1	Origin of the analytical ¹⁸³ W effect and its implications
2	for tungsten isotope analyses
3	
4	
5	Gerrit Budde ^{*a,b,c} , Gregory J. Archer ^b , François L. H. Tissot ^c , Sebastian Tappe ^d ,
6	Thorsten Kleine ^{b,e}
7	
8	^a Department of Earth, Environmental and Planetary Sciences, Brown University,
9	Providence, RI 02912, USA
10	^b Institut für Planetologie, University of Münster, 48149 Münster, Germany
11	°The Isotoparium, Division of Geological and Planetary Sciences, California Institute of
12	Technology, Pasadena, CA 91125, USA
13	^d Department of Geosciences, UiT The Arctic University of Norway, N-9037 Tromsø,
14	Norway
15	^e Max Planck Institute for Solar System Research, 37077 Göttingen, Germany
16	
17	
18	*corresponding author: gerrit_budde@brown.edu
19	
20	
21	
22	
23	
24	accepted for publication in
25	Journal of Analytical Atomic Spectrometry
26	https://doi.org/10.1039/D2JA00102K
27	
28	

29 Abstract

30

31 Mass-independent tungsten isotope variations provide critical insights into the timing 32 and nature of processes that occurred in the early Solar System and during planetary 33 differentiation. However, W isotope analyses are often compromised by an analytical 34 artifact manifesting itself as an apparent deficit in ¹⁸³W, whose origin and nature have 35 remained enigmatic. Here, by evaluating previously published high-precision W isotope 36 data for a large and diverse set of terrestrial samples, we demonstrate that this artifact 37 occurs independent of the type of mass spectrometer and confirm that it can be attributed to mass-independent fractionation of ¹⁸³W. Contrary to previous proposals, we find that 38 39 this 'analytical ¹⁸³W effect' cannot be explained by a nuclear field shift, but may instead 40 reflect a magnetic isotope effect. Regardless of its exact origin, our investigation reveals 41 that this artifact is induced during the chemical separation of W, and that the specific 42 combination of chromatographic purification and dry-down procedure determines its 43 overall magnitude. Within a given analytical protocol, however, its size is strongly 44 controlled by the amount of W that is processed, where the ¹⁸³W effect increases with 45 decreasing amount of W. Therefore, this work resolves apparent inconsistencies 46 between previous studies regarding the occurrence and magnitude of the ¹⁸³W effect, 47 and provides directions for its mitigation and reliable correction. This in turn is crucial for 48 the accurate interpretation of W isotope data with respect to radiogenic and 49 nucleosynthetic anomalies for both terrestrial and meteoritic materials.

51 **1. Introduction**

52 Mass-independent tungsten (W) isotope variations are a versatile tool in 53 cosmochemical and geochemical research, as they provide critical insights into the 54 timing and nature of processes that range from the formation of the Solar System to the 55 inner workings of the ancient and modern silicate Earth (see review by Kleine and 56 Walker¹). For instance, radiogenic variations, resulting from decay of short-lived ¹⁸²Hf to 57 ¹⁸²W ($t_{1/2} \approx 8.9 \text{ Ma})^2$, have proven uniquely useful for constraining the timescales of planetary accretion and differentiation.^{e.g., 3} Moreover, there is growing evidence for the 58 59 presence of widespread nucleosynthetic W isotope anomalies among Solar System 60 materials, including meteoritic components as well as bulk meteorites.^{e.g., 4-9} These 61 anomalies arise from the heterogeneous distribution of presolar matter and, as such, 62 carry important information on the origin and genetic relationships of meteoritic and 63 planetary materials.

64 Using state-of-the-art multicollector inductively-coupled plasma mass spectrometers 65 (MC-ICP-MS) as well as refined techniques for negative thermal ionization mass 66 spectrometry (N-TIMS), it has become possible to determine W isotope ratios with a precision of a few parts per million (ppm).^{e.g., 10–13} However, most high-precision MC-ICP-67 MS studies report a significant (*i.e.*, up to a few tens of ppm), albeit variable, analytical 68 69 artifact that compromises the isotopic data and occurs independent of sample matrix, 70 measurement protocol, and MC-ICP-MS model. This artifact manifests itself as spurious 71 W isotope anomalies that reflect an apparent deficit in ¹⁸³W (relative to the even-72 numbered W isotopes), and is hereafter referred to as the 'analytical ¹⁸³W effect'. As 73 demonstrated in Fig. 1, this results in a complex interplay of natural and analytical effects 74 that severely complicates the interpretation of W isotope data and, consequently, a 75 precise quantification of the ¹⁸³W effect is crucial for identifying and disentangling 76 genuine W isotope anomalies.

77 It is currently unclear, however, when and how the ¹⁸³W effect is created, and why its 78 magnitude varies between different studies and even among different samples within the 79 same study. Previously, this artifact was attributed to mass-independent fractionation by the nuclear field shift (NFS) effect; e.g., 14 but, as we will demonstrate here, such NFS-80 driven W isotope fractionation is difficult to reconcile with revised nuclear parameters and 81 82 other characteristics of this artifact. Moreover, the interpretation that the ¹⁸³W effect is induced during the chemical separation of W^{e.g., 13,15} appears to be at odds with the fact 83 that studies utilizing N-TIMS did not recognize such an artifact, e.g., 16,17 which would imply 84 85 that it is specific to MC-ICP-MS measurements.

86 Consequently, major unknowns regarding the analytical ¹⁸³W effect have remained to 87 date, which we address here by evaluating high-precision W isotope data for diverse

terrestrial samples from numerous recent studies. Our investigation yields novel insights into the origin and nature of the ¹⁸³W effect with important implications for its mitigation and correction, which will aid in the reliable interpretation of W isotope data with respect to radiogenic and nucleosynthetic anomalies. Finally, we use data for different W solution standards and the observations from this study to better constrain the W isotope composition of bulk silicate Earth (BSE), which is an important prerequisite for the evaluation of isotopic variations in terrestrial and meteoritic materials.

95 96

97 2. Materials and Methods

98 2.1. Samples and data sources

99 In this study, we primarily evaluate W isotope data obtained by MC-ICP-MS in the 100 Institut für Planetologie (IfP) at the University of Münster (since 2012), as these studies 101 generally followed the same analytical protocol (Section 2.2) and provided comprehensive sets of W isotope ratios and normalizations.^{4,6,7,11,18–25} Because many of 102 103 the investigated (mostly meteoritic) samples have radiogenic or nucleosynthetic 104 anomalies, which complicates the assessment of any analytical artifacts (Fig. 1), we here 105 consider only terrestrial samples for which the presence of such natural W isotope 106 anomalies can essentially be ruled out.

107 In particular, we focus on a recently obtained data set for a comprehensive suite of 108 kimberlites (30 individual analyses) from 18 occurrences across sub-Saharan Africa.²⁶ 109 These high-precision W concentration and isotope data reveal no radiogenic or 110 nucleosynthetic variations (Section 4), but show that these samples are characterized by 111 large variations in W concentrations and in the magnitude of the analytical ¹⁸³W effect. 112 As such, the kimberlite sample set, combined with data for other geological reference 113 materials measured at the IfP (BHVO-2, BCR-2, JB-2, JG-1, JA-2, DTS-2b, AGV-2, SRM 114 129c), provides a unique opportunity for investigating the origin and nature of the 115 analytical ¹⁸³W effect. For further comparison, we also compiled MC-ICP-MS data from 116 other laboratories as well as W isotope data obtained by N-TIMS (for references see 117 Sections 3 and 5.1).

118

119 2.2. Chemical separation and isotope ratio measurements of W

As will be discussed below (Sections 4.2 and 5.2), the magnitude of the analytical ¹⁸³W effect depends on details of the analytical protocol and, therefore, the methods for the chemical separation of W and isotope composition measurements commonly used at the IfP are briefly summarized here (details of the established procedures are described in numerous previous studies^{7,11,19}). In general, sample powders are digested
in Savillex[®] PFA vials on a hotplate using concentrated HF–HNO₃(–HClO₄), followed by
treatments with HNO₃ or aqua regia (HCl–HNO₃) to re-dissolve fluoride precipitates. At
this point, complete dissolution is achieved in dilute HCl (+trace HF), from which a small
aliquot is typically taken to determine W (and Hf) concentrations by isotope dilution using
a mixed ¹⁸⁰Hf-¹⁸³W tracer.²⁷

130 The purification of W from the remaining solution is accomplished by a two-stage 131 anion exchange chromatography utilizing AG1-X8 resin, where W is first separated from 132 most of the sample matrix and, subsequently, from high-field-strength elements (HFSEs) 133 using different HCI-HF($-H_2O_2$) mixtures. To destroy (*i.e.*, oxidize and volatilize) resin-134 derived organic material, the W cuts from both chromatography stages are generally 135 evaporated with ~50 µl of conc. HClO₄ and then dried down at 180–200°C, during which 136 a few drops of conc. HF are added several times to wash down condensed HCIO₄ from 137 the beaker wall. Once all HClO₄ is removed, the samples are fluxed in conc. HF (+trace HNO₃) over night at 130°C before further processing. This dry-down procedure has 138 139 proven effective at preventing organic interferences during the mass spectrometric 140 analyses.^{4,7} The total procedural yield is typically 60–80%, which refers to the amount of 141 W left after the chemical separation procedure, as inferred from the signal intensity of 142 the sample solution (relative to that of the bracketing solution standard), compared to the 143 initial amount derived from the isotope dilution analyses.

144 Tungsten isotope compositions are determined using a Thermo Scientific[®] Neptune 145 Plus MC-ICP-MS, which is equipped with a Cetac® Aridus II desolvator and a 146 combination of (Ni) Jet sampler and X skimmer cones. The measurements are performed 147 in low-resolution mode using analyte concentrations of usually ~30-50 ng/ml W and 148 consume, for example, ~200 ng W for high-precision guintuple measurements. 149 Instrumental mass bias is corrected by internal normalization to $^{186}W/^{184}W = 0.92767$ 150 (denoted '6/4') or $^{186}W/^{183}W = 1.98590$ (denoted '6/3') using the exponential law.²⁸ The 151 W isotope data are reported as ε -unit (*i.e.*, parts per 10,000) or μ -unit (*i.e.*, parts per 152 million) deviations relative to the bracketing Alfa Aesar[®] solution standard (prepared from 153 a pure W metal, batch no. 22312; ref. 27), where $\mu^{i/k}W = [(W/kW)_{sample} / (W/kW)_{standard} - (W/kW$ 154 1] × 10⁶ (*i*, *k* = 182, 183, 184, 186; unless stated otherwise, k is the denominator of the 155 normalization ratio). Typically, an external reproducibility (uncertainty for a single 156 measurement consuming \sim 40 ng W, as defined by the 2SD for repeated analyses of rock 157 standards) of ~10 ppm is obtained for all W isotope ratios, and a precision of ≤5 ppm 158 (95% CI) is routinely achieved by repeated ($n \ge 5$) measurements (Kruijer and Kleine¹¹; 159 Table S1). Note that no ¹⁸⁰W data were obtained in most of the aforementioned studies 160 because of its very low abundance (~0.1%) and anomalous fractionation effects for ¹⁸⁰W 161 measurements using X skimmer cones (see Cook and Schönbächler¹⁴ for further
162 discussion).

- 163
- 164

165 **3. Results**

The W isotope data, literature sources, and further details for the investigated 166 167 kimberlite samples and several geological reference materials are summarized in Table 168 S1, which also reports some additional isotope ratios and normalizations that were not 169 provided in the original publications. The data set evaluated in this study is characterized 170 by very different sample matrices (silicates and metals) as well as highly variable W 171 concentrations, ranging from about 0.01–0.16 μ g/g (DTS-2b, kimberlite 'K2') up to 21.8 172 µg/g (kimberlite 'K18'). Depending on the amount of sample material digested (mostly 173 ~ 0.5 g), the total amount of W that was processed through the entire analytical protocol 174 varies by almost three orders of magnitude, ranging between ~0.04 and ~12 µg W. We 175 note, however, that the large W amounts processed for many kimberlites are not 176 representative of samples typically processed at the IfP (usually <0.5 µg W).

177 None of these samples show resolved variations in $\mu^{182}W$ (6/4) relative to the 178 bracketing solution standard. By contrast, isotope ratios involving ¹⁸³W show variable and resolved anomalies of up to ~15-30 ppm, which are well correlated and consistently 179 largest for μ^{182} W (6/3). The $\mu^{183/184}$ W values (6/4- and 6/3-normalized) are characterized 180 181 by negative anomalies, whereas other ratios [e.g., $\mu^{182}W$ (6/3), $\mu^{184}W$ (6/3)] display 182 excesses relative to the solution standard. As demonstrated in Fig. 2, these variations 183 are best described as pure deficit in ¹⁸³W, where the largest measured anomalies 184 correspond to a deficit of ~ 2.3 per 10⁵ atoms of ¹⁸³W. These observations were not only 185 made throughout the analyses at the IfP (Kruijer and Kleine¹¹, and references in Section 186 2.1), but similar systematics were also reported for processed terrestrial standards in 187 high-precision MC-ICP-MS studies conducted in numerous other laboratories (e.g., Cook 188 and Schönbächler¹⁴, ETH Zürich; Holst et al.²⁹, University of Copenhagen; Shirai and 189 Humayun³⁰, Florida State University; Takamasa et al.³¹, JAMSTEC; Tusch et al.¹⁵, University of Cologne; Willbold *et al.*¹³, University of Bristol). 190

Given the internal normalization of the isotopic data (Section 2.2), any natural and analytical mass-dependent W isotope fractionation following the exponential law is cancelled out. As such, the residual $\mu^{i}W$ variations observed for isotope ratios involving ¹⁸³W either reflect non-exponential mass fractionation effects or, more likely, are massindependent in nature. In addition to the internally normalized isotope ratios, we also determined $\delta^{186/184}W$ values using the standard-sample bracketing technique (from the same measurements), which represent the permit deviations of the raw ¹⁸⁶W/¹⁸⁴W

relative to the IfP (Alfa Aesar) solution standard. Given that natural mass-dependent variations are generally small for W,^{*e.g.*, 32} these $\delta^{186/184}$ W values, which range between about –0.4 and +0.1 ‰ (Table S1), can be used as a first-order measure of massdependent W isotope fractionation induced during the chemical separation procedure.

