1187A-009R-04W), Rizo et al. (2016a), using NTIMS, reported one of the
102 largest $\mu^{182}W$ excesses measured so far for terrestrial samples ($\mu^{182}W$ = +24±5). However, Willbold
103 et al. (2011), using MC-ICPMS, found no such $\mu^{182}W$ excess in another OJP sample from the same
104 drill core ($\mu^{182}W$ = –7±6 ppm; 192-1187A-006R-06W). In the same study, Rizo et al. (2016a) also
105 reported an even larger $\mu^{182}W$ excess of +48±5 ppm for samples from Baffin Bay. Understanding the
106 cause of the disparate results for the OJP samples is important not only for understanding as to
107 whether there is a $\mu^{182}W$ anomaly in these samples, but also because the $\mu^{182}W$ excesses for OJP and
108 Baffin Bay reported by Rizo et al. (2016a) would be difficult to account for by late accretion. Thus, if
109 these ^{182}W excesses are confirmed, then this would be strong evidence that vestiges of Earth's earliest
110 differentiation, predating the formation of the Moon, have been preserved in Earth's mantle until the
111 present day.

112   The objectives of the present study are to evaluate and document the accuracy and
113 reproducibility of W isotope measurements by MC-ICMPS, compare this to the NTIMS technique,
114 and to ultimately assess whether there is a $\mu^{182}W$ anomaly in the OJP source. To this end new $\mu^{182}W$
115 data for Ontong Java samples as well as for terrestrial reference materials (BHVO-2, BCR-2) are
116 reported.

2. Samples and analytical methods

2.1. Sample preparation and chemical separation

For this study, different digestions (~0.5 g) of the geological reference material BHVO-2 was analyzed several times, and the results for these two samples are presented together with BHVO-2 and BCR-2 data obtained in the Münster laboratory since 2012. For the OJP samples, two drill core samples, provided by the Ocean Drilling Program (ODP), were selected for high-precision W isotope analyses (192-1187A-04W 15-17; 192-1187A-04W 118.5-120). These samples are from the same drill core section (Site 1187; Core A) and are the exact same lithology and lava flow as the sample analyzed by Rizo et al. (2016a) (192-1187A-04W 125-138). Moreover, one of the two samples from this study (192-1187A-04W 118.5-120) was collected only a few cm apart from the sample analyzed by Rizo et al. (2016a) (Fig. S1). Of note, the total amount of OJP sample used here for a high-precision W isotope measurement by MC-ICPMS is ~9.5 g, significantly smaller than the ~44 g required for a NTIMS measurement of similar precision (Rizo et al., 2016a).

The analytical techniques for sample digestion, chemical separation of W, and W isotope ratio measurements by MC-ICPMS are based on methods described in several prior studies from the Münster laboratory (*e.g.*, Budde et al., 2016; Kruijer et al., 2015, 2014). The OJP samples were received as rock fragments and visually inspected upon arrival. No obvious signs of alteration were observed and the samples most likely stem from the interior parts of the drill core. It should be noted already here that, because all investigated OJP samples exhibit very low and uniform W concentrations (Section 5-6; Table 1), significant W contamination from W-enriched source (*e.g.*, the drill bit) can effectively be ruled out. The OJP samples were cleaned with abrasive paper, then ultrasonically cleaned and rinsed with ethanol, and finally crushed and ground to a fine powder in an agate mortar. Powders of terrestrial rock standards and OJP samples were split into ~2 g powder fractions and then digested in 40 ml concentrated $HF–HNO_3$ at ~120-130 °C in 60 ml Savillex vials on a hotplate for ~2 days. Following digestion, the samples were dried in concentrated HNO_3 several times, and then converted to Cl^--form by repeatedly drying the samples in 6 M HCl–0.06 M HF at ~120 °C. Finally, the samples were re-dissolved completely in 40 ml 6 M HCl–0.06 M HF. From these solutions ~5-10 % aliquots were spiked with a [183]W tracer that was previously calibrated against a pure W metal (Kleine et al., 2004) for the determination of W concentrations by isotope dilution.

For the isotope composition measurements, W was separated from the sample matrix using a two-stage anion exchange chromatography (Kruijer et al., 2015, 2014). The first column consists of a polyethylene transfer pipette (30 cm × 4 mm ⌀) filled with 4 ml of anion exchange resin (Biorad® AG1×8, 200-400 mesh), and serves to separate W from most matrix elements. Since the chromatographic separation is optimized for samples weighing <0.5 g, the individual digestions of the OJP samples (i.e. ~1.1 to ~2.1 g) were split in corresponding fractions of ~0.5 g equivalent sample weight. Thus, prior to the chromatography, each OJP sample was dried, and then re-dissolved in appropriate volumes of loading solution. Each sample fraction corresponding to ~0.5 g sample weight was loaded onto the column in 75 ml 0.5 M HCl–0.5 M HF. Following a rinse using 10 ml 0.5 M HCl–0.5 M HF, W was eluted in 15 ml 6 M HCl–1 M HF. After evaporating the sample solutions to dryness, a few drops of concentrated $HClO_4$ were added and then evaporated at 190-200 °C on a hotplate. This step was repeated once or twice. Subsequently, several drops of concentrated HF were added and evaporated at 200 °C several times until all $HClO_4$ was removed. Using such high temperature dry-downs in $HClO_4$ has several important advantages. First, $HClO_4$ efficiently destroys any organic molecules added to the sample during column chromatography. Second, as Os is highly volatile, drying samples in $HClO_4$ at high temperature ensures that any Os potentially remaining after the chemistry is effectively removed, resulting in sample solutions having [188]Os/[183]W of <0.00001.

163   Such small Os amounts cause any isobaric interferences from Os on W isotopes to be minimal
164   (Section 2.2). Third, using $HClO_4$ results in significantly higher total W yields after chemical
165   separation. This is because W tends to adhere to Teflon, resulting in loss of W in Savillex beakers.
166   Finally, and related to the previous point, addition of $HClO_4$ appears to reduce the magnitude of any
167   analytical [183]W effect (Section 4).

168   Following the $HClO_4$ and HF dry-downs, the samples were re-dissolved in 3.6 ml of 1 M HF.
169   The purpose of the second column is to separate W from most other high field strength elements
170   (HFSE; Nb, Hf, Ti, Zr). Approximately ~20 min. prior to loading, 0.080 ml H_2O_2 (30% w/w) and 2.32
171   ml H_2O were added to the 3.6 ml 1 M HF sample solutions, and then placed on a hotplate (~100 °C)
172   for ~15 min. Commercial 10 ml Biorad® Polyprep columns were filled with 1 ml anion exchange
173   resin (BioRad® AG1×8, 200-400 mesh). After cleaning and conditioning of the resin, the sample
174   solutions are loaded in 6 ml 0.6 M HF–0.4% H_2O_2. This is followed by a rinse with 10 ml 1 M HCl–
175   2% H_2O_2 in which most of the Ti, Zr, and Nb are eluted. Following elution of the remaining Ti, Zr,
176   and Ag with 9 ml 8 M HCl–0.01 M HF, W was collected using 8.5 ml 6 M HCl–1 M HF. After
177   evaporating the W cuts to dryness, several drops of concentrated $HClO_4$ (180-200 °C) were added and
178   evaporated. Following the dry downs in $HClO_4$ the W cuts were converted to F⁻-form by evaporating
179   the samples to dryness in concentrated HF several times, and subsequently re-dissolved in a 0.56 M
180   HNO_3–0.24 M HF running solutions. The total yields of the chemical separation for W were ~70-
181   95%. Total procedural blanks were ~50-100 pg W for the isotope composition analyses and ~1-7 pg
182   for the isotope dilution analyses, in both cases insignificant given the amounts analyzed (~25-30 ng
183   W).