202 203

204 **4. Origin of the analytical ¹⁸³W effect**

205 The samples investigated here yield well-defined correlation lines in diagrams of μW 206 versus $\mu^{j}W$ (Fig. 2), indicating that the isotopic variations are dominated by a single 207 process. As illustrated in Fig. 1, however, the measured isotope systematics cannot be 208 of nucleosynthetic or radiogenic origin, which is evident from the lack of $\mu^{182}W$ (6/4) 209 anomalies. For instance, nucleosynthetic variations (affecting all isotope ratios) would be 210 most pronounced in μ^{182} W (6/4), about 1.4 times the anomaly in μ^{183} W (6/4)³³, meaning that resolvable μ^{182} W (6/4) excesses of up to ~30 ppm would be expected. Moreover, a 211 radiogenic origin (from ¹⁸²Hf decay) can be ruled out as it would only affect ratios 212 213 involving ¹⁸²W and thus result in (1:1) correlated μ^{182} W (6/4) and μ^{182} W (6/3) variations. 214 which is not observed (Fig. 2a). As such, these isotopic anomalies are not genuine 215 signatures of the samples, but result from an analytical artifact that manifests itself as an apparent ¹⁸³W deficit. In line with previous studies, we thus conclude that this analytical 216 217 ¹⁸³W effect is created in the laboratory, either during the isotope composition 218 measurements or during the chemical separation of W. As will be shown below, the data 219 compiled in this study provide critical new insights into the origin and nature of the ¹⁸³W 220 effect; in particular, as to why its magnitude varies between different studies and even 221 among samples within the same study (e.g., the kimberlite data set²⁶).

222

223 4.1. Mass spectrometric artifacts

224 During mass spectrometric analyses, spurious isotope anomalies can potentially arise 225 from unaccounted interferences or an inaccurate correction of instrumental mass bias. 226 The observed W isotope variations, however, cannot reflect isobaric or molecular 227 interferences, as has already been demonstrated in a previous MC-ICP-MS study that 228 reports similar systematics.¹³ This is, for example, because the measured anomalies 229 reflect variable deficits in ¹⁸³W (Fig. 2), which is contrary to the effect of organic 230 interferences on mass 183 that occasionally occurred in some studies. e.g., 5,29,34 231 Moreover, the generation of W hydrides, as suggested by Breton and Quitté³⁵, cannot explain the observed isotope systematics, as this predicts, for example, a slope of about 232 -0.8 for μ^{182} W versus μ^{183} W (6/4), which is inconsistent with the measured variations 233 234 (Fig. 2b). The observed anomalies are also unlikely to reflect unaccounted mass-

235 dependent fractionation effects that do not follow the exponential law. This is, for example, indicated by the inverse correlation of $\mu^{182/184}$ W and $\mu^{183/184}$ W (6/3) as well as 236 the lack of a correlation for μ^{182} W and μ^{183} W (6/4), which would have slopes of about 237 238 +3.0 and +2.7, respectively, in such a case (Fig. 2e,b). Moreover, consistent with the 239 observations by Cook et al.²¹, the internally normalized ratios do not scale with the raw isotope ratios (quantified here as $\delta^{186/184}$ W), meaning that there is no correlation between 240 241 the magnitude of the analytical ¹⁸³W effect and the extent of (analytical) mass-dependent 242 isotope fractionation that is not accounted for by the standard-sample bracketing 243 technique (Fig. 3a).

244 Analytical artifacts during isotope ratio measurements can also arise from mass-245 independent fractionation processes at the interface region of the MC-ICP-MS^{e.g., 30}. particularly for the combination of Jet sampler and X skimmer cones that is typically used 246 247 in recent W isotope studies.^{e.g., 4,7} For instance, the application of such high-sensitivity 248 cones resulted in anomalous fractionation effects for Nd and for the low-abundance isotope ¹⁸⁰W.^{21,36,37} However, W isotope studies that used combinations of standard 249 sampler and either standard skimmer^{14,21,25,38} or X skimmer^{13,15} cones report essentially 250 251 the same systematics (for the major W isotopes) as observed for the Jet-X combination. 252 As such, the use of a specific cone design cannot be responsible for the spurious W 253 isotope anomalies.

254 Of note, almost all samples discussed in this study were measured under identical 255 conditions (e.g., analyte W concentration, cone setup, sample matrix) and often during 256 the same analytical session. Thus, if the W isotope variations were induced during the 257 mass spectrometric analyses, they would be expected to be approximately constant, but 258 not highly variable as observed here. Moreover, aliquots of bracketing solution 259 standards^{13,25,31} as well as the DTS-2b rock standard doped (to ~80%) with W from the 260 solution standard²⁰, which were processed through the entire analytical protocol, showed 261 the same systematic deviations from the unprocessed solution standard. Finally, Cook 262 and Schönbächler¹⁴ pointed out that the W isotope anomalies observed in many studies 263 occur independent of the MC-ICP-MS instrument, measurement protocol, bracketing 264 solution standard, and sample matrix. These observations combined strongly suggest 265 that the spurious W isotope variations do not have a mass spectrometric origin, which is 266 consistent with the conclusions reached in most of the aforementioned studies.

267

268 4.2. Fractionation during chemical separation

Since it can essentially be ruled out that the observed W isotope anomalies are genuine signatures of the samples or reflect artifacts from the isotope composition measurements, they most likely result from the chemical separation procedure. In most 272 analytical protocols (e.g., IfP protocol, Section 2.2; Peters et al.³⁹; Touboul and Walker¹²), 273 bulk samples are loaded onto the first ion exchange column in a weak HCI-HF mixture 274 from which often significant amounts of Ca,Mg,Al-fluorides precipitate, which can be 275 accompanied by sequestration (and potentially isotopic fractionation) of certain trace 276 elements.^{e.g., 40} However, this process cannot account for the analytical ¹⁸³W effect 277 because tests have shown that only negligible amounts of W co-precipitate with these 278 fluorides,⁴¹ and because this artifact also occurs for sample matrices that do not form 279 fluorides in general (e.g., metals, solution standards) as well as for protocols that avoid 280 fluoride precipitation.¹⁵ The most plausible scenario is, therefore, that these spurious 281 isotope anomalies are induced either during the chromatographic purification or during 282 the subsequent dry-down procedure (*i.e.*, evaporation, oxidation, and re-dissolution) for 283 the W cuts. Furthermore, as residual effects from an inadequate correction of (natural 284 and chemistry-induced) mass-dependent fractionation can (for the same reasons as 285 unaccounted instrumental mass bias; Section 4.1) be excluded, the ¹⁸³W effect most 286 likely reflects a fractionation process that is mass-independent. This is, for example, 287 supported by the fact that numerous studies report such mass-independent isotope 288 fractionation in laboratory-scale chemical exchange reactions for various elements (see 289 Fujii et al.42 and references therein).

290 As the total W yield of the chemical separation procedure is typically <90%, analytical 291 artifacts could potentially originate from anomalous fractionation effects during the ion 292 exchange chromatography. For instance, Breton and Quitté³⁵ have shown that a non-293 quantitative recovery of W can result in significant mass-dependent isotope fractionation. 294 While such mass-dependent fractionation itself cannot explain the observed W isotope 295 variations, this process can potentially be accompanied by mass-independent isotope 296 fractionation, as has, for example, been observed for Nd.43 In this case, an inverse 297 correlation between the spurious W isotope anomalies and the W yield of the chemical 298 separation procedure would be expected. Indeed, the magnitude of the analytical ¹⁸³W 299 effect increases with decreasing yield (Fig. 3c), meaning that samples with a high yield 300 (>80%) are barely affected, whereas those with a low yield (50–60%) show the largest 301 ¹⁸³W effect. Unexpectedly, however, the total procedural yield also scales with the 302 amount of W that was processed through the chemical separation procedure, where 303 samples with a large amount of W generally show a higher yield (Fig. 3d). We note that 304 neither of these parameters is a function of the amount of sample matrix loaded onto the 305 ion exchange columns; in fact, samples with the same amount of material processed (~0.5 g) span virtually the entire range of W yields and amounts (as well as ¹⁸³W effect) 306 307 observed here (Table S1).

308 As a corollary of the above interrelations, our data set also reveals a clear correlation 309 between the analytical ¹⁸³W effect and the amount of W processed. As demonstrated in 310 Fig. 4, this relationship is for all W isotope ratios best described by a logarithmic function, 311 where the magnitude of the ¹⁸³W effect decreases with increasing (initial) W amount. 312 These empirical correlations are combined in Fig. 5, and show that this artifact is 313 particularly relevant for samples containing several tens to hundreds of ng of W (as is 314 the case for most MC-ICP-MS studies), but becomes barely resolvable when several µg 315 of W are processed. Overall, the regressions obtained here display only little excess 316 scatter (MSWD \approx 2.3; Fig. 4), indicating that the magnitude of the ¹⁸³W effect is 317 predominantly controlled by the amount of W that is processed, while other processes 318 have only small, if any, effects. This conclusion is supported by the fact that replicate 319 digestions processed under identical conditions (*i.e.*, same analytical protocol and 320 amount of W) yield very consistent results (e.g., reference materials in Budde et al.^{4,19}; 321 Kruijer et al.²²). While this observation is based on data generated at the IfP, the broad 322 correlation of the ¹⁸³W effect and W amount in a data subset from Tusch *et al.*¹⁵ (Fig. S1) 323 demonstrates that it is not unique to the analytical protocol or sample set discussed here.

324 The finding that the magnitude of the ¹⁸³W effect as well as the total W yield of the 325 separation procedure depend on the amount of W processed (Figs. 3d and 4) is difficult 326 to reconcile with this artifact originating from the chromatographic purification, because 327 in this case a causal relationship would only be expected between the yield and the ¹⁸³W effect. This conclusion is further supported by the fact that Willbold *et al.*¹³ occasionally 328 329 observed significant loss of W during their dry-down procedure for W cuts, which these 330 authors attributed to the formation of insoluble oxide compounds. Moreover, Tusch et 331 al.¹⁵ report a significant increase of the ¹⁸³W effect, combined with much (~20%) lower 332 total W yields, in case of an insufficient oxidation of the W cuts. While the latter points to 333 organic compounds (rather than oxides) playing a major role, these observations 334 combined indicate that significant W loss accompanied by a preferential sequestration 335 of ¹⁸³W can occur during the treatment of W cuts from the ion exchange chromatography 336 (see Section 5.2 for further discussion).

Consequently, a successful model for the origin of the analytical ¹⁸³W effect must be capable of explaining (*i*) that it is induced by mass-independent W isotope fractionation during the dry-down procedure, (*ii*) that the associated W loss dominates the total procedural yield, (*iii*) that its magnitude is strongly controlled by the amount of W processed, and (*iv*) that it occurs for very different sample matrices (silicates, metals, processed solution standards).

344 4.3. The case against a nuclear field shift effect

345 It has been demonstrated that most mass-independent isotope fractionation effects 346 observed in laboratory-scale chemical exchange reactions^{e.g., 42} can be explained by a 347 nuclear field shift (NFS), which is an anomalous isotope effect resulting from differences 348 in nuclear sizes and shapes.^{44–46} To first order, this effect scales proportionally to $|\Psi(0)|^2$ $\delta < r^2 >$, where $|\Psi(0)|^2$ is the total electron density at the nucleus and $\delta < r^2 >$ is the difference 349 in mean-square nuclear charge radii of the respective isotopes.^{e.g., 45,47} As such, a NFS 350 351 is most significant for heavy elements (e.g., REEs, U) and, since odd isotopes typically 352 have disproportionately small nuclear charge radii relative to the adjacent even isotopes, e.g., 42,46 it is often accompanied by a diagnostic odd-even isotope fractionation. 353 354 Hence, this effect could potentially account for the observed deficits in ¹⁸³W relative to 355 the other (even) W isotopes; in fact, a recent study has attributed the analytical ¹⁸³W 356 effect to mass-independent fractionation by a NFS.¹⁴ As we will demonstrate below, 357 however, such NFS-driven isotope fractionation is inconsistent with revised nuclear 358 parameters and other systematics observed in this study.