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2.2. Mass spectrometry

186   The W isotope measurements were performed using a ThermoScientific® Neptune *Plus* MC-
187   ICPMS at the Institut für Planetologie in Münster. Samples and standards for W isotope analyses were
188   introduced using self-aspirating C-flow PFA nebulizers (~50μl/min) connected to a Cetac® Aridus II
189   desolvator. The W isotope measurements were performed in low-resolution mode using high-
190   sensitivity 'Jet' sample and 'X'-skimmer cones, which yielded total ion beams of ~1.5-2.5 ×10^{-10} A
191   for a ~30 ppb W standard solution at an uptake rate of ~50 μl/min. All four major W isotopes ([182]W,
192   [183]W, [184]W, [186]W) were measured simultaneously. Electronic baselines (60 s) were obtained prior to
193   each sample measurement by deflecting the beam using the electrostatic analyzer and then subtracted
194   from sample signal intensities. A single W isotope measurement comprised 200 cycles of 4.2 s
195   integration time each. Note that, following the chemical separation, the different W cuts of the two
196   OJP samples derived from individual columns were recombined so that ~25-30 ng of W was available
197   for each individual sample measurement. Using this approach, the total available amount of W
198   separated from the OJP samples was sufficient for five isotope ratio measurements of 200 cycles
199   (Table 1). The reference materials analyzed here (BHVO-2, BCR-2) have higher W concentrations,
200   and so each processed standard (~0.5 g) was analyzed several times (*i.e.*, 2-4 times 200 cycles). Small
201   isobaric interferences from [184]Os and [186]Os on W isotope ratios were corrected by monitoring
202   interference-free [188]Os, and were smaller than 10 parts-per-million (ppm) on [182]W/[184]W and hence
203   insignificant. Instrumental mass bias was corrected by internal normalization to [186]W/[184]W = 0.92767
204   (denoted '6/4') or [186]W/[183]W = 1.9859 (denoted '6/3') using the exponential law. The W isotope
205   analyses of samples were bracketed by measurements of terrestrial solution standards (Alfa Aesar®,
206   batch no. 22312) and results are reported as μ-unit deviations from the mean W isotope ratios of the
207   bracketing solution standards, whose concentrations matched those of the sample solutions to within
208   ~10%. Note that analyses of a different commercially available solution standard (NIST SRM 3163)

209 which has been used in several other W isotope studies by MC-ICPMS (*e.g.*, Willbold et al., 2011,
210 2015; Krabbe et al., 2017) yield W isotope compositions identical to the Alfa Aesar bracketing
211 standard solution (see Kruijer et al., 2012).

3. Results

213   The terrestrial reference materials (BHVO-2, BCR-2) analyzed here exhibit μ^{182}W (6/4) values
214 that are indistinguishable from the bracketing solution standard analyses (Table S1; Fig. 1-3), with a
215 mean μ^{182}W (6/4) of −1.9±11.0 (2s.d., *N*=132). However, the same reference materials also exhibit
216 small and variable W isotope anomalies for normalizations involving ^{183}W (Fig. 2, 3), with coupled
217 excesses in μ^{182}W (6/3) [up to +30 ppm] and μ^{184}W (6/3) [up to +15 ppm], and corresponding deficits
218 in μ^{183}W (6/4) [down to −23 ppm] (Fig. 2c, 2d). Of note, similar W isotope systematics are observed
219 for the OJP samples analyzed in this study. Again, the OJP samples analyzed here exhibit μ^{182}W (6/4)
220 values that are indistinguishable from the bracketing standard solution analyses (Table 1; Fig. 2, 4),
221 where the mean μ^{182}W (6/4) of five replicate measurements corresponds to −0.4±5.1 (95% conf., *N*=5;
222 Table 1). Nevertheless, similar to the reference materials, the same OJP samples also exhibit small
223 and variable W isotope anomalies for normalizations involving ^{183}W (Table 1; Fig. 2, 4), with coupled
224 excesses in μ^{182}W (6/3) [up to +33 ppm] and μ^{184}W (6/3) [up to +17 ppm], and corresponding
225 deficits in μ^{183}W (6/4) [down to −25 ppm] (Fig. 2c, 2d). Finally, the five OJP samples analyzed here
226 display very similar and relatively low W concentrations of between ~13 and ~17 ppb.

4. Accuracy and reproducibility of W isotope measurements by MC-ICPMS

228   The accuracy and reproducibility of the W isotope measurements by MC-ICPMS were assessed
229 through analyses of terrestrial reference materials (BHVO-2, BCR-2) that were digested, processed
230 and analyzed alongside the OJP samples. Although these two reference materials have higher W
231 contents than the OJP samples analyzed, they were nevertheless selected because a large body of
232 high-precision W isotopic data from different laboratories (Bristol, Maryland, Münster) and acquired
233 using different measurement techniques (MC-ICPMS, NTIMS) exists for these reference materials.
234 Moreover, the analyses performed here are complemented by additional analyses of BHVO-2 and
235 BCR-2 performed in the Münster lab since 2012, allowing assessment of the long-term reproducibility
236 of the measurements from the present study. The mean μ^{182}W (6/4) values for BHVO-2 and BCR-2
237 obtained in the present study, and including data from the Münster laboratory since 2012, are −
238 2.2±11.2 (2s.d., *N*=107) and 0.7±7.9 (*N*=13), respectively. Thus, for both samples, μ^{182}W is
239 statistically indistinguishable from the composition of the solution standard (Fig. 1a). The two-
240 standard deviation (2s.d.) of ±11 ppm obtained for the BHVO-2 measurements provides a
241 conservative estimate of the external reproducibility of a *single* W isotope measurement (200 cycles).
242 Of note, a similar reproducibility is obtained for analyses of a terrestrial metal standard NIST129c
243 (Mean μ^{182}W = +1.3±9.3, 2s.d., *N*=53) (Fig. 1b), and our method for high-precision W isotope
244 analyses can therefore also be used to analyze metal samples including iron meteorites (see *e.g.*,
245 Kruijer et al., 2014). Altogether, the technique thus yields accurate and precise μ^{182}W (6/4) values for
246 a measurement consuming as little as 30 ng of W. Provided sufficient W is available, the precision for
247 a single W isotope measurement as quoted above can be further improved by pooling several
248 individual W isotope measurements (*i.e.*, solution replicates) of any given sample. Such a pooled W
249 isotope measurement typically consumes ~150 ng W (*i.e.*, 5× 30 ng) and yields an uncertainty on
250 μ^{182}W (6/4) of *ca.* 5 ppm (95% conf., with *N*=5), where the 95% conf. limits are calculated according
251 to (s.d. × $t_{0.95, N-1}$)/$\sqrt{N}$. For the processed reference materials, the mean μ^{182}W (6/4) of BHVO-2 and
252 NIST129c calculated in this manner correspond to −2.3±5.6 ppm (95% conf., *N*=20) and 1.0±5.5 ppm

253   (*N*=12), demonstrating that W isotope compositions of natural samples can be accurately be
254   determined to high precision.