359 To explain the occurrence of the NFS effect during the dry-down procedure for W cuts 360 (as discussed in Section 4.2), Cook and Schönbächler¹⁴ proposed a redox reaction 361 between insoluble oxide/organic compounds and the aqueous solution (*i.e.*, the solution 362 that will eventually be analyzed), where W has a higher oxidation state (most likely W^{6+}) 363 in the insoluble compounds relative to the W species in solution (e.g., oxyanions, fluoride 364 complexes). As the loss of 5d electrons during progressive oxidation beyond W^{2+} results in a higher electron density at the nucleus,⁴⁸ this would cause a preferential incorporation 365 of light isotopes into the oxide/organic compounds.44,45 Hence, if the odd isotope ¹⁸³W 366 367 were to have an exceptionally small nuclear charge radius, relative to the (mass-368 dependent) trend defined by the even W isotopes (see below), this incorporation would be disproportionally high for ¹⁸³W, as it would essentially behave as it had a lower atomic 369 370 mass.⁴⁴ In this hypothetical scenario, a non-quantitative precipitation (or re-dissolution) 371 of W could potentially result in the expected relative enrichment of ¹⁸³W in the insoluble 372 compounds and a complementary deficit in the aqueous solution. However, it remains 373 unclear whether W in the aqueous species actually has a lower oxidation state, and this 374 process seems difficult to reconcile with the causal relationship between the magnitude 375 of the ¹⁸³W deficit and the relative loss of W, as well as with the fact that both are inversely 376 correlated with the amount of W processed (Figs. 3d and 4). This is because the NFS 377 effect generally occurs in equilibrium systems and, therefore, its magnitude is not 378 expected to scale with the fraction of W incorporated into the oxide/organic compounds. 379 Moreover, a NFS would presumably be accompanied by significant correlated mass-380 dependent isotope fractionation, which is not observed here (Fig. 3a).

381 Most importantly, however, the interpretation from Cook and Schönbächler¹⁴ was 382 based on the nuclear charge radii compiled in Angeli⁴⁹, which are inappropriate for 383 assessing whether or not the spurious W isotope anomalies represent a NFS. Taken at 384 face value, the Angeli⁴⁹ data set suggests that the $\delta < r^2 >$ is essentially a linear function 385 of the atomic mass for the even W isotopes, whereas the odd isotope ^{183}W ($\delta < r^2 > \approx -0.4$ 386 fm²) is characterized by a substantial deviation from this trend (see Fig. 2 in Cook and 387 Schönbächler¹⁴). If these data were correct, the NFS effect would manifest itself as a virtually pure ¹⁸³W deficit (or excess) in internally normalized isotope ratios (Table S2), 388 389 which would be consistent with the observed W isotope anomalies. A close inspection of 390 this compilation, however, reveals major problems with the reported nuclear charge 391 radius for ¹⁸³W: The magnitude of its deficit (~0.03 fm compared to what would be 392 expected from an ¹⁸²W-¹⁸⁴W interpolation) seems physically implausible, and its 393 uncertainty (±0.15 fm) is two orders of magnitude larger than those of the other W 394 isotopes (~5 times larger than the proposed deviation itself). Of note, apparently due to 395 a lack of alternative data, only the value for ¹⁸³W in Angeli⁴⁹, which is a compilation that 396 primarily focused on absolute nuclear charge radii, is based on nuclear parameters from 397 De Wit *et al.*⁵⁰ The results of the latter study are compiled in Angeli⁵¹, which shows that 398 the nuclear charge radii derived from the De Wit *et al.*⁵⁰ parameters are generally highly imprecise and characterized by considerable systematic deficits relative to other studies 399 400 (including elements other than W).

401 It is important to recognize that this questionable value for ¹⁸³W from Angeli⁴⁹ has 402 been abandoned in the most recent compilation of nuclear charge radii by Angeli and 403 Marinova⁵², which, instead, provides a self-consistent data set that is in line with direct 404 measurements of differences in mean-square nuclear charge radii for W isotopes using 405 optical isotope shifts (OIS). Despite utilizing different techniques, such studies have 406 obtained very consistent $\delta < r^2 >$ values,^{53–55} which is testament to the generally high 407 accuracy and precision of data obtained by OIS. These $\delta < r^2 >$ values show only subtle 408 deviations from a mass-dependent trend (most pronounced for ¹⁸⁰W and ¹⁸²W) and, 409 therefore, do not support a disproportionally small nuclear charge radius of ¹⁸³W (Fig. 6a). Based on these data, the internal normalization to ¹⁸⁶W/¹⁸³W or ¹⁸⁶W/¹⁸⁴W would 410 411 result in roughly complementary anomalies in μ^{180} W and μ^{182} W that are significantly 412 larger than those in μ^{183} W and μ^{184} W (Fig. 6b). Thus, the predicted W isotope variations 413 resulting from the NFS effect are inconsistent with the observed ¹⁸³W deficits, as had 414 already been noted by Shirai and Humayun³⁰. In fact, in diagrams of µⁱW versus µ^jW, the 415 predicted NFS-lines are roughly perpendicular to the regressions defined by the 416 investigated samples (Fig. 2).

417 As the analytical ¹⁸³W effect cannot be attributed to a NFS, another mass-independent 418 fractionation process is required to explain the spurious W isotope anomalies. One 419 possibility is that this artifact reflects a magnetic isotope effect (MIE), which arises from 420 chemical reactions that involve a spin-selective step, resulting in the fractionation of 421 isotopes according to their nuclear spin and corresponding magnetic moment.^{e.g., 56} This 422 rather exotic effect is, for example, generally thought to be responsible for the substantial 423 fractionation of odd Hg isotopes, which have a magnetic moment unlike the even 424 isotopes, observed in natural and experimental systems.⁵⁷ Similarly, the nuclear spins of 425 the even W isotopes are all zero, while the odd isotope ¹⁸³W is characterized by a spin 426 of $-\frac{1}{2}$ and thus a magnetic moment and hyperfine structure.^{e.g., 55} A MIE, therefore, could 427 selectively fractionate ¹⁸³W and potentially result in a significant ¹⁸³W deficit (or excess) 428 that is unrelated to any potential mass-dependent fractionation, as is observed in this 429 study (Fig. 3a). Moreover, this effect typically occurs during reactions involving organic 430 components and is purely kinetic by nature (see Dauphas and Schauble⁵⁸ and 431 references therein). As such, the MIE would be consistent with the hypothesis that W is 432 lost by incorporation into insoluble oxide/organic compounds (Section 4.2) and with the 433 fact that the ¹⁸³W deficit scales with the fraction of W that is sequestered (Fig. 3c), which 434 points to disequilibrium fractionation of W isotopes between the aqueous species and 435 oxide/organic compounds. In this scenario, a certain amount of W is incorporated into 436 the insoluble compounds, which represents a larger fraction for samples with less W (Fig. 437 3d). Accordingly, the associated MIE-driven sequestration of ¹⁸³W is then also expected 438 to be more pronounced for lower amounts of W, resulting in a larger ¹⁸³W deficit in the 439 corresponding solution. Although this remains speculative, isotope fractionation by a 440 magnetic isotope effect seems to represent a viable mechanism to produce the analytical 441 ¹⁸³W effect and to account for its systematic variation with the total procedural yield and 442 the amount of W processed.

443 Further experimental and theoretical investigations, which are beyond the scope of 444 this study, are needed to fully understand the analytical ¹⁸³W effect. Regardless of its 445 exact origin, however, the results of our investigation reveal that the ¹⁸³W effect is an 446 analytical artifact that can essentially be described as pure ¹⁸³W deficit and that its 447 magnitude is (at least within a given analytical protocol) strongly controlled by the amount 448 of W that is processed through the chemical separation procedure. These key 449 observations have important implications for high-precision W isotope analyses in 450 general, as they resolve apparent inconsistencies from previous studies, and because they allow the development of a method for the accurate correction of the analytical ¹⁸³W 451 452 effect.

454

455 **5. Implications for W isotope analyses**

456 5.1. Comparison with N-TIMS studies

457 The methods for W isotope ratio measurements by N-TIMS utilized in early studies 458 were only capable of obtaining high-precision ¹⁸²W/¹⁸⁴W data, using ¹⁸³W/¹⁸⁴W for a second-order mass fractionation correction. e.g., 12,59-61 Recent improvements of the 459 measurement protocol,^{10,62} however, now allow determining the full range of W isotope 460 461 ratios with the same precision (i.e., a few ppm) achieved by MC-ICP-MS, making it 462 possible to identify nucleosynthetic isotope anomalies as well as a potential analytical 463 ¹⁸³W effect. Surprisingly though, studies using this refined N-TIMS technique did not recognize such an artifact,^{16,17,63–68} implying that the ¹⁸³W effect originates in the MC-ICP 464 465 mass spectrometer, which in turn would be in conflict with our conclusion that it is induced 466 during the chemical separation procedure.

467 A major difference between most MC-ICP-MS and N-TIMS studies is the amount of 468 W that is processed, which exerts a strong control on the magnitude of the analytical 469 ¹⁸³W effect (Section 4.2). Due to the lower ionization efficiency in the N-TIMS source, 470 significantly more sample material is required, meaning that typically 0.75-1.5 µg W is 471 processed through the chemical separation procedure (as opposed to several tens to 472 few hundreds of ng for most samples measured by MC-ICP-MS at the IfP). Hence, even 473 though the empirical correlations defined in this study (Fig. 4) cannot be transferred 474 directly to other analytical protocols (Section 5.2), the general observation that the ¹⁸³W 475 effect decreases with increasing amount of W implies that this artifact (if present) is likely 476 less pronounced and thus difficult to resolve for typical N-TIMS analyses (Fig. 5). A 477 detailed evaluation of the N-TIMS data is further complicated by the fact that details on 478 the amount of W processed are often lacking, and that most studies do not report all 479 relevant W isotope ratios and normalizations, particularly µ¹⁸²W (6/3) for which the ¹⁸³W 480 effect would be most pronounced. Moreover, only very few processed terrestrial 481 standards, for which natural (mass-independent) isotope anomalies can be ruled out, 482 have been measured using the refined N-TIMS technique to date.

483 Nonetheless, some recent N-TIMS studies conducted at the Isotope Geochemistry Laboratory (IGL) at the University of Maryland^{16,63,69–71} provide combined $\mu^{182}W$ (6/4), 484 485 $\mu^{182/184}$ W (6/3), and μ^{183} W (6/4) data, which allows a more quantitative assessment of the 486 presence of the ¹⁸³W effect. Since most of the samples from these studies display 487 radiogenic W isotope variations, as evident from the broadly correlated μ^{182} W (6/4) and $\mu^{182/184}$ W (6/3) deficits, we here use the difference between the two normalizations 488 $\left[\Delta\mu^{182}W = \mu^{182/184}W\right]$ (6/3)_{meas} - $\mu^{182}W$ (6/4)_{meas}], which cancels out any radiogenic 489 490 contribution. The non-radiogenic W isotope variations for these samples are generally

491 small (<15 ppm) and mostly unresolved, and (except for one sample) the data from 492 Mundl et al.^{16,63} scatter around zero within the expected range (Fig. 7). However, the other three data sets display a clear bias toward negative $\mu^{183}W$ (6/4) (-3 ppm on 493 494 average) combined with excesses in $\Delta \mu^{182}$ W. Of note, these anomalies are even more 495 pronounced relative to the Alfa Aesar solution standard used at the IfP, which has a 496 slightly different W isotope composition than the Alfa Aesar Specpure Plasma standard 497 relative to which these N-TIMS data are reported (see Section 6). While nucleosynthetic anomalies would theoretically follow the same inverse correlation (Fig. 7), these $\Delta \mu^{182}W$ -498 μ^{183} W systematics are most readily attributed to a small ¹⁸³W effect. 499

500 Recently, such an analytical origin was also proposed for W isotope anomalies 501 measured in an earlier N-TIMS study⁶¹, which reported large µ¹⁸²W (corrected for 502 second-order mass fractionation using ¹⁸³W/¹⁸⁴W) excesses of 24 and 48 (±5) ppm for 503 basalts/picrites from the Ontong Java Plateau (OJP) and Baffin Bay ('Pd-2'), 504 respectively. These data are in disagreement with several MC-ICP-MS studies that found no resolvable μ^{182} W anomalies in other samples from these two locations,^{11,13,72} and 505 Kruijer and Kleine¹¹ argued that the apparent µ¹⁸²W excesses from Rizo *et al.*⁶¹ most 506 likely reflect a substantial ¹⁸³W effect. This interpretation is supported by the fact that 507 508 these samples were subjected to an extensive chromatographic purification and dry-509 down procedure, and are characterized by low W yields (54 and 50%), consistent with 510 our findings presented in Section 4.2.

511 Together, these observations strongly suggest that the analytical ¹⁸³W effect is also 512 present in some N-TIMS data sets, which supports our conclusion that it is induced 513 during the chemical separation procedure and not unique to MC-ICP-MS. Further 514 systematic investigations are, however, necessary to better understand potential 515 differences between these two mass spectrometer types; for instance, whether the 516 specific sample introduction and ionization can influence the measured ¹⁸³W effect. 517 Regardless, this highlights that also for N-TIMS measurements the ¹⁸³W effect, even 518 though it is comparatively small or imperceptible in most studies, should be precisely 519 quantified to ensure an accurate interpretation of W isotope data, especially when 520 advances in analytical methods allow for smaller amounts of W to be measured with this 521 technique.

522

523 5.2. Mitigating the analytical ¹⁸³W effect

524 While the size of the analytical ¹⁸³W effect is generally a function of the amount of W 525 that is processed (Section 4.2), there are substantial variations in its overall magnitude 526 between different studies that cannot be explained by this observation alone. Although 527 the majority of high-precision MC-ICP-MS studies report a significant ¹⁸³W effect, in some

528 MC-ICP-MS^{15,73–76} and many N-TIMS studies^{16,17,63–67} this artifact was generally small or 529 even absent. This was likely facilitated by the relatively large amounts of W processed 530 in such studies (mostly 500–1000 ng); however, several observations indicate that these 531 different outcomes primarily reflect differences in the analytical protocols, particularly in 532 the dry-down procedures (*i.e.*, evaporation, oxidation, and re-dissolution) for W cuts from 533 the ion exchange chromatography.

534 For instance, Tusch et al.¹⁵ demonstrated that a change in their dry-down procedure 535 from a 'weak' [dilute HNO₃-HF + H₂O₂ (9:1); 1×] to a 'strong' oxidation [conc. HNO₃ + 536 H₂O₂ (1:1); 3× at max. 60°C] resulted in higher W yields (~80% instead of ~60%) and an 537 imperceptible ¹⁸³W effect. While most N-TIMS studies (as well as Mei et al.⁷⁴) also 538 successfully applied an HNO₃–H₂O₂ oxidation step, others observed a significant ¹⁸³W 539 effect with such a procedure^{13,14} and found that an improvement was achieved instead by fluxing W cuts alternately with conc. HNO₃ and HF at 150°C over night.⁷⁶ Similarly, a 540 541 dry-down procedure [conc. HNO₃ + H₂O₂ (1:1), 2–3× at max. 80°C] virtually identical to 542 the 'strong' oxidation from Tusch et al.¹⁵ had opposite effects when applied at the IfP.^{77,78} 543 It not only caused more frequent problems with organic interferences (on mass 183) 544 during the MC-ICP-MS measurements, but also resulted in lower yields and a ¹⁸³W effect 545 that was generally larger (up to about -60 ppm on μ^{183} W) and, most importantly, more 546 erratic in magnitude, compared to the high-temperature HCIO₄ dry-down procedure 547 (Section 2.2).

548 These contradictory observations are likely related to the specific matrix elements and 549 organic materials present in the W cut, or even to the operator-specific execution of the 550 dry-down procedure. For instance, HFSEs (Ti, Zr, Hf, Nb, Ta), which are usually eluted 551 together with W during the initial chromatography stage, can form insoluble oxides during 552 dry-downs with HClO₄⁴⁰ that could potentially also sequester W. While large amounts of 553 HFSEs (mainly Ti) might hamper an efficient oxidation, such a precipitation of oxide 554 compounds itself (of W alone or in combination with HFSEs) cannot be the origin of the 555 analytical ¹⁸³W effect, as it also occurs in the absence of HFSEs (metal samples, 556 processed solution standards) and when no $HClO_4$ is used for the dry-down procedure. 557 Based on the observation that the ¹⁸³W effect (and corresponding W loss) is not induced 558 by simple evaporation/re-dissolution of W solutions (neither with HClO₄ nor with H_2O_2), 559 but only if the solution has been subjected to ion exchange chromatography (even 560 without dry-down steps, or when the solution was doped with W only after 561 chromatography and dry-downs), it has recently been suggested that eluted organic material from the resin is responsible for this artifact.^{31,79} Consequently, the particular 562 563 type of ion exchange resin used for different chromatography stages and, therefore, the 564 amount and physicochemical properties of resin-derived organic material in the W cut,

565 may play a critical role in the generation of the ¹⁸³W effect. It is noteworthy that the IfP 566 protocol (and some others^{13,14}) uses only anion exchange resin (AG1-X8), whereas 567 studies that better mitigated the ¹⁸³W effect by an HNO₃–H₂O₂ oxidation step utilized 568 cation exchange resin (AG50W-X8) for the initial separation of W (+HFSEs) from the 569 sample matrix, and sometimes extraction chromatography resins (TEVA, DGA) for the 570 subsequent purification.^{12,15,39,74}

571 Although the exact processes involved remain enigmatic, it seems clear that not the 572 details of the dry-down procedure alone (e.g., reagents, temperature), but the specific 573 combination of the chromatographic purification protocol (*i.e.*, the organic material, and 574 possibly matrix elements, present in the W cut) and the dry-down procedure determines 575 the overall magnitude of the ¹⁸³W effect. While some studies were generally successful 576 in mitigating this artifact (see above), it should be noted that even for those protocols a 577 noticeable ¹⁸³W effect may still occur occasionally. For instance, the vast majority of 578 analyses from Mei et al.⁷³ and Tusch et al.⁷⁵ display no resolvable (*i.e.*, <3 ppm) µ¹⁸³W anomalies, but several samples show a significant ¹⁸³W effect (-6 to -11 ppm), in 579 580 particular when smaller amounts (~150 ng) of W were processed. This indicates that no 581 analytical protocol should be relied on to fully prevent the ¹⁸³W effect, necessitating a 582 close inspection of measured W isotope data for every individual sample. In some 583 circumstances, it might even be more beneficial to apply a protocol that produces an 584 elevated but very reproducible ¹⁸³W effect (as for the HClO₄ dry-down procedure 585 preferred at the IfP; Section 4.2), which then can be corrected adequately (Section 5.3). 586 This requires increased efforts and leads to slightly larger uncertainties, but it may yield 587 more accurate and reliable results under certain conditions.

Taken together, the findings discussed above resolve the apparent inconsistencies between previous studies, as they demonstrate that the substantial variations in the overall magnitude of the analytical ¹⁸³W effect observed in different studies are primarily caused by differences in the analytical protocols, while there are systematic variations within a given protocol depending on the amount of W processed. As such, the combined observations from this study provide directions to better mitigate the effect in the first place as well as means to accurately correct it if necessary.

595

596 5.3. Quantification and correction

597 The observations that the analytical ¹⁸³W effect is inconsistent with a NFS origin but 598 best described as pure ¹⁸³W deficit, and that its magnitude is (within a given analytical 599 protocol) strongly controlled by the amount of W that is processed through the chemical 600 separation procedure (Section 4.2), have important implications for the correction of this 601 analytical artifact. Previous MC-ICP-MS studies have employed two different 602 approaches, where the measured W isotope ratios are corrected either internally using 603 empirically or theoretically determined $\mu^{i}W - \mu^{j}W$ slopes,^{e.g., 11,25} or externally using 604 processed geological reference materials as a proxy.^{e.g., 4,7}

605 The internal correction is generally applied to terrestrial rock samples and reference 606 materials that are assumed to have no nucleosynthetic W isotope anomalies. In this 607 simple scenario, all variations in the non-radiogenic ratios $[\mu^{183}W (6/4), \mu^{184}W (6/3),$ 608 $\mu^{183/184}$ W (6/3)] can be attributed to the ¹⁸³W effect. Accordingly, these values can then, combined with the theoretical slopes for a pure ¹⁸³W deficit (Table S2), be used to correct 609 610 the measured μ^{182} W of a given sample: μ^{182} W (6/3)_{corr} = μ^{182} W (6/3)_{meas} - 2 × μ^{184} W $(6/3)_{\text{meas}}$ and $\mu^{182/184}$ W $(6/3)_{\text{corr}} = \mu^{182/184}$ W $(6/3)_{\text{meas}} - (-1) \times \mu^{183/184}$ W $(6/3)_{\text{meas}}$. These 611 corrected μ^{182} W values should then be indistinguishable from μ^{182} W (6/4), which is not 612 613 modified by the ¹⁸³W effect and does thus not require any correction. For consistency, 614 the non-radiogenic isotope ratios can be corrected using the measured $\mu^{182}W$ (6/3) and 615 $\mu^{182/184}$ W (6/3) of a given sample [the μ^{182} W (6/4) cannot be used as it does not scale with the ¹⁸³W effect], following the same approach as above: $\mu^{183}W$ (6/4)_{corr} = $\mu^{183}W$ 616 $(6/4)_{meas} - (-0.75) \times \mu^{182}W (6/3)_{meas}$ and $\mu^{184}W (6/3)_{corr} = \mu^{184}W (6/3)_{meas} - 0.5 \times \mu^{182}W$ 617 $(6/3)_{\text{meas}}$ and $\mu^{183/184}$ W $(6/3)_{\text{corr}} = \mu^{183/184}$ W $(6/3)_{\text{meas}} - (-1) \times \mu^{182/184}$ W $(6/3)_{\text{meas}}$. For samples 618 619 with no radiogenic ¹⁸²W variations, these corrected values should then be 620 indistinguishable from the bracketing solution standard (compare Table S1). We note 621 that corrections using the slopes from Cook and Schönbächler¹⁴ performed in some recent studies^{e.g., 11,15} are still accurate. Although these slopes were based on the 622 623 assumption that the analytical ¹⁸³W effect represents a NFS (Section 4.3), the data used 624 by Cook and Schönbächler¹⁴ yielded µW–µW slopes that are virtually identical to those 625 for a pure ¹⁸³W deficit (Table S2).

626 Matters become, however, much more complicated for samples potentially having 627 nucleosynthetic W isotope anomalies, which result in correlated μ^{182} W and μ^{183} W (or 628 μ^{184} W) variations (Fig. 1). Several studies have demonstrated that significant 629 nucleosynthetic (s- or r-process) W isotope variations [often >100 ppm on μ^{183} W (6/4)] 630 exist in diverse Solar System materials such as calcium-aluminum-rich inclusions 631 (CAIs)^{5,7}, chondritic components (chondrules, matrix, metal)^{4,19}, and acid leachates of primitive meteorites^{33,80,81}. Of note, significant W isotope anomalies have recently been 632 633 shown to also exist at the bulk meteorite scale. While most meteorites belonging to the 634 *'non-carbonaceous*' suite show no or slightly negative (about –5 ppm) µ¹⁸³W anomalies 635 relative to the terrestrial standard, 'carbonaceous' (i.e., carbonaceous chondrite-related) 636 meteorites are characterized by resolved excesses in μ^{183} W, which are typically ~10 ppm but can be as high as ~50 ppm.6,9,19 These observations demonstrate that for 637 638 extraterrestrial (meteoritic) samples, and potentially even some exotic (*i.e.*, ancient or

deep mantle-derived) terrestrial rocks (Section 5.3), it cannot be ruled out *a priori* thatthey have nucleosynthetic W isotope anomalies.

641 For such samples, the interpretation of the W isotope data is severely complicated by the complex interplay of the analytical ¹⁸³W effect as well as radiogenic and 642 643 nucleosynthetic variations, which affects every isotope ratio in a different way (Fig. 1). 644 For instance, the ¹⁸⁶W/¹⁸³W-normalized μ^{182} W values are most affected by the ¹⁸³W effect 645 but show only a small, often negligible, effect of nucleosynthetic isotope anomalies. 646 Conversely, the ${}^{186}W/{}^{184}W$ -normalized $\mu{}^{182}W$ values are not compromised by the ${}^{183}W$ 647 effect, but are strongly affected by nucleosynthetic isotope anomalies. Correction of the 648 latter (in order to unveil radiogenic contributions), however, requires knowledge of the 649 true μ^{183} W (6/4) of a given sample,^{4,7,33} but this ratio again is modified by the ¹⁸³W effect. 650 Hence, for samples with nucleosynthetic anomalies the chronological interpretation not 651 only of the μ^{182} W (6/3), but indirectly also of the μ^{182} W (6/4) values, critically depends on 652 the accurate correction of the ¹⁸³W effect. However, in this case none of the original (*i.e.*, 653 pre-¹⁸³W effect) isotope ratios are known, meaning that the internal correction procedure 654 described above cannot be applied and, instead, an independent quantification of the 655 ¹⁸³W effect is required.

656 For this, studies typically utilize geological reference materials that are assumed to 657 have no radiogenic or nucleosynthetic W isotope anomalies (e.g., BHVO-2, BCR-2, JB-658 2, SRM 129c), which are processed through the entire analytical protocol and analyzed 659 together with the actual samples. The W isotope ratios of the samples are then corrected 660 by simply subtracting the average µⁱW values measured for the reference material from 661 those of the samples.^{e.g., 4,7,31} While this external correction is a reasonable approach that has generally proven capable of correcting the ¹⁸³W effect, it relies on the assumption 662 663 that the effect observed for the reference materials is representative for the investigated 664 samples. Our results demonstrate, however, that this may not always be justified 665 because the magnitude of the ¹⁸³W effect strongly depends on the amount of W 666 processed (Figs. 4 and 5).

667 Hence, it is crucial that the amount of W processed through the analytical protocol for 668 all samples is well known and closely matches that of the corresponding reference material that is used to quantify the analytical ¹⁸³W effect. A more reliable correction, 669 670 particularly if the investigated samples show a large range in W contents, can probably 671 be achieved by analyzing a suite of reference materials with varying W amounts. This will yield an empirical correlation between the magnitude of the ¹⁸³W effect and the 672 673 amount of W processed, which can then be used to individually correct the measured W isotope ratios of each sample: $\mu^{i}W_{corr} = \mu^{i}W_{meas} - (m \times \ln[W] + b)$, where *m* and *b* are the 674 675 slope and intercept, respectively, of the corresponding μ^{W} –ln[W] regression defined by 676 the reference materials. We emphasize again that such correlations are specific to a 677 certain analytical protocol (and maybe even operator) and not applicable to other data 678 sets (Section 5.2). Thus, the correction parameters must be determined separately for 679 each chemical separation procedure employed for high-precision W isotope analyses.