255   In contrast to the $\mu^{182}W$ (6/4) values discussed above, the W isotope normalizations involving
256   ^{183}W exhibit considerably more scatter. In particular, geological reference materials (BHVO-2, BCR-
257   2) as well as the metal standard (NIST129c) exhibit small, but in some cases resolvable deficits in
258   $\mu^{183}W$ (6/4) that are coupled with small excesses in $\mu^{182}W$ (6/3) and $\mu^{184}W$ (6/3) (Fig. 2a, 2b). These
259   coupled W isotope variations have been observed in several prior high-precision W isotope studies
260   (*e.g.*, Budde et al., 2016; Cook et al., 2014; Dale et al., 2017; Kruijer et al., 2012; Willbold et al.,
261   2011) and are caused by an analytical mass-independent isotope fractionation resulting in apparent
262   deficits in ^{183}W (henceforth referred to as 'analytical ^{183}W effect'). Previous studies demonstrated that
263   this analytical ^{183}W effect is probably not caused by the column chromatography, but instead is most
264   likely caused by incomplete re-dissolution of W following evaporation of solutions in Savillex vials
265   (Kruijer et al., 2012; Willbold et al., 2011). Moreover, Cook and Schönbächler (2016) showed that the
266   W isotope systematics related to the ^{183}W effect are consistent with a nuclear field shift effect
267   resulting in a mass-independent isotope fractionation affecting primarily the odd W isotopes (*i.e.*,
268   ^{183}W). For each individual sample, the $\mu^{182}W$ (6/3) values can therefore be corrected using its
269   measured $\mu^{184}W$ (6/3) and the following relation (Kruijer et al., 2012; Cook and Schönbächler,
270   2016): $\mu^{182}W$ (6/3)$_{corrected}$ = $\mu^{182}W$ (6/3)$_{measured}$ − 1.962 × $\mu^{184}W$ (6/3). Even though the nuclear field
271   shift theoretically also slightly modifies $\mu^{182}W$ (6/4) values, the magnitude of this effect is ~16 times
272   smaller than the effect on $\mu^{184}W$ (6/3), and hence, essentially negligible. Nevertheless, to be fully
273   consistent, the above approach was used here to correct both the $\mu^{182}W$ (6/4) and $\mu^{182}W$ (6/3) of
274   individual BHVO-2 and BCR-2 standards. After the correction, the mean $\mu^{182}W$ (6/4) and $\mu^{182}W$
275   (6/3) for BHVO-2 and BCR-2 are indistinguishable to within <0.1 ppm (Table S1), demonstrating
276   that the nuclear field shift effect very accurately describes the observed difference between $\mu^{182}W$
277   (6/4) and $\mu^{182}W$ (6/3) for processed standards and samples.

278   The analytical ^{183}W effect presents somewhat of a challenge when precise analyses of non-
279   radiogenic W isotopes are required (*i.e.*, $\mu^{183}W$ and $\mu^{184}W$), as in studies focused on identifying
280   nucleosynthetic W isotope heterogeneities in meteorites and their components (*e.g.*, Burkhardt et al.,
281   2012; Kruijer et al., 2014). Accordingly, in such studies the magnitude of any analytical ^{183}W effect
282   must be closely monitored by analyzing a wide range of terrestrial reference materials. Nevertheless,
283   for studies where only precise $\mu^{182}W$ data are required, the analytical ^{183}W effect does not present an
284   issue. This is because the ^{183}W effect affect modifies $\mu^{182}W$ (6/4) values only to a very minor degree,
285   and consequently most recent MC-ICPMS studies investigating $\mu^{182}W$ variations in terrestrial and
286   (some) extraterrestrial samples have exclusively used the $\mu^{182}W$ (6/4) normalization (Dale et al.,
287   2017; Kruijer et al., 2017, 2015). Thus, the ^{183}W effect is irrelevant when precisely determining $\mu^{182}W$
288   (6/4) variations by MC-ICPMS in terrestrial rocks, including the OJP samples analyzed here.
289   Nevertheless, some previous NTIMS studies, including the OJP study of Rizo et al. (2016), relied on a
290   double normalization procedure employing $\mu^{183}W$, and consequently, as discussed below, the ^{183}W
291   effect may pose an issue for obtaining accurate $\mu^{182}W$ data using this technique.

292   **5. Agreement between recent high-precision W isotope studies**

293   The potential presence of an analytical ^{183}W effect raises the question of how good the agreement
294   is between different recent high-precision W isotope studies. Tungsten isotope analyses of the same
295   samples but conducted by different laboratories generally reproduce very well (Fig. 5). For example,
296   for a pillow basalt sample from Isua, Greenland (SM/GR/00/26), two MC-ICPMS studies, conducted
297   in different labs, obtained indistinguishable $\mu^{182}W$ excesses of *ca.* +11 to +13 ppm (Dale et al., 2017;

298 Willbold et al., 2011). Similarly, for two KREEP-rich lunar samples (68115, 68815), two recent
299 studies reported indistinguishable $\mu^{182}W$ excesses of *ca.* +25 ppm (Kruijer et al., 2015; Touboul et al.,
300 2015). Similar good agreement is seen for analyses of meteorites. For instance, for the IVB iron
301 meteorite Skookum, indistinguishable $\mu^{182}W$ values of –330±4 and –335±6 were obtained by MC-
302 ICPMS and NTIMS (Kruijer et al., 2013, 2014; Archer et al., 2017). Collectively, these examples
303 demonstrate that reproducible and precise $\mu^{182}W$ data can be obtained using both MC-ICPMS and N-
304 TIMS techniques.

305   However, in detail some disparities between laboratories become apparent for materials that have
306 been analyzed very often, such as geological reference material BHVO-2 (Fig. 5). Whereas the mean
307 $\mu^{182}W$ values for BHVO-2 obtained here and by Willbold et al. (2011, 2015) are essentially
308 indistinguishable from other standards, geological reference materials and most modern terrestrial
309 rocks, Mundl et al. (2017) and Mei et al. (2018) reported small but resolved deficits for BHVO-2
310 down to *ca.* –9 ppm. The exact cause of these apparent small-scale ^{182}W variations for BHVO-2
311 remains unclear, and resolving this issue will require future W isotope analyses of the same BHVO-2
312 powder digestion by different laboratories. Overall the BHVO-2 data highlight that determining
313 $\mu^{182}W$ variations of < ~10 ppm is analytically extremely challenging. In particular, as will be
314 illustrated below, at this level precision other analytical effects, including the nuclear field shift effect
315 described above, potentially become problematic.