680

681 5.4. Significance of the analytical ¹⁸³W effect

682 Although the analytical ¹⁸³W effect is typically <20 ppm and often smaller than the 683 analytical uncertainty, it can have a significant impact on the evaluation of measured W 684 isotope data. For instance, µ¹⁸²W values of iron meteorites are used to date core formation in their parent bodies by calculating ¹⁸²Hf-¹⁸²W model ages (see Kleine and 685 Walker¹). The precision and accuracy of these ages, however, critically depend on those 686 of the used μ^{182} W and are thus very sensitive to the ¹⁸³W effect, regardless of which 687 688 isotope ratio is used. For example, the μ^{182} W (6/3) are directly affected by this analytical 689 artifact, meaning that an unrecognized ¹⁸³W effect shifting this ratio by +10 ppm (a typical 690 value for MC-ICP-MS analyses) would result in an apparent model age that is ~0.9 Ma too young. In contrast, the μ^{182} W (6/4) are not directly compromised by the ¹⁸³W effect 691 692 and thus commonly used for Hf-W chronology. However, the μ^{182} W (6/4) can be strongly 693 affected by nucleosynthetic isotope anomalies that need to be quantified using the 694 corresponding μ^{183} W (6/4), which are in turn modified by this artifact (Fig. 1, Section 5.3). 695 For example, a ¹⁸³W effect of only -7 ppm on μ^{183} W (6/4), which is misinterpreted (and 696 corrected for) as nucleosynthetic anomaly, would cause a shift of +10 ppm in μ^{182} W (6/4), 697 again resulting in a model age that is ~ 0.9 Ma too young. Hence, directly or indirectly, even a moderate unaccounted ¹⁸³W effect can result in inaccurate Hf-W model ages, 698 699 exceeding the typical uncertainties (~0.5-0.7 Ma) obtained in recent high-precision studies.^{e.g., 6,24} Of note, the slightly negative, albeit unresolved, $\mu^{183}W$ (6/4) values of 700 701 many 'non-carbonaceous' iron meteorites (Section 5.3) are commonly attributed to an 702 insufficient correction of the analytical ¹⁸³W effect. However, it is also possible that these 703 small µ¹⁸³W deficits are real, and would then reflect small nucleosynthetic W isotope anomalies. In this case, the reported Hf-W model ages based on the measured µ¹⁸²W 704 705 (6/4), which have not been corrected for nucleosynthetic anomalies, may be too old by 706 up to several hundred thousand years.

707Over the past decade, W isotope variations in terrestrial samples have become the708focus of sustained attention, as they provide critical insights into past and present709workings of the silicate Earth. Several MC-ICP-MS and N-TIMS studies report small710(mostly <15 ppm) μ^{182} W anomalies for some ancient (*i.e.*, Hadean to Archean) komatiites711and supracrustal rocks as well as for modern plume-related basalts (see Zhang and Liu⁸²712for references and a recent data compilation), which provide evidence for the existence

713 and preservation of isotopically anomalous portions of the mantle.¹ Generally, these 714 variations are interpreted to solely reflect radiogenic anomalies; however, a full 715 assessment of the origin of these variations is often not possible, for example, because some studies report only $\mu^{182/184}$ W (6/3) or μ^{182} W (6/3) values that may potentially be 716 717 affected by the ¹⁸³W effect. Of note, the observation that bulk meteorites (and thus the 718 assumed building blocks of Earth) show significant nucleosynthetic W isotope anomalies 719 (Section 5.3), combined with the recent discovery of nucleosynthetic Ru isotope 720 anomalies in some ancient terrestrial rocks,⁸³ implies that nucleosynthetic W isotope 721 variations might not only have existed during Earth's early formative period but could 722 even have been preserved until today, either in primordial mantle domains or in rocks 723 that formed very early in Earth's history. Hence, it cannot be ruled out a priori that such 724 exotic (*i.e.*, ancient or deep mantle-derived) terrestrial rocks have small nucleosynthetic 725 W isotope anomalies. This in turn means that for some of these samples the observed 726 μ^{182} W variations may, at least in part, reflect unrecognized nucleosynthetic contributions, 727 which is particularly relevant for the $\mu^{182}W$ (6/4) values.

728 These examples highlight that even a small analytical ¹⁸³W effect can severely 729 compromise the chronological interpretation of µ¹⁸²W variations and hamper the 730 identification of nucleosynthetic W isotope anomalies in meteoritic and terrestrial 731 samples. Resolving the above issues, therefore, requires a very precise quantification of 732 the ¹⁸³W effect in the analyses of such samples, which will become even more important 733 as the analytical precision improves and sample sizes decrease in the future. As such, 734 increased efforts to accurately correct the ¹⁸³W effect will be pivotal for establishing a 735 fine-scale Hf-W chronology of the early Solar System as well as for improving our 736 understanding of Earth's accretion and differentiation history.

737

738

739 6. Tungsten isotope composition of bulk silicate Earth

740 With respect to mass-independent (*i.e.*, internally normalized) isotope variations, it is 741 generally assumed that high-purity elemental standards, relative to which the measured 742 data are reported, are representative of the isotopic composition of bulk silicate Earth 743 (BSE). However, several studies have demonstrated that this assumption may not 744 always be valid because solution standards can display anomalous (i.e., mass-745 independent or non-exponential mass-dependent) isotope fractionation effects, 746 potentially induced during the elemental purification/enrichment in the production 747 process or during the genesis of the ores from which these standards were made (e.g., 748 Akram and Schönbächler⁸⁴, Zr; Budde et al.⁸⁵, Mo; Steele et al.⁸⁶, Ni; Zhang et al.⁸⁷, Ti).

749 In the case of W isotopes, this issue is emphasized by the fact that different solution 750 standards have slightly different isotopic compositions (Fig. 8). For this study, we have 751 repeatedly measured the two most commonly used W isotope standards against each 752 other (by MC-ICP-MS) and found that the Alfa Aesar Specpure Plasma standard, which 753 is used for N-TIMS analyses in the IGL at the University of Maryland (Section 5.1), is 754 characterized by a small offset from the Alfa Aesar standard used in the IfP at the 755 University of Münster (Table S1; Fig. 2). Although these µW deviations are only on the 756 order of 1–2 ppm and barely resolvable, they are internally consistent and, given the 757 small magnitude of natural variations, of significance for the adequate comparison and interpretation of W isotope data. We note that Mundl et al.¹⁶ did not find a difference 758 759 between the two standards during a cross-calibration by N-TIMS; however, their 760 uncertainties (~5–9 ppm; n=4) were much larger than the differences identified here. 761 Regardless, the above observations combined raise the question of how accurately 762 these solution standards reflect the W isotope composition of BSE in general. Note that 763 an anomalous isotopic composition of a solution standard could only lead to a constant 764 offset from terrestrial rock samples and, therefore, cannot account for the large range of 765 W isotope variations observed here and in previous studies for processed samples and 766 solution standards.

767 Generally, the validity of using a given solution standard as proxy for the BSE can be 768 assessed by the analyses of a comprehensive suite of terrestrials rocks. In the case of 769 W, however, this is hampered by the widespread analytical ¹⁸³W effect that is induced 770 during the chemical separation of W, because any measured difference between 771 terrestrial samples and the solution standard could partly or wholly reflect this artifact. 772 Nevertheless, the data for processed rock samples compiled in this study allow placing 773 important constraints on BSE's W isotope signature. In particular, these samples yield 774 well-defined correlation lines in the W isotope diagrams (Fig. 2), which represent the 775 direction of the ¹⁸³W effect-induced shift. A corollary of this is that the original composition 776 of the samples and, therefore, the true signature of BSE lies on these $\mu^{i}W - \mu^{i}W$ 777 regressions. This assumption is justified by the lack of $\mu^{182}W$ (6/4) anomalies in the 778 investigated samples, which indicates that the ¹⁸³W effect is the sole origin of the 779 measured anomalies and that there is no systematic (geological) bias in this data set 780 (Section 3).

One way to constrain the BSE position on the $\mu^{i}W - \mu^{j}W$ regression lines is based on the correlation between the magnitude of the ¹⁸³W effect and the W yield of the chemical separation procedure (as exemplified for $\mu^{182}W$ (6/3) in Fig. 3c). Extrapolating these linear regression lines to a yield of 100%, provides $\mu^{i}W$ values which represent a theoretical composition [*e.g.*, $\mu^{183}W$ (6/4) ≈ 4] that is presumably free of the ¹⁸³W effect. 786 These '100%-intercepts' deviate systematically in the opposite direction than processed 787 rock samples and plot on the $\mu^{i}W - \mu^{j}W$ regressions defined by these samples (Fig. 8), 788 indicating that the deviation from the IfP standard is significant, albeit not resolved 789 [except for μ^{182} W (6/3)] (Table S1). One problem with this approach is, however, that the 790 ¹⁸³W effect might not further decrease linearly in the interval between ~90% and 100% 791 yield (*i.e.*, there might be a disproportionately large effect at very high yields). As such, 792 the 100%-intercepts rather represent only an upper limit, meaning that the true BSE 793 composition is likely closer to that of the solutions standards. In contrast, a lower limit for 794 the µW values of BSE can be inferred directly from the processed rock samples with the 795 smallest ¹⁸³W effect. Considering the associated uncertainties, the data obtained by MC-796 ICP-MS allow, for example, for a small deficit in $\mu^{183}W$ (6/4) of about -3 ppm (Fig. 8), 797 which would also still be within uncertainty of some samples with slightly positive $\mu^{183}W$ 798 analyzed by N-TIMS (Fig. 7). Taken together, these constraints provide a conservative 799 estimate of BSE's W isotope signature, where the μ^{183} W (6/4) of BSE is between about 800 -3 and +4 ppm relative to the IfP standard.

801 It is noteworthy that the $\mu^{i}W - \mu^{i}W$ correlation lines pass exactly (*i.e.*, within ~1 ppm) 802 through the IfP as well as IGL solution standards (Fig. 2), which implies that both are 803 probably very close to the true composition of the BSE. This is because any significant 804 anomalous (*i.e.*, non-exponential) isotope fractionation would likely have resulted in 805 distinct W isotope systematics and caused a deviation from those regressions. 806 Furthermore, the IfP standard represents an endmember composition, meaning that all 807 analyzed rock samples, for which effects of nucleosynthetic isotope anomalies can be 808 excluded, as well as other solution standards (IGL standard, NIST SRM 3163) deviate in the direction of the analytical ¹⁸³W effect (*i.e.*, ¹⁸³W deficit) (Fig. 8). It remains unclear, 809 810 however, whether this indicates that the IfP standard is the most appropriate proxy for 811 the BSE composition. In any case, further work is necessary to more precisely define the 812 W isotope signature of bulk silicate Earth as well as to assess the extent of potential 813 heterogeneities in the mantle. This will, for instance, be important for obtaining a better 814 understanding of BSE's position relative to the dichotomous nucleosynthetic W isotope 815 anomalies in 'carbonaceous' and 'non-carbonaceous' meteorites (e.g., ref. 6 and 9 816 Section 5.3), and for investigating geological processes that may generate W isotope 817 anomalies in the silicate Earth.⁸⁸

- 818
- 819

820 7. Conclusions

821 Our evaluation of high-precision W isotope data for diverse terrestrial samples from 822 numerous recent studies demonstrates that W isotope analyses are often compromised 823 by an analytical artifact that manifests itself as an apparent deficit in ¹⁸³W. This analytical 824 ¹⁸³W effect can be present in MC-ICP-MS as well as TIMS data, and can be attributed to a mass-independent fractionation of ¹⁸³W that is inconsistent with a nuclear field shift but 825 826 may instead reflect a magnetic isotope effect. Regardless of its exact origin, our 827 investigation reveals that this widespread artifact is induced during the chemical 828 separation of W and that the specific combination of chromatographic purification and 829 dry-down procedure determines its overall magnitude. Within a given analytical protocol, 830 however, its size is strongly controlled by the amount of W that is processed, where the 831 ¹⁸³W effect increases with decreasing amount of W. This work, therefore, provides directions for mitigating the ¹⁸³W effect and resolves apparent inconsistencies between 832 833 previous studies regarding its occurrence and magnitude. Further, our observations 834 make it possible to precisely quantify and correct the analytical ¹⁸³W effect using an 835 empirical correlation between its magnitude and the W amount processed, which can be 836 obtained by analyzing a suite of geological reference materials. This approach will result 837 in an overall improved precision and accuracy of W isotope ratios involving ¹⁸³W, which 838 is essential for identifying and disentangling radiogenic and nucleosynthetic anomalies 839 and, therefore, a prerequisite for the adequate interpretation of isotopic data for terrestrial 840 and meteoritic materials.