316 **6. No ^{182}W anomaly in the Ontong Java Plateau Source**

317   Despite the overall good agreement between several W isotope studies, W isotope measurements
318 of drill core samples from the Ontong Java Plateau do exhibit inconsistencies. In particular, the mean
319 $\mu^{182}W$ (6/4) obtained for the OJP samples analyzed here corresponds to −0.4±5.1 ppm (95% conf.,
320 *N*=5). This value is indistinguishable from the value of the present-day bulk silicate Earth as defined
321 by the bracketing solution standard as well as the processed terrestrial reference materials analyzed in
322 this study. Moreover, the same OJP samples exhibit coupled variations in $\mu^{182}W$ (6/3), $\mu^{184}W$ (6/3),
323 and $\mu^{183}W$ (6/4) which closely mirror those observed for the terrestrial reference materials in this
324 study (Fig. 2,4). These variations, therefore, must be analytical in origin, and are very likely caused by
325 a nuclear field shift effect induced during sample preparation (Section 4). Consequently, our results
326 do not provide evidence for a resolved $\mu^{182}W$ anomaly in rocks from the Ontong Java Plateau. This is
327 consistent with the findings of Willbold et al. (2011), who analyzed a OJP sample from the same drill
328 core (*i.e.*, 192-1187A-006R-06W) and also did not find a resolved ^{182}W anomaly. Furthermore,
329 Willbold et al. (2011) also reported 'normal' $\mu^{182}W$ compositions for a sample from another OJP core
330 (192-1185A), as well as for several samples from two other large igneous provinces in the western
331 Pacific Ocean, including the related Manihiki-Plateau and the Shatsky Rise.

332   Contrary to the results from this and the Willbold et al. (2011) study, Rizo et al (2016a) reported
333 a well-resolved $\mu^{182}W$ excess of *ca.* +24 ppm in an OJP sample (192-1187A-009R-04W). One
334 potential explanation for the discrepancy between the studies is that there are true $\mu^{182}W$
335 heterogeneities within the Ontong Java Plateau. However, not only are the samples from this study
336 and that of Rizo et al. (2016a) from the same drill core, they also derive from the same lava flow and
337 were sampled in very close proximity to each other (as little as ~6 cm apart; see Fig. S1). Moreover,
338 all samples from this part of the core belong to the same lithologic unit (Kroenke type; Fitton and
339 Godard, 2004) and as such exhibit strong geochemical similarities. Consequently, it seems extremely
340 unlikely that $\mu^{182}W$ heterogeneities exist among the OJP samples analyzed here and by Rizo et al.
341 (2016a). Another explanation for the disparity between the studies could be that the source $\mu^{182}W$
342 signatures of the OJP samples are variably affected by contamination with W from a 'normal' $\mu^{182}W$

343   source (*i.e.*, $\mu^{182}W = 0$). However, both OJP samples analyzed here (Table 1) and those by Rizo et al.
344   (2016a) exhibit very similar and low W concentrations between ~13 and ~23 ppb, where the samples
345   from the present study have W concentrations at the lower end of this range. Thus, W contamination
346   from another source (*e.g.* from the drill core, crustal rocks, or seawater) can effectively be ruled as the
347   cause of the disparity in $\mu^{182}W$ between the studies.

348   This leaves an unaccounted analytical ^{183}W effect as the most likely cause for the disparate ^{182}W
349   results for OJP samples reported in this and the Rizo et al. (2016a) study. The $\mu^{183}W$ analyses of the
350   terrestrial reference materials and OJP samples in the present study (Table 1) demonstrate that
351   analytical $\mu^{183}W$ deficits of up to several tens of ppm are not atypical. This is especially true for large
352   samples with relatively low yields such as the OJP samples analyzed by Rizo et al. (2016a) (see also
353   below). Such analytical $\mu^{183}W$ deficits are problematic in case of W isotope measurements by NTIMS
354   because such analyses require a double normalization to correct for instrumental mass fractionation
355   and therefore have to utilize W isotope ratios involving ^{183}W. More specifically, for W isotope
356   compositions determined by N-TIMS, the measured (and mass fractionation corrected) $^{182}W/^{184}W$ and
357      $^{183}W/^{184}W$ of standards exhibit a residual positive correlation (Touboul and Walker, 2011). These
358   correlated W isotope ratios have been attributed to a changing mass-dependent isotope fractionation
359   of O isotopes in the TIMS source that causes variations in measured W-oxide isotope compositions,
360   ultimately leading to residual variations in measured $\mu^{182}W$ compositions on the order of ~100-150
361   ppm (Touboul and Walker, 2011). Because the slope of the correlation line is invariant over time, the
362   measured $\mu^{182}W$ of a sample is typically corrected for this second order mass fractionation effect
363   using the (constant) slope of the correlation line together with the measured $^{183}W/^{184}W$ ratio of the
364   sample (Fig. 6). This approach results in final $\mu^{182}W$ values with a precision of ±5 ppm (2s.d.) as long
365   as the corresponding $\mu^{183}W$ values are accurately and precisely determined (Touboul and Walker,
366   2012). However, because measured $\mu^{183}W$ values are needed to correct the $\mu^{182}W$ values for this
367   second-order mass fractionation, the N-TIMS method used by Rizo et al. (2016a) does not yield an
368   independent measurement of $\mu^{183}W$. Thus, any mass-independent analytical effect on $\mu^{183}W$ would go
369   unnoticed in the NTIMS analyses. It therefore seems possible that the +24 ppm $\mu^{182}W$ anomaly
370   inferred for the OJP sample analyzed by Rizo et al. (2016) is caused by such an effect. For instance,
371   an apparent +24 ppm $\mu^{182}W$ anomaly would be inferred if the same sample had an analytical $\mu^{183}W$
372   deficit of similar magnitude, *i.e.*, –24 ppm (Fig. 6). It is important to note that this magnitude for the
373   ^{183}W effect is well within the range of observed effects, including some of the OJP samples analyzed
374   in the present study (Table 1). Accordingly, the +24 ppm $\mu^{182}W$ anomaly reported by Rizo et al.
375   (2016a) may be caused by an analytical effect on ^{183}W.

376   Although Rizo et al. (2016a) found resolved $\mu^{182}W$ excesses for two samples (OJP sample 192-
377   1187A-009R-04W and one Baffin Bay sample), they did not find such anomalies for the other
378   samples they investigated. This raises the question as to why this might be the case, particularly given
379   that the latter samples would likely also have been subjected to the analytical ^{183}W effect. The answer
380   may lie in the relatively low W concentrations of both the OJP and Baffin Bay samples (<23 ppb W)
381   in comparison to the other samples as well as the terrestrial standards. As a consequence, whereas for
382   most samples 'only' several grams of sample material had to be processed in order to have sufficient
383   W for a single NTIMS analysis (~500 ng W), significantly larger sample amounts were required for
384   the OJP sample and the Baffin Bay sample Pd-2 (~34 g and ~44 g, respectively). For this reason, the
385   chemical separation for these two samples required the use of a large number of chromatography
386   columns, and accordingly, the evaporation of large volumes of sample solution in Savillex vials on a
387   hotplate. Given that the analytical ^{183}W effect is very likely generated during incomplete re-
388   dissolution of W in Savillex vials (Section 4), this extensive W separation procedure for the OJP and
389   Baffin Bay samples might have magnified any analytical ^{183}W effect in comparison to samples with

390   higher W amounts. Note that the relatively low procedural W yields for these two samples (~50%)
391   would be consistent with this interpretation.

392   In summary, we have not reproduced the +24 ppm μ^{182}W excess reported by Rizo et al. (2016a)
393   for OJP samples, and the data presented here demonstrate that there is no ^{182}W excess in rocks from
394   the Ontong Java Plateau. As such, the results from this study also cast some doubt on the validity of
395   the +48 ppm μ^{182}W excess reported for a sample from Baffin Bay (Pd-2) as determined by NTIMS in
396   the same analytical campaign (Rizo et al., 2016a). Reassessing the μ^{182}W composition for samples
397   from Baffin Bay will therefore be an important future task, ideally utilizing both MC-ICPMS and
398   NTIMS studies. Finally, we note that Archer et al. (2017) recently developed a new N-TIMS
399   technique for high-precision W isotope analysis that permits the independent and simultaneous
400   measurement of ^{18}O/^{16}O on WO$_3^-$. As a consequence, this new TIMS technique no longer relies on
401   accurate μ^{183}W analyses for obtaining precise μ^{182}W measurements. Using this technique, it should in
402   principle be possible to assess the occurrence of the analytical ^{183}W effect in NTIMS analyses and to
403   evaluate as to whether it has the same magnitude as in MC-ICPMS studies.

404   7. Conclusions

405   The results presented here and elsewhere demonstrate that an analytical ^{183}W effect can
406   potentially occur in any high-precision W isotope study. Thus, to avoid erroneous data and resulting
407   misinterpretation, any high-precision W isotope study conducted by MC-ICPMS or NTIMS should
408   assess whether such potential analytical ^{183}W effects are significant. Such an assessment requires (i) a
409   measurement technique permitting an independent measurement of μ^{183}W, and (ii) the analysis of a
410   sufficient number of terrestrial reference materials alongside the samples. Nevertheless, once the ^{183}W
411   effect is taken into account, both MC-ICPMS and NTIMS can provide W isotope data that is accurate
412   to within a very high level of precision (*i.e.*, down to *ca.* 5 ppm, 95% conf.).

413   The new data for OJP samples presented here demonstrate that there is no resolvable ^{182}W excess
414   in the Ontong Java Plateau source. This is consistent with results from a prior MC-ICPMS study
415   (Willbold et al., 2011), but is in disagreement with the +24 ppm ^{182}W excess reported for OJP samples
416   in an NTIMS study (Rizo et al., 2016a). As such, these results also cast some doubt on the validity of
417   the ^{182}W excess reported for a single Baffin Bay sample in the same study that reported a resolved
418   ^{182}W excess for the OJP samples (Rizo et al., 2016a). Assessing the ^{182}W composition of Baffin Bay
419   samples, therefore, will necessitate new high-precision W isotope measurements, ideally using both
420   MC-ICPMS and NTIMS.

421   One important implication of the present study is that μ^{182}W excesses in terrestrial rocks seem to
422   be restricted to a narrow range between *ca.* +10 and +15 ppm relative to the modern bulk silicate
423   Earth. Excesses of this magnitude can readily be accounted for by late accretion, implying that these
424   ^{182}W excesses do not require the preservation of early mantle heterogeneities that have been generated
425   prior to the Moon-forming impact.

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533

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Figure captions

Fig. 1: μ^{182}W compositions of terrestrial reference materials. Each data point represents a single W isotope measurement of a reference material that was processed through the full chemical separation (a) Basalt standards (BHVO-2 and BCR-2), and (b) metal standard NIST 129c. Error bars denote two standard errors (2s.e.) obtained from internal run statistics. The external reproducibility (2 s.d.) of a single W isotope measurement (200 cycles) as inferred from replicate standard analyses is shown as a light gray filled bar, and the corresponding 95% confidence limits as a dark gray bar. Data sources: This study (open symbols), Budde et al. (2016, 2017) and Kruijer et al. (2015, 2017a, 2017b, 2017c) (closed symbols).

Fig. 2: μ^{182}W vs. μ^{183}W (or μ^{184}W) data of reference materials and OJP samples analyzed in this study. Each data point represents a single W isotope analysis (200 cycles) and error bars represent two standard errors (2s.e.) obtained from internal run statistics. (a) Terrestrial reference materials (BHVO-2, BCR-2, NIST129c), and (b) OJP samples plotted together with reference material analyses. Distinguished are BHVO-2 data from this study (open symbols) and from prior studies (closed symbols) conducted by the Münster group. Solid lines depict trajectories predicted for analytical ^{183}W deficits (Kruijer et al., 2012; Cook and Schönbächler, 2016). Data sources: This study (open symbols), Budde et al. (2016, 2017) and Kruijer et al. (2015, 2017a, 2017b, 2017c).

Fig. 3: Quintuple μ^{182}W measurements of terrestrial reference materials BHVO-2, BCR-2, and NIST129c. Each data point represents the mean of five W isotope measurements (200 cycles) and error bars denote 95% conf. limits. Shaded area shows the mean of all quintuple measurements (*N*=35) and the associated reproducibility (2s.d).

Fig. 4: μ^{182}W vs. μ^{183}W (or μ^{184}W) data of OJP samples analyzed in this work. The μ^{182}W value reported by Rizo et al. (2016) is plotted for comparison (green shaded area). Each data point represents a single analysis of an OJP sample and error bars represent two standard errors (2s.e.) obtained from internal run statistics.

Fig. 5: Compilation of μ^{182}W data obtained in recent high-precision W isotope studies. Plotted are data for samples that were analyzed by at least two laboratories. Error bars denote external uncertainties (2σ). Distinguished are W isotope analyses by MC-ICPMS (closed symbols) and by NTIMS (open symbols). Data sources: (1) Rizo et al., 2016a, (2) Willbold et al., 2011, (3) Mundl et al. (2017), (4) Dale et al., 2017, (5) Kruijer et al., 2015, (6) Touboul et al., 2015. The measured μ^{182}W value for the individual Isua sample (SM/GR/98/26) analyzed by Willbold et al. (2011) was corrected for a small analytical effect on ^{183}W using its measured μ^{183}W (following the equations reported in Kruijer et al., 2012; Cook and Schönbächler, 2016). For BHVO-2 the mean μ^{182}W value of each study is reported.