841

843 844 **Conflicts of interest** 845 There are no conflicts to declare. 846 847 848 Acknowledgments 849 We are grateful to E.A. Schauble (UCLA) for initial discussions regarding mass-850 independent isotope fractionation, J. Tusch (University of Cologne) for providing 851 additional data, as well as to R.J. Walker (University of Maryland) and A. Mundl-852 Petermeier (now University of Vienna) for providing the IGL W isotope solution standard. 853 We thank several reviewers for their constructive comments on different versions of this 854 manuscript and C. Sutton for the editorial handling. This study was supported by the 855 Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 856 263649064 - TRR 170 (to T.K.), a Geochemistry Option Postdoctoral Fellowship by 857 Caltech (to G.B.), and start-up funds by Caltech (to F.T.). This is TRR 170 publication 858 no. 160. 859

860 **References**

- T. Kleine and R. J. Walker, Tungsten Isotopes in Planets, *Annu. Rev. Earth Planet. Sci.*, 2017, **45**, 389–417.
- 2 C. Vockenhuber, F. Oberli, M. Bichler, I. Ahmad, G. Quitté, M. Meier, A. N. Halliday,
 D.-C. Lee, W. Kutschera, P. Steier, R. J. Gehrke and R. G. Helmer, New Half-Life
 Measurement of ¹⁸²Hf: Improved Chronometer for the Early Solar System, *Phys. Rev. Lett.*, 2004, **93**, 172501.
- T. Kleine, M. Touboul, B. Bourdon, F. Nimmo, K. Mezger, H. Palme, S. B. Jacobsen,
 Q.-Z. Yin and A. N. Halliday, Hf–W chronology of the accretion and early evolution of
 asteroids and terrestrial planets, *Geochim. Cosmochim. Acta*, 2009, **73**, 5150–5188.
- 4 G. Budde, T. Kleine, T. S. Kruijer, C. Burkhardt and K. Metzler, Tungsten isotopic constraints on the age and origin of chondrules, *Proc. Natl. Acad. Sci. USA*, 2016, 113, 2886–2891.
- 5 C. Burkhardt, T. Kleine, B. Bourdon, H. Palme, J. Zipfel, J. M. Friedrich and D. S. Ebel, Hf–W mineral isochron for Ca,Al-rich inclusions: Age of the solar system and the timing of core formation in planetesimals, *Geochim. Cosmochim. Acta*, 2008, **72**, 6177–6197.
- 878 6 T. S. Kruijer, C. Burkhardt, G. Budde and T. Kleine, Age of Jupiter inferred from the
 879 distinct genetics and formation times of meteorites, *Proc. Natl. Acad. Sci. USA*, 2017,
 880 **114**, 6712–6716.
- 7 T. S. Kruijer, T. Kleine, M. Fischer-Gödde, C. Burkhardt and R. Wieler,
 Nucleosynthetic W isotope anomalies and the Hf–W chronometry of Ca–Al-rich
 inclusions, *Earth Planet. Sci. Lett.*, 2014, **403**, 317–327.
- 884 8 L. Qin, N. Dauphas, M. Wadhwa, A. Markowski, R. Gallino, P. E. Janney and C.
 885 Bouman, Tungsten Nuclear Anomalies in Planetesimal Cores, *Astrophys. J.*, 2008,
 886 674, 1234–1241.
- 887 9 E. A. Worsham, C. Burkhardt, G. Budde, M. Fischer-Gödde, T. S. Kruijer and T.
 888 Kleine, Distinct evolution of the carbonaceous and non-carbonaceous reservoirs:
 889 Insights from Ru, Mo, and W isotopes, *Earth Planet. Sci. Lett.*, 2019, **521**, 103–112.
- 890 10G. J. Archer, A. Mundl, R. J. Walker, E. A. Worsham and K. R. Bermingham, High 891 precision analysis of ¹⁸²W/¹⁸⁴W and ¹⁸³W/¹⁸⁴W by negative thermal ionization mass
 892 spectrometry: Per-integration oxide corrections using measured ¹⁸O/¹⁶O, *Int. J. Mass* 893 *Spectrom.*, 2017, **414**, 80–86.
- 894 11 T. S. Kruijer and T. Kleine, No ¹⁸²W excess in the Ontong Java Plateau source, *Chem.* 895 *Geol.*, 2018, **485**, 24–31.
- 12M. Touboul and R. J. Walker, High precision tungsten isotope measurement by
 thermal ionization mass spectrometry, *Int. J. Mass Spectrom.*, 2012, **309**, 109–117.
- 13M. Willbold, T. Elliott and S. Moorbath, The tungsten isotopic composition of the
 Earth's mantle before the terminal bombardment, *Nature*, 2011, **477**, 195–198.
- 14D. L. Cook and M. Schönbächler, High-precision measurement of W isotopes in Fe–
 Ni alloy and the effects from the nuclear field shift, *J. Anal. At. Spectrom.*, 2016, **31**,
- 902 1400–1405.
- 15J. Tusch, P. Sprung, J. van de Löcht, J. E. Hoffmann, A. J. Boyd, M. T. Rosing and C.
 Münker, Uniform ¹⁸²W isotope compositions in Eoarchean rocks from the Isua region,
 SW Greenland: The role of early silicate differentiation and missing late veneer, *Geochim. Cosmochim. Acta*, 2019, **257**, 284–310.
- 16A. Mundl, R. J. Walker, J. R. Reimink, R. L. Rudnick and R. M. Gaschnig, Tungsten182 in the upper continental crust: Evidence from glacial diamictites, *Chem. Geol.*,
 2018, **494**, 144–152.
- 910 17H. Rizo, D. Andrault, N. R. Bennett, M. Humayun, A. Brandon, I. Vlastelic, B. Moine,
 911 A. Poirier, M. A. Bouhifd and D. T. Murphy, ¹⁸²W evidence for core-mantle interaction
 912 in the source of mantle plumes, *Geochem. Persp. Let.*, 2019, **11**, 6–11.
- 913 18G. J. Archer, G. A. Brennecka, P. Gleißner, A. Stracke, H. Becker and T. Kleine, Lack
- 914 of late-accreted material as the origin of ¹⁸²W excesses in the Archean mantle:

- 915 Evidence from the Pilbara Craton, Western Australia, *Earth Planet. Sci. Lett.*, 2019,
 916 **528**, 115841.
- 917 19G. Budde, T. S. Kruijer and T. Kleine, Hf-W chronology of CR chondrites: Implications
 918 for the timescales of chondrule formation and the distribution of 26Al in the solar
 919 nebula, *Geochim. Cosmochim. Acta*, 2018, **222**, 284–304.
- 920 20 G. Budde, T. S. Kruijer, M. Fischer-Gödde and T. Kleine, Planetesimal differentiation
 921 revealed by the Hf–W systematics of ureilites, *Earth Planet. Sci. Lett.*, 2015, **430**, 316–
 922 325.
- 21D. L. Cook, T. S. Kruijer, I. Leya and T. Kleine, Cosmogenic ¹⁸⁰W variations in meteorites and re-assessment of a possible ¹⁸⁴Os-¹⁸⁰W decay system, *Geochim. Cosmochim. Acta*, 2014, **140**, 160–176.
- 22T. S. Kruijer, T. Kleine, L. E. Borg, G. A. Brennecka, A. J. Irving, A. Bischoff and C. B.
 Agee, The early differentiation of Mars inferred from Hf–W chronometry, *Earth Planet*. *Sci. Lett.*, 2017, **474**, 345–354.
- 929 23T. S. Kruijer, T. Kleine, M. Fischer-Gödde and P. Sprung, Lunar tungsten isotopic
 930 evidence for the late veneer, *Nature*, 2015, **520**, 534–537.
- 24T. S. Kruijer, M. Touboul, M. Fischer-Gödde, K. R. Bermingham, R. J. Walker and T.
 Kleine, Protracted core formation and rapid accretion of protoplanets, *Science*, 2014,
 344, 1150–1154.
- 25T. S. Kruijer, P. Sprung, T. Kleine, I. Leya, C. Burkhardt and R. Wieler, Hf–W
 chronometry of core formation in planetesimals inferred from weakly irradiated iron
 meteorites, *Geochim. Cosmochim. Acta*, 2012, **99**, 287–304.
- 26S. Tappe, G. Budde, A. Stracke, A. Wilson and T. Kleine, The tungsten-182 record of
 kimberlites above the African superplume: Exploring links to the core-mantle
 boundary, *Earth Planet. Sci. Lett.*, 2020, **547**, 116473.
- 940 27 T. Kleine, K. Mezger, C. Münker, H. Palme and A. Bischoff, ¹⁸²Hf-¹⁸²W isotope
 941 systematics of chondrites, eucrites, and martian meteorites: Chronology of core
 942 formation and early mantle differentiation in Vesta and Mars, *Geochim. Cosmochim.*943 *Acta*, 2004, **68**, 2935–2946.
- 28J. Völkening, M. Köppe and K. G. Heumann, Tungsten isotope ratio determinations
 by negative thermal ionization mass spectrometry, *Int. J. Mass Spectrom. Ion Process.*, 1991, **107**, 361–368.
- 947 29 J. C. Holst, C. Paton, D. Wielandt and M. Bizzarro, Tungsten isotopes in bulk
 948 meteorites and their inclusions—Implications for processing of presolar components
 949 in the solar protoplanetary disk, *Meteorit. Planet. Sci.*, 2015, **50**, 1643–1660.
- 30N. Shirai and M. Humayun, Mass independent bias in W isotopes in MC-ICP-MS
 instruments, *J. Anal. At. Spectrom.*, 2011, 26, 1414–1420.
- 31A. Takamasa, K. Suzuki, Y. Fukami, T. Iizuka, M. L. G. Tejada, W. Fujisaki, Y. Orihashi
 and T. Matsumoto, Improved method for highly precise and accurate ¹⁸²W/¹⁸⁴W
 isotope measurements by multiple collector inductively coupled plasma mass
 spectrometry and application for terrestrial samples, *Geochem. J.*, 2020, **54**, 117–127.
- 32N. Krabbe, T. S. Kruijer and T. Kleine, Tungsten stable isotope compositions of terrestrial samples and meteorites determined by double spike MC-ICPMS, *Chem. Geol.*, 2017, **450**, 135–144.
- 33C. Burkhardt and M. Schönbächler, Intrinsic W nucleosynthetic isotope variations in
 carbonaceous chondrites: Implications for W nucleosynthesis and nebular vs. parent
 body processing of presolar materials, *Geochim. Cosmochim. Acta*, 2015, **165**, 361–
 375.
- 34M. Becker, D. C. Hezel, T. Schulz, B.-M. Elfers and C. Münker, Formation timescales
 of CV chondrites from component specific Hf–W systematics, *Earth Planet. Sci. Lett.*,
 2015, 432, 472–482.
- 35T. Breton and G. Quitté, High-precision measurements of tungsten stable isotopes
 and application to earth sciences, *J. Anal. At. Spectrom.*, 2014, **29**, 2284–2293.
- 36K. Newman, Effects of the sampling interface in MC-ICP-MS: Relative elemental
 sensitivities and non-linear mass dependent fractionation of Nd isotopes, *J. Anal. At. Spectrom.*, 2012, **27**, 63–70.
 - 27

- 971 37T. Schulz, C. Münker and S. T. M. Peters, p-Process ¹⁸⁰W anomalies in iron 972 meteorites: Nucleosynthetic versus non-nucleosynthetic origins, Earth Planet. Sci. 973 Lett., 2013, 362, 246-257.
- 974 38A. C. Hunt, D. L. Cook, T. Lichtenberg, P. M. Reger, M. Ek, G. J. Golabek and M. 975 Schönbächler, Late metal-silicate separation on the IAB parent asteroid: Constraints 976 from combined W and Pt isotopes and thermal modelling, Earth Planet. Sci. Lett., 977 2018, **482**, 490–500.
- 978 39B. J. Peters, A. Mundl-Petermeier, M. F. Horan, R. W. Carlson and R. J. Walker, 979 Chemical Separation of Tungsten and Other Trace Elements for TIMS Isotope Ratio Measurements Using Organic Acids, Geostand. Geoanal. Res., 2019, 43, 245-259. 980
- 981 40T. Yokoyama, A. Makishima and E. Nakamura, Evaluation of the coprecipitation of 982 incompatible trace elements with fluoride during silicate rock dissolution by acid 983 digestion, Chem. Geol., 1999, 157, 175-187.
- 41Z.-Y. Chu, J.-J. Xu, C.-F. Li, Y.-H. Yang and J.-H. Guo, A Chromatographic Method 984 985 for Separation of Tungsten (W) from Silicate Samples for High-Precision Isotope 986 Analysis Using Negative Thermal Ionization Mass Spectrometry, Anal. Chem., 2020, 987 **92**, 11987–11993.
- 42 T. Fujii, F. Moynier and F. Albarède, The nuclear field shift effect in chemical exchange 988 989 reactions, Chem. Geol., 2009, 267, 139-156.
- 990 43N. S. Saji, D. Wielandt, C. Paton and M. Bizzarro, Ultra-high-precision Nd-isotope 991 measurements of geological materials by MC-ICPMS, J. Anal. At. Spectrom., 2016, 992 **31**, 1490–1504.
- 993 44J. Bigeleisen, Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements, J. Am. Chem. Soc., 1996, 118, 3676-3680. 994
- 995 45E. A. Schauble, Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements, *Geochim.* 996 997 Cosmochim. Acta, 2007, 71, 2170–2189.
- 998 46S. Yang and Y. Liu, Nuclear field shift effects on stable isotope fractionation: a review, 999 Acta Geochim., 2016, 35, 227-239.
- 1000 47W. H. King, Isotope Shifts in Atomic Spectra, Springer, New York, 1984.
- 1001 48A. E. Kramida and T. Shirai, Energy levels and spectral lines of tungsten, W III through 1002 W LXXIV, Atom. Data Nucl. Data, 2009, 95, 305-474.
- 1003 491. Angeli, A consistent set of nuclear rms charge radii: properties of the radius surface 1004 R(N,Z), Atom. Data Nucl. Data, 2004, 87, 185–206.
- 1005 50S. A. De Wit, G. Backenstoss, C. Daum, J. C. Sens and H. L. Acker, Measurement 1006 and analysis of muonic X-ray spectra in deformed nuclei, Nucl. Phys., 1966, 87, 657-1007 702.
- 1008 511. Angeli, Table of nuclear root mean square charge radii, International Atomic Energy 1009 Agency.
- 1010 521. Angeli and K. P. Marinova, Table of experimental nuclear ground state charge radii: An update, Atom. Data Nucl. Data, 2013, 99, 69-95. 1011
- 1012 53P. Aufmuth, A. Steudel, W. Tegtmeier and E. Wobker, Isotope shifts and electron 1013 densities in W I. II. Theoretical field shifts and configuration mixing, J. Phys. B: At. 1014 Mol. Opt. Phys., 1988, 21, 2253-2260.
- 54W. G. Jin, M. Wakasuqi, T. T. Inamura, T. Murayama, T. Wakui, H. Katsuragawa, T. 1015 1016 Ariga, T. Ishizuka, M. Koizumi and I. Sugai, Isotope shift and hyperfine structure in Lu 1017 I and W I, Phys. Rev. A, 1994, 49, 762–769.
- 1018 55J. Lee, J. Chen and A. E. Leanhardt, High resolution isotope shifts and hyperfine structure measurements of tungsten by laser-induced fluorescence spectroscopy. J. 1019 1020 Phys. B: At. Mol. Opt. Phys., 2013, 46, 075003.
- 1021 56A. L. Buchachenko, Magnetic isotope effect, Theor. Exp. Chem., 1995, 31, 118-126.
- 1022 57B. A. Bergquist and J. D. Blum, Mass-Dependent and -Independent Fractionation of 1023 Hg Isotopes by Photoreduction in Aquatic Systems, Science, 2007, **318**, 417–420.
- 1024
- 58N. Dauphas and E. A. Schauble, Mass Fractionation Laws, Mass-Independent Effects, and Isotopic Anomalies, Annu. Rev. Earth Planet. Sci., 2016, 44, 709-783. 1025