Fig. 6: Explanatory diagram of μ^{182}W *vs.* μ^{183}W illustrating how an analytical ^{183}W effect can lead to apparent μ^{182}W excesses following the second order mass bias correction used in NTIMS measurements.

(a) Terrestrial silicate rock standards (single measurements)

BHVO-2
BCR-2

$\mu^{182}W$ (6/4)

BHVO-2:
$\mu^{182}W = -2.2\pm11.2$ (2s.d., N=107)

BCR-2:
$\mu^{182}W = 0.7\pm7.9$ (2s.d., N=13)

(b) Terrestrial metal standard NIST129c (single measurements)

$\mu^{182}W$ (6/4)

NIST129c:
Mean $\mu^{182}W = 1.3\pm9.3$ (2s.d., N=53)

(a)
- ● NIST129c
- ◆ BHVO-2
- ■ BCR-2

$\mu^{182}W$ (6/4) vs $\mu^{183}W$ (6/4)

^{183}W deficit

(b)
$\mu^{182}W$ (6/3) vs $\mu^{184}W$ (6/3)

^{183}W deficit

(c)
- ◆ OJP

$\mu^{182}W$ (6/4) vs $\mu^{183}W$ (6/4)

(d)
$\mu^{182}W$ (6/3) vs $\mu^{184}W$ (6/3)
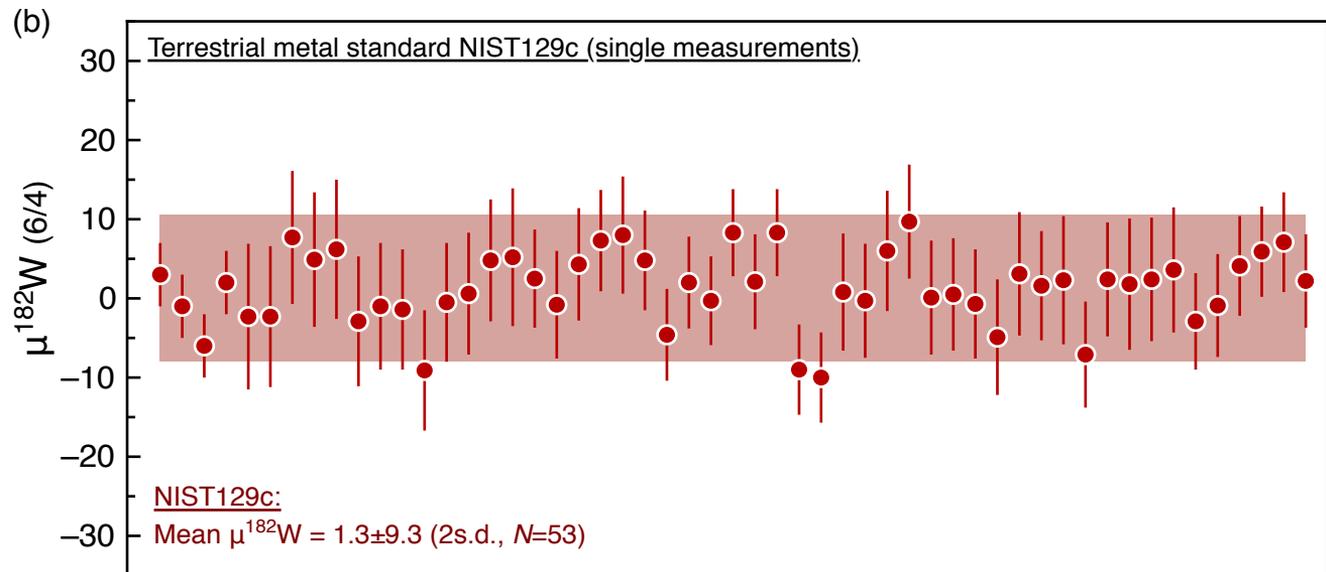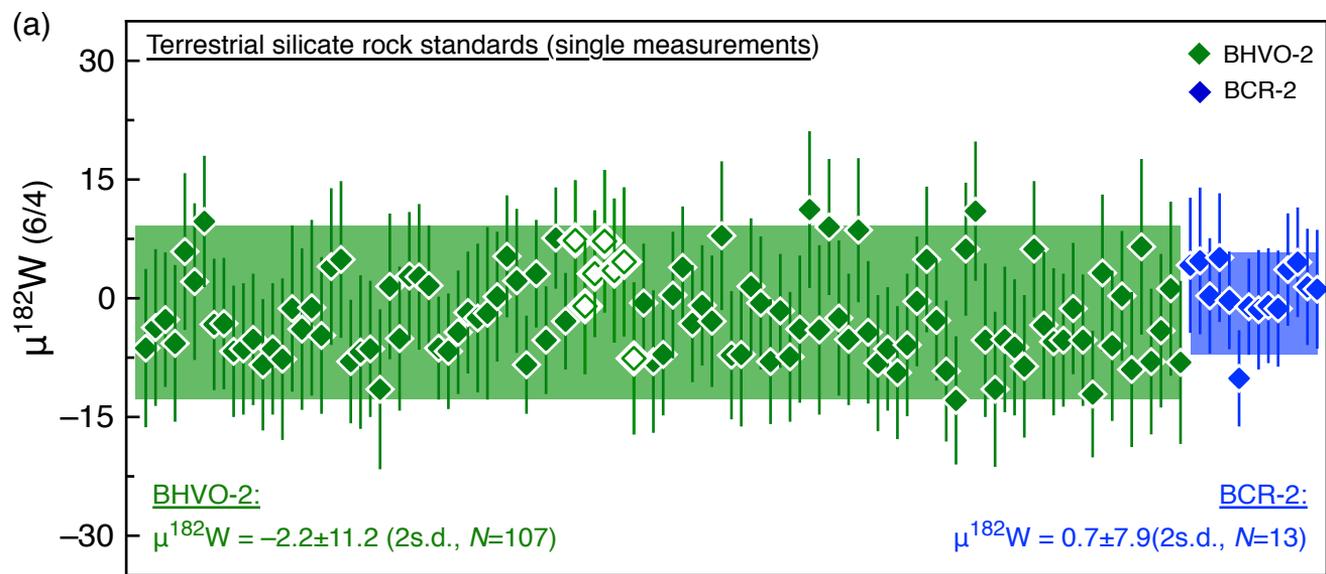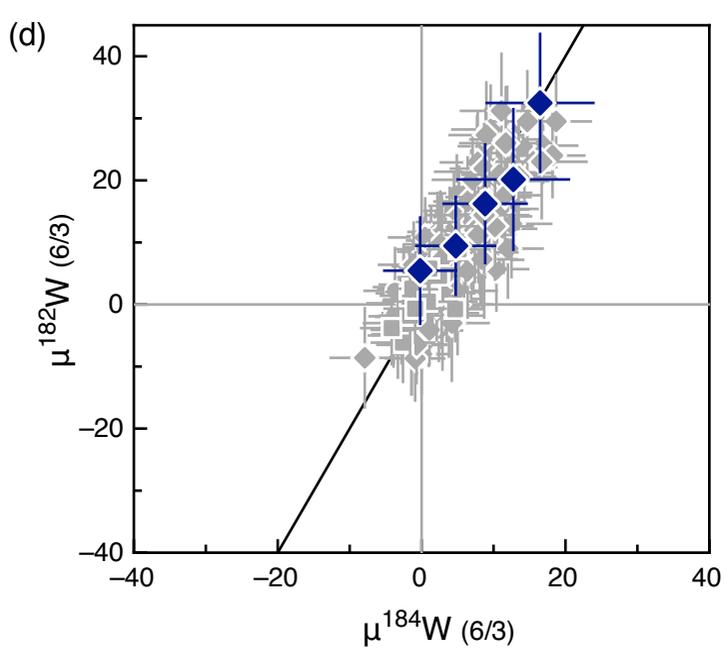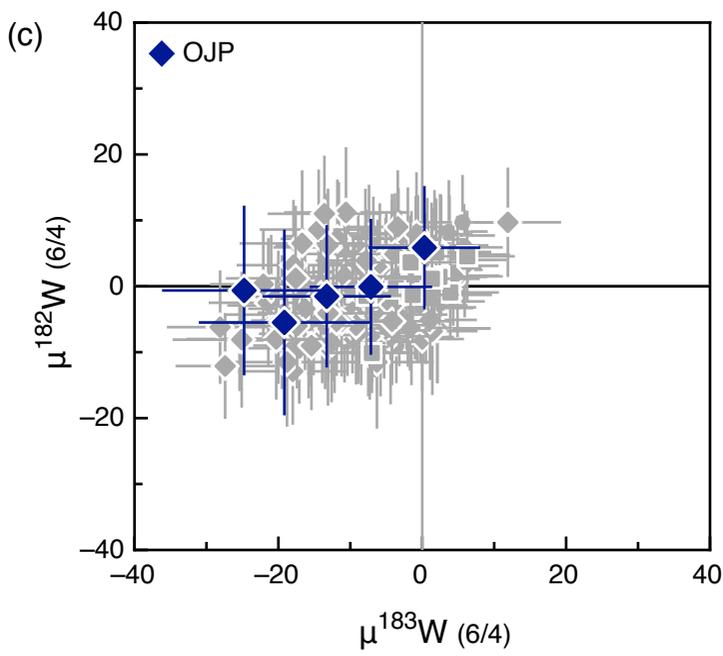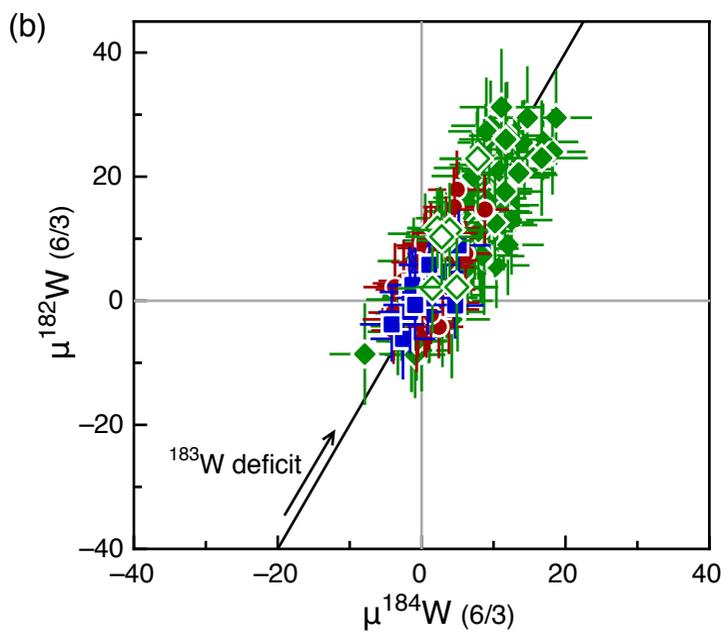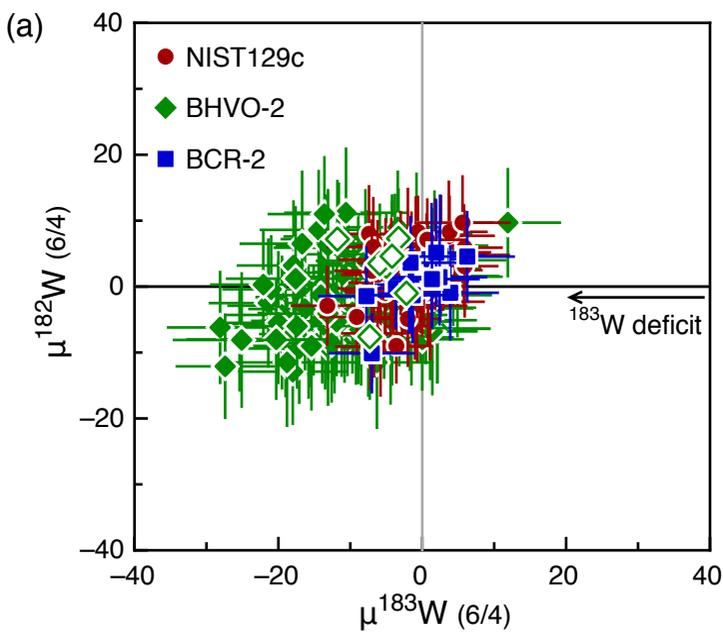
Quintuple measurements of terrestrial reference materials