- 1026 59 J. Liu, M. Touboul, A. Ishikawa, R. J. Walker and D. G. Pearson, Widespread tungsten
 1027 isotope anomalies and W mobility in crustal and mantle rocks of the Eoarchean Saglek
 1028 Block, northern Labrador, Canada: Implications for early Earth processes and W
 1029 recycling, *Earth Planet. Sci. Lett.*, 2016, **448**, 13–23.
- 601. S. Puchtel, J. Blichert-Toft, M. Touboul and R. J. Walker, ¹⁸²W and HSE constraints
 from 2.7 Ga komatiites on the heterogeneous nature of the Archean mantle, *Geochim. Cosmochim. Acta*, 2018, **228**, 1–26.
- 1033 61 H. Rizo, R. J. Walker, R. W. Carlson, M. F. Horan, S. Mukhopadhyay, V. Manthos, D.
 1034 Francis and M. G. Jackson, Preservation of Earth-forming events in the tungsten isotopic composition of modern flood basalts, *Science*, 2016, **352**, 809–812.
- 1036 62A. Trinquier, M. Touboul and R. J. Walker, High-Precision Tungsten Isotopic Analysis
 1037 by Multicollection Negative Thermal Ionization Mass Spectrometry Based on
 1038 Simultaneous Measurement of W and ¹⁸O/¹⁶O Isotope Ratios for Accurate
 1039 Fractionation Correction, *Anal. Chem.*, 2016, **88**, 1542–1546.
- 1040 63A. Mundl, M. Touboul, M. G. Jackson, J. M. D. Day, M. D. Kurz, V. Lekic, R. T. Helz
 1041 and R. J. Walker, Tungsten-182 heterogeneity in modern ocean island basalts,
 1042 Science, 2017, 356, 66–69.
- 64 A. Mundl-Petermeier, R. J. Walker, R. A. Fischer, V. Lekic, M. G. Jackson and M. D.
 Kurz, Anomalous ¹⁸²W in high ³He/⁴He ocean island basalts: Fingerprints of Earth's core?, *Geochim. Cosmochim. Acta*, 2020, **271**, 194–211.
- 1046 65A. Mundl-Petermeier, R. J. Walker, M. G. Jackson, J. Blichert-Toft, M. D. Kurz and S.
 1047 A. Halldórsson, Temporal evolution of primordial tungsten-182 and ³He/⁴He signatures in the Iceland mantle plume, *Chem. Geol.*, 2019, **525**, 245–259.
- 1049 66 J. R. Reimink, A. Mundl-Petermeier, R. W. Carlson, S. B. Shirey, R. J. Walker and D.
 1050 G. Pearson, Tungsten Isotope Composition of Archean Crustal Reservoirs and 1051 Implications for Terrestrial μ¹⁸²W Evolution, *Geochem. Geophys. Geosyst.*, 2020, **21**, 1052 e2020GC009155.
- 1053 67 B. J. Peters, A. Mundl-Petermeier, R. W. Carlson, R. J. Walker and J. M. D. Day,
 1054 Combined Lithophile-Siderophile Isotopic Constraints on Hadean Processes
 1055 Preserved in Ocean Island Basalt Sources, *Geochem. Geophys. Geosyst.*, 2021, 22,
 1056 e2020GC009479.
- 1057 681. S. Puchtel, A. Mundl-Petermeier, M. Horan, E. J. Hanski, J. Blichert-Toft and R. J.
 1058 Walker, Ultra-depleted 2.05 Ga komatiites of Finnish Lapland: Products of grainy late
 1059 accretion or core-mantle interaction?, *Chem. Geol.*, 2020, **554**, 119801.
- 69G. J. Archer, R. J. Walker, J. Tino, T. Blackburn, T. S. Kruijer and J. L. Hellmann,
 Siderophile element constraints on the thermal history of the H chondrite parent body, *Geochimica et Cosmochimica Acta*, 2019, **245**, 556–576.
- 1063
 1064
 1064
 1065
 70N. Nakanishi, A. Giuliani, R. W. Carlson, M. F. Horan, J. Woodhead, D. G. Pearson
 and R. J. Walker, Tungsten-182 evidence for an ancient kimberlite source, *Proc. Natl.*1065 *Acad. Sci. USA*, 2021, **118**, e2020680118.
- 1066 71 E. A. Worsham, K. R. Bermingham and R. J. Walker, Characterizing cosmochemical
 1067 materials with genetic affinities to the Earth: Genetic and chronological diversity within
 1068 the IAB iron meteorite complex, *Earth Planet. Sci. Lett.*, 2017, **467**, 157–166.
- 72M. W. Jansen, J. Tusch, C. Münker, A. Bragagni, R. Avanzinelli, F. Mastroianni, F. M.
 Stuart and F. Kurzweil, Upper mantle control on the W isotope record of shallow level
 plume and intraplate volcanic settings, *Earth Planet. Sci. Lett.*, 2022, **585**, 117507.
- 1072 73Q.-F. Mei, J.-H. Yang, Y.-F. Wang, H. Wang and P. Peng, Tungsten isotopic
 1073 constraints on homogenization of the Archean silicate Earth: Implications for the
 1074 transition of tectonic regimes, *Geochim. Cosmochim. Acta*, 2020, **278**, 51–64.
- 1075 74Q.-F. Mei, J.-H. Yang and Y.-H. Yang, An improved extraction chromatographic
 1076 purification of tungsten from a silicate matrix for high precision isotopic measurements
 1077 using MC-ICPMS, *J. Anal. At. Spectrom.*, 2018, **33**, 569–577.
- 1078 75J. Tusch, C. Münker, E. Hasenstab, M. Jansen, C. S. Marien, F. Kurzweil, M. J. Van
 1079 Kranendonk, H. Smithies, W. Maier and D. Garbe-Schönberg, Convective isolation of
 1080 Hadean mantle reservoirs through Archean time, *Proc. Natl. Acad. Sci. USA*, 2021,
 1081 **118**, e2012626118.

- 1082 76M. Willbold, S. J. Mojzsis, H.-W. Chen and T. Elliott, Tungsten isotope composition of 1083 the Acasta Gneiss Complex, *Earth Planet. Sci. Lett.*, 2015, **419**, 168–177.
- 1084 77 J. L. Hellmann, T. S. Kruijer, K. Metzler, M. Patzek, A. Pack, J. Berndt and T. Kleine,
 1085 Hf-W chronology of a macrochondrule from the L5/6 chondrite Northwest Africa 8192,
 1086 *Meteorit. Planet. Sci.*, 2020, **55**, 2241–2255.
- 1087 78 J. L. Hellmann, T. S. Kruijer, J. A. Van Orman, K. Metzler and T. Kleine, Hf-W 1088 chronology of ordinary chondrites, *Geochim. Cosmochim. Acta*, 2019, **258**, 290–309.
- 1089 79H. Enomoto, T. Iizuka, Y. Homma, O. Kobayashi, K. Suzuki and T. Kashiwabara,
 1090 Experimental constraints on the origin of analytical ¹⁸³W deficits, *Goldschmidt* 1091 *Conference*, 2021, #4728.
- 80C. Burkhardt, T. Kleine, N. Dauphas and R. Wieler, Nucleosynthetic tungsten isotope
 anomalies in acid leachates of the Murchison chondrite: Implications for hafniumtungsten chronometry, *Astrophys. J.*, 2012, **753**, L6.
- 1095 81B.-M. Elfers, P. Sprung, M. Pfeifer, F. Wombacher, S. T. M. Peters and C. Münker,
 1096 Variable distribution of s-process Hf and W isotope carriers in chondritic meteorites –
 1097 Evidence from ¹⁷⁴Hf and ¹⁸⁰W, *Geochim. Cosmochim. Acta*, 2018, **239**, 346–362.
- 1098 82Y. Zhang and Y. Liu, ¹⁸²W anomalies in mantle: a brief review, *Acta Geochim.*, , DOI:10.1007/s11631-022-00536-z.
- 1100 83M. Fischer-Gödde, B.-M. Elfers, C. Münker, K. Szilas, W. D. Maier, N. Messling, T.
 1101 Morishita, M. Van Kranendonk and H. Smithies, Ruthenium isotope vestige of Earth's pre-late-veneer mantle preserved in Archaean rocks, *Nature*, 2020, **579**, 240–244.
- 84W. Akram and M. Schönbächler, Zirconium isotope constraints on the composition of
 Theia and current Moon-forming theories, *Earth Planet. Sci. Lett.*, 2016, 449, 302–
 310.
- 1106 85G. Budde, C. Burkhardt and T. Kleine, Molybdenum isotopic evidence for the late 1107 accretion of outer Solar System material to Earth, *Nat. Astron.*, 2019, **3**, 736–741.
- 86 R. C. J. Steele, T. Elliott, C. D. Coath and M. Regelous, Confirmation of massindependent Ni isotopic variability in iron meteorites, *Geochim. Cosmochim. Acta*,
 2011, **75**, 7906–25.
- 1111 87 J. Zhang, N. Dauphas, A. M. Davis, I. Leya and A. Fedkin, The proto-Earth as a significant source of lunar material, *Nat. Geosci.*, 2012, **5**, 251–255.
- 1113 88Y. Zhang and Y. Liu, How to produce isotope anomalies in mantle by using extremely
 1114 small isotope fractionations: A process-driven amplification effect?, *Geochim.*1115 *Cosmochim. Acta*, 2020, **291**, 19–49.
- 89T. Fujii, F. Moynier and F. Albarède, Nuclear field vs. nucleosynthetic effects as cause
 of isotopic anomalies in the early Solar System, *Earth Planet. Sci. Lett.*, 2006, 247, 1–
 9.
- 90 M. Wang, G. Audi, F. G. Kondev, W. J. Huang, S. Naimi and X. Xu, The AME2016
 atomic mass evaluation (II). Tables, graphs and references, *Chin. Phys. C*, 2017, 41, 030003.
- 1122
- 1123
- 1124

- 1125 Figure captions
- 1126

1127 1128

1129 Fig. 1. Schematic diagrams illustrating different origins of mass-independent W isotope variations. Radiogenic variations (from ¹⁸²Hf decay) only affect ¹⁸²W, whereas 1130 nucleosynthetic anomalies and the nuclear field shift (see Fig. 6 for details) result in 1131 correlated ¹⁸²W and ¹⁸³W (or ¹⁸⁴W) variations. The analytical ¹⁸³W effect, which essentially 1132 1133 represents a pure ¹⁸³W deficit (Section 4), directly affects all ratios except ¹⁸²W/¹⁸⁴W (6/4). Isotope ratios are internally normalized to ¹⁸⁶W/¹⁸⁴W (a) or ¹⁸⁶W/¹⁸³W (b). For clarity. 1134 1135 cosmogenic variations (from interaction with galactic cosmic rays) that predominantly affect ¹⁸²W are not shown. Slopes for nucleosynthetic variations of 1.41 (a) and -0.12 (b) 1136 1137 are from Burkhardt and Schönbächler³³; other slopes are provided in Table S2.

1138 1139

1140 Fig. 2. W isotope diagrams for kimberlite samples (blue) and geological reference materials (green) obtained by MC-ICP-MS. While the µ¹⁸²W (6/4) values are 1141 indistinguishable from the (IfP) solution standard, there are well-resolved anomalies in 1142 1143 isotope ratios involving ¹⁸³W. These variations are inconsistent with the predicted effects 1144 of a nuclear field shift (NFS), but in excellent agreement with a pure deficit in ¹⁸³W (Table S2). Isotope ratios are internally normalized to ¹⁸⁶W/¹⁸⁴W ('6/4') or ¹⁸⁶W/¹⁸³W ('6/3'). 1145 1146 Regressions (solid lines) were calculated using the 'Model 1 fit' of Isoplot (v3.76); 1147 uncertainties represent 95% CI. Selected data from other studies/laboratories are shown 1148 for comparison (orange triangles); red open squares represent the IGL solution standard 1149 (Section 5.1). All data and references are provided in Table S1.

1150 1151

1152 Fig. 3. The samples investigated here (same as in Fig. 2) display no correlation between 1153 the extent of (analytical) mass-dependent isotope fractionation ($\delta^{186/184}W$) and the magnitude of the analytical ¹⁸³W effect (a) or the total procedural W yield (b). By contrast, 1154 1155 the correlations in (c) and (d) reveal an interrelationship between the ¹⁸³W effect, the 1156 relative loss of W, and the amount of W that was processed through the chemical separation procedure (see also Fig. 4). The ¹⁸³W effect is quantified here as µ¹⁸²W 1157 (normalized to ¹⁸⁶W/¹⁸³W), for which this artifact is most pronounced. For interpretation 1158 of the '100%-intercept' (c) see Section 6; uncertainty on the yield is estimated to be ±5 1159 1160 percentage points.