BHVO-2:
$\mu^{182}W = -2.3 \pm 5.6$ (2s.d., $N=20$)

NIST129c:
$\mu^{182}W = 1.0 \pm 5.5$ (2s.d., $N=12$)

$\mu^{182}W$ (6/4)

◆ BHVO-2
● NIST129c

Rizo et al. (2016)

μ¹⁸²W (6/4) vs μ¹⁸³W (6/4)

Rizo et al. (2016)

μ¹⁸²W (6/3) vs μ¹⁸⁴W (6/3)

Ontong Java Plateau

192-1187A 9R (1)
192-1187A 6R (2)
192-1187A 9R (This study)

BHVO-2

(2)
(1)
(3)
(This study)

Isua

SM/GR/98/26 (2)
SM/GR/98/26 (6)

Moon

68115 (5)
68115 (6)
68815 (5)
68815 (6)

$\mu^{182}W$

−20   0   20   40

Figure axis labels:
- x-axis: $\mu^{183}W\ (6/4)$
- y-axis: $\mu^{182}W\ (6/4)$

Labels within figure:
- Inferred MF
- ^{183}W deficit
- MF
- Inferred OJP
- Secondary MF line
- True OJP
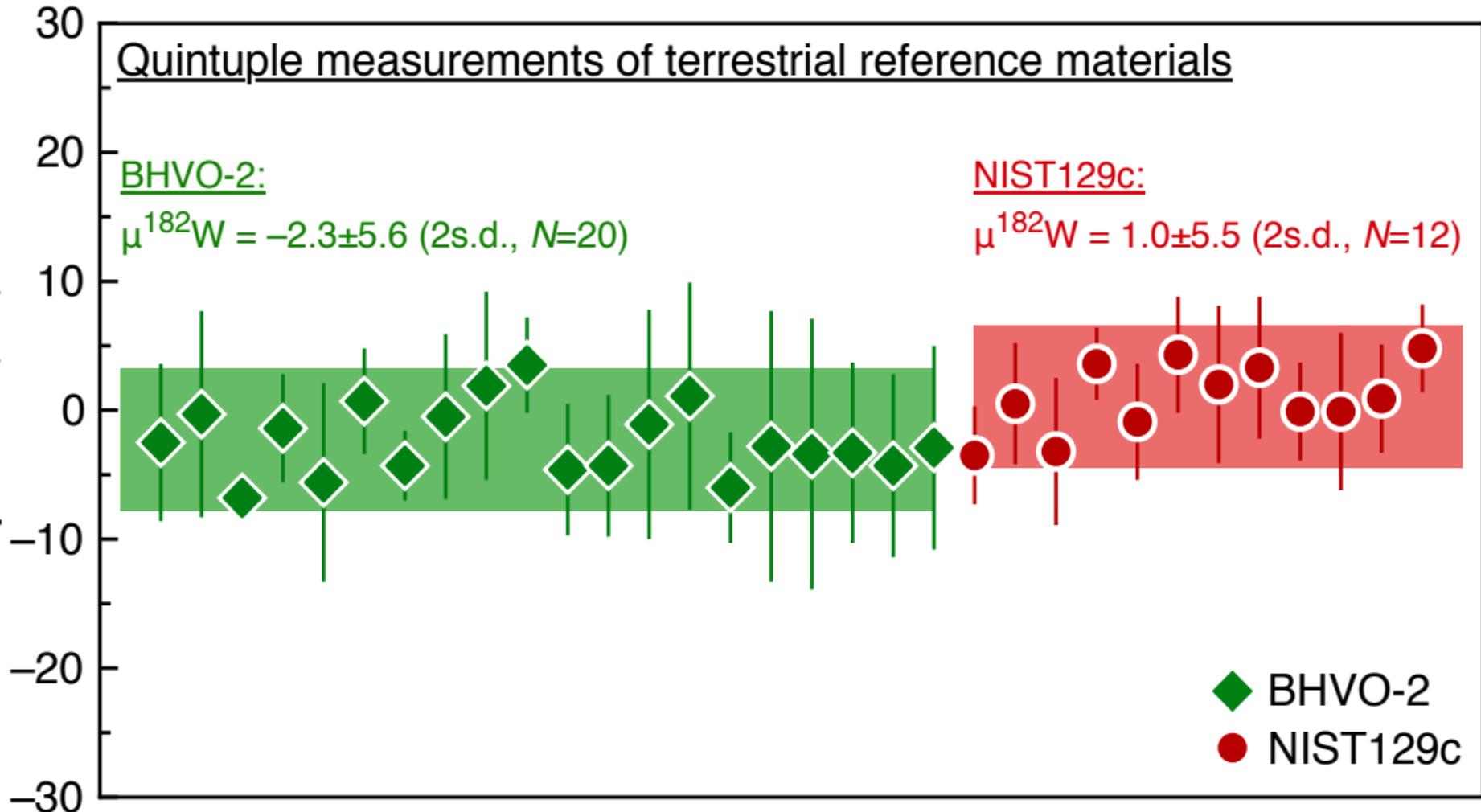
Table 1
Tungsten isotopic compositions of Ontong Java Plateau drill core samples and reference materials determined by MC-ICPMS.

Sample	ID	Weight (g)	W (ng/g)	Normalized to $^{186}W/^{184}W = 0.92767$				Normalized to $^{186}W/^{183}W = 1.9859$				$\mu^{182}W_{corr.}$	$(\pm2\sigma)^a$
				$\mu^{182}W_{meas.}$	$(\pm2\sigma)$	$\mu^{183}W_{meas.}$	$(\pm2\sigma)$	$\mu^{182}W_{meas.}$	$(\pm2\sigma)$	$\mu^{184}W_{meas.}$	$(\pm2\sigma)$		
OJP drill core samples													
192-1187A-009R-04W (118.5-120)	CM01	2.11	17.3	-0.1	± 10.3	-7.1	± 8.5	9.5	± 8.1	4.7	± 5.7	0.1	± 13.9
192-1187A-009R-04W (118.5-120)	CN01A	1.27	17.3	5.9	± 9.3	0.3	± 7.8	5.4	± 8.8	-0.2	± 5.2	5.8	± 13.5
192-1187A-009R-04W (118.5-120)	CN01BC	2.08	13.4	-5.5	± 14.1	-19.2	± 11.9	20.1	± 11.5	12.8	± 7.9	-4.9	± 19.6
192-1187A-009R-04W (15-17)	CM02	2.08	16.2	-1.5	± 10.8	-13.3	± 8.9	16.2	± 9.8	8.8	± 5.9	-1.1	± 15.4
192-1187A-009R-04W (15-17)	CN02AB	1.89	15.6	-0.6	± 12.9	-24.8	± 11.4	32.5	± 11.3	16.5	± 7.6	0.2	± 18.9
192-1187A-009R-04W	**Mean (N=5)**	±2 s.d.		**-0.4**	**± 8.2**	-12.8	± 19.7	16.8	± 21.0	8.5	± 13.1	**0.0**	**± 7.7**
		±95% conf.			**± 5.1**		± 12.2		± 13.0		± 8.1	**0.0**	**± 4.8**
Geological reference materials (Mean values)													
BHVO-2		Mean (N=107)	±2 s.d.	-2.2	± 11.2	-9.7	± 15.6	10.9	± 19.6	6.5	± 10.4	-1.8	± 11.2
BCR-2		Mean (N=13)	±2 s.d.	0.7	± 7.9	-0.4	± 7.9	1.2	± 7.7	0.2	± 5.3	0.7	± 7.8
NIST 129c		Mean (N=53)	±2 s.d.	1.3	± 9.3	-1.8	± 8.0	3.7	± 10.6	1.2	± 5.4	1.3	± 9.2

Each analysis represents a single W isotope measurement (200 cycles). Uncertainties on measured μ^iW values of OJP samples (subscript 'meas.') are two standard errors (2s.e.) obtained from internal run statistics.
[a] $\mu^{182}W_{corr.}$: Corrected for an analytical effect on ^{183}W according to $\mu^{182}W_{corr.} = \mu^{184}W_{meas.} - 1.962 \times \mu^{184}W_{meas.}$ (Cook and Schönbächler, 2016; Kruijer et al., 2012).
The added uncertainty induced by this correction is propagated in the reported uncertainties of corrected μ^iW values.