1161 1162

1163 Fig. 4. W isotope anomalies as function of the amount of W that was processed through 1164 the chemical separation procedure (same samples as in Fig. 2). For most of the observed 1165 range, the samples define a linear correlation between the magnitude of the analytical 1166 ¹⁸³W effect and the W amount (on a logarithmic scale). Note that all data used here were 1167 obtained following the identical analytical protocol and by the same operator, in order to 1168 avoid any systematic variations potentially arising from differences in ion exchange 1169 chromatography, dry-down protocol, or mass spectrometric analyses. Kimberlite sample 1170 'K18' (highest W amount) was excluded from regressions, which were calculated using 1171 the 'Model 1 fit' of *Isoplot* (v3.76); uncertainties represent 95% CI.

1172 1173

Fig. 5. Summary of empirically defined correlations from Fig. 4, demonstrating that the analytical ¹⁸³W effect (displayed as μ^i W variations) decreases logarithmically with increasing amount of W. Vertical bars represent W amounts typically processed for highprecision MC-ICP-MS (orange) and N-TIMS (purple) studies to achieve an uncertainty of about ±5 ppm (gray bar). We note that these trends are specific to a certain analytical protocol and not directly transferrable to other studies and data sets (Section 5.2). As such, the vertical bars are only shown for reference, indicating that a potential ¹⁸³W effect is generally expected to be less pronounced in typical N-TIMS analyses compared tomost MC-ICP-MS data.

1183

1184

1185 Fig. 6. Theoretical effect of a nuclear field shift (NFS) on internally normalized W isotope ratios. (a) Overall, the difference in mean-square nuclear charge radii ($\delta < r^2 >$) is a linear 1186 function of the isotope mass (uncertainties are smaller than symbols); only ¹⁸⁰W and ¹⁸²W 1187 1188 show subtle deviations from the mass-dependent trend (dashed line). Shown are data from Lee et al.55, which are consistent with previous (OIS) studies but of higher precision 1189 (see Section 4.3 for details). (b) Internal normalization to ¹⁸⁶W/¹⁸³W ('6/3') or ¹⁸⁶W/¹⁸⁴W ('6/4') results in roughly complementary anomalies for μ^{180} W and μ^{182} W that are 1190 1191 significantly larger than those for μ^{183} W and μ^{184} W. Values were calculated using Eqt. 1 1192 1193 from Fujii et al.⁸⁹, based on $\delta < r^2 >$ from (a) and isotope masses from Wang et al.⁹⁰; error bars represent propagated uncertainties of all $\delta < r^2 >$ values involved. 1194

1195 1196

Fig. 7. Diagram of $\Delta \mu^{182}$ W versus μ^{183} W (6/4) for samples analyzed by N-TIMS [Archer 1197 et al.⁶⁹ (A19); Mundl et al.^{16,63} (M17,18); Nakanishi et al.⁷⁰ (N21); Worsham et al.⁷¹ (W17)]. 1198 1199 The $\Delta \mu^{182}$ W values represent the difference between measured $\mu^{182/184}$ W (6/3) and μ^{182} W 1200 (6/4) values (all uncertainties propagated); red area corresponds to the long-term reproducibility (±6 ppm for μ^{183} W)⁷⁰. All data are reported relative to the Alfa Aesar 1201 1202 Specpure Plasma standard used at the IGL in Maryland, which shows a small offset from 1203 the Alfa Aesar standard used at the IfP in Münster (green diamond; Section 6). In such 1204 a diagram samples naturally follow the displayed slope of 0.667 (dashed gray line); nonetheless, some data sets are biased toward negative µ¹⁸³W coupled with excesses 1205 in $\Delta \mu^{182}$ W, which is consistent with a small analytical ¹⁸³W effect (Section 5.1). 1206

1207 1208

Fig. 8. Diagram of μ^{183} W (6/4) versus μ^{182} W (6/3) showing different W isotope solution 1209 1210 standards and constraints on the composition of bulk silicate Earth (BSE). All data are 1211 reported relative to the Alfa Aesar standard used in the IfP at the University of Münster 1212 $(\mu^{i}W \equiv 0)$. The '100%-intercepts' are theoretical values that presumably represent an 1213 upper limit for BSE's W isotope signature; a conservative estimate of the BSE 1214 composition is highlighted in blue (see Section 6). Data for NIST SRM 3163 is from 1215 Kruijer et al.²⁵; regression line and processed rock samples (gray symbols) are the same 1216 as shown in Fig. 2c.



¹⁸²W/¹⁸⁴W













µ¹⁸³W (6/4)



V (6/3)

Table S1. W isote	pe data for kir	nberlites, g	eological ri	eterence m	iaterials,	and solution star	idards evaluated in	n this study.										
Sample	ID	Mass	Winitial	Yield	n	µ ¹⁸² W _{meas} .	µ ¹⁸³ W _{meas} .	µ183Wcorr.*	µ ¹⁸² W _{meas} .	µ ¹⁸² W _{corr} .*	µ ¹⁸⁴ W _{meas} .	µ184Wcorr.*	µ ^{182/184} W _{meas} .	µ ^{182/184} W _{corr.} *	µ183/184Wmeas.	µ ^{183/184} W _{corr.} *	δ ^{186/184} W	Ref.
		(g)	(ng)	(%)		(± 20)	(± 2σ)	(± 20)	(± 20)	(± 20)	(± 20)	(± 2σ)	(± 2σ) 183w = 4.00500 //	(± 2σ)	(± 20)	(± 20)	(± 20)	
normalized to								normalized to ""W/""W = 1.98590 ("6/3")										
BOT17-03	К1	0.529	142	70	2	39 + 86	-11.1 + 9.0	28 + 112	185 + 88	38 + 149	74 + 60	-10 + 74	112 + 62	38 + 87	-74 + 60	38 + 87	-0.22 + 0.36	T20
BOT 17-05	К2	0.510	84	66	1	02 + 86	-13.3 + 9.0	04 + 112	182 + 88	0.5 + 14.9	88 + 60	-03 + 74	91 + 62	0.3 + 87	-88 + 60	0.3 + 8.7	-0.08 + 0.36	T20
BOT17-09	КЗ	0.504	347	77	7	-0.3 ± 3.3	-14.2 ± 2.9	0.1 ± 3.2	19.1 ± 1.7	0.2 ± 4.2	9.5 ± 2.0	-0.1 ± 2.1	9.4 ± 1.7	-0.1 ± 2.6	-9.5 ± 2.0	-0.1 ± 2.6	-0.31 ± 0.10	T20
CIM15-72	K4	0.513	277	66	5	1.2 ± 5.3	-12.0 ± 4.8	1.2 ± 7.2	17.7 ± 7.3	1.7 ± 9.6	8.0 ± 3.2	-0.9 ± 4.8	9.2 ± 5.2	1.2 ± 6.1	-8.0 ± 3.2	1.2 ± 6.1	-0.31 ± 0.19	T20
CIM15-80	K5	0.515	272	63	5	0.3 ± 6.1	-13.4 ± 4.5	0.7 ± 7.2	18.7 ± 7.5	0.9 ± 9.6	8.9 ± 3.0	-0.5 ± 4.8	9.8 ± 6.0	0.8 ± 6.7	-8.9 ± 3.0	0.8 ± 6.7	-0.37 ± 0.16	T20
ANG14-287	K6	0.553	1190	79	10	0.4 ± 1.3	-11.3 ± 2.6	0.1 ± 3.8	15.1 ± 3.8	0.1 ± 5.1	7.5 ± 1.7	-0.1 ± 2.5	8.1 ± 2.2	0.6 ± 2.8	-7.5 ± 1.7	0.6 ± 2.8	-0.46 ± 0.11	T20
IH57	K7	0.533	811	75	10	-6.0 ± 3.1	-14.3 ± 2.9	-4.6 ± 4.0	13.0 ± 3.7	-6.0 ± 5.3	9.5 ± 1.9	3.0 ± 2.6	3.5 ± 2.6	-6.1 ± 3.2	-9.5 ± 1.9	-6.1 ± 3.2	-0.44 ± 0.08	T20
LES17-02	K8	0.502	591	77	9	2.1 ± 3.0	-9.3 ± 3.4	1.1 ± 4.2	13.9 ± 3.3	1.5 ± 5.6	6.2 ± 2.2	-0.7 ± 2.8	7.9 ± 2.5	1.7 ± 3.3	-6.2 ± 2.2	1.7 ± 3.3	-0.23 ± 0.13	T20
SAF17-11	K9	0.509	461	68	8	0.0 ± 4.7	-11.7 ± 3.1	0.0 ± 3.9	15.5 ± 3.1	0.0 ± 5.2	7.8 ± 2.1	0.0 ± 2.6	7.6 ± 3.2	-0.1 ± 3.8	-7.8 ± 2.1	-0.1 ± 3.8	-0.33 ± 0.13	120
SAF17-15	K10	0.530	15/0	/8	10	0.6 ± 3.6	-7.2 ± 4.5	0.5 ± 5.3	10.4 ± 3.7	0.7 ± 7.0	4.8 ± 3.0	-0.4 ± 3.5	5.6 ± 2.2	0.8 ± 3.7	-4.8 ± 3.0	0.8 ± 3.7	-0.25 ± 0.07	120
LE317-02	K12	0.661	1200	74	9	-1.4 ± 3.2	-10.9 ± 3.4	-1.0 ± 4.1	13.2 ± 3.1	-1.3 ± 5.5	7.3 ± 2.2	0.0 ± 2.7	0.0 ± 2.3	-1.2 ± 3.2	-7.3 ± 2.2	-1.2 I 3.2	-0.25 ± 0.10	T20
IH 17 IH 53	K12	0.531	369	57	7	-3.0 ± 2.7	-7.9 ± 2.0	-2.1 ± 3.9	10.1 ± 3.0	-2.0 ± 5.1	5.2 ± 1.7	1.4 ± 2.0 0.5 + 3.4	2.5 ± 2.9 9.2 + 3.4	-2.0 ± 3.4	-3.2 ± 1.7	-2.0 I 3.4	-0.39 ± 0.13	T20
ITA-1	K14	0.558	1418	69	10	-21 + 31	-80 + 29	-18 + 38	83 + 33	-24 + 51	53 + 19	12 + 25	30 + 26	-23 + 32	-53 + 19	-23 + 32	-0.37 + 0.10	T20
BOT17-01	K15	0.541	242	59	4	01 + 86	-156 + 67	03 + 94	211 + 88	0.4 + 12.5	10.3 + 4.4	-02 + 62	107 + 62	04 + 77	-10.3 + 4.4	04 + 77	-0.33 + 0.25	T20
ANG14-325	K16	0.549	2688	80	9	-1.0 ± 3.1	-5.0 ± 2.3	-0.3 ± 3.1	6.2 ± 2.8	-0.4 ± 4.1	3.3 ± 1.5	0.2 ± 2.1	2.6 ± 1.9	-0.7 ± 2.5	-3.3 ± 1.5	-0.7 ± 2.5	-0.07 ± 0.20	T20
ANG14-366	K17	0.562	208	59	4	-3.6 ± 7.8	-20.2 ± 5.3	-2.9 ± 5.3	23.0 ± 1.1	-3.9 ± 7.1	13.4 ± 3.5	1.9 ± 3.6	9.7 ± 4.2	-3.7 ± 5.5	-13.4 ± 3.5	-3.7 ± 5.5	-0.32 ± 0.20	T20
NAM18-02	K18	0.548	11959	91	10	0.2 ± 2.7	-2.8 ± 2.3	0.2 ± 3.8	4.0 ± 4.1	0.2 ± 5.1	1.9 ± 1.5	-0.1 ± 2.5	2.3 ± 3.0	0.4 ± 3.4	-1.9 ± 1.5	0.4 ± 3.4	0.13 ± 0.12	T20
SAF18-51	K19	0.548	4380	81	10	-3.0 ± 2.2	-4.3 ± 3.2	-2.0 ± 4.4	3.2 ± 4.1	-2.6 ± 5.9	2.9 ± 2.1	1.3 ± 2.9	0.0 ± 2.6	-2.9 ± 3.3	-2.9 ± 2.1	-2.9 ± 3.3	-0.20 ± 0.11	T20
SAF18-57	K20	0.562	247	60	4	-0.7 ± 4.8	-16.8 ± 5.0	0.2 ± 8.3	22.7 ± 8.8	0.3 ± 11.0	11.2 ± 3.3	-0.2 ± 5.5	11.1 ± 6.2	-0.1 ± 7.1	-11.2 ± 3.3	-0.1 ± 7.1	-0.41 ± 0.24	T20
SAF18-59	K21	0.568	1229	67	10	4.0 ± 2.6	-7.5 ± 1.9	3.1 ± 3.3	14.1 ± 3.6	4.2 ± 4.4	5.0 ± 1.3	-2.1 ± 2.2	9.1 ± 2.8	4.1 ± 3.0	-5.0 ± 1.3	4.1 ± 3.0	-0.38 ± 0.10	T20
LES17-02	K22	1.063	1252	72	10	0.2 ± 3.9	-10.0 ± 3.4	0.0 ± 4.6	13.4 ± 4.0	0.1 ± 6.1	6.7 ± 2.3	0.0 ± 3.1	7.2 ± 3.4	0.5 ± 4.1	-6.7 ± 2.3	0.5 ± 4.1	-0.03 ± 0.12	T20
LES17-01	K23	1.069	535	60	8	0.9 ± 3.4	-13.3 ± 3.9	0.4 ± 5.5	18.4 ± 5.2	0.6 ± 7.3	8.9 ± 2.6	-0.3 ± 3.7	10.0 ± 3.4	1.1 ± 4.3	-8.9 ± 2.6	1.1 ± 4.3	0.14 ± 0.13	T20
LES17-03	K24	1.069	840	61	9	0.7 ± 2.9	-14.2 ± 3.4	0.3 ± 4.0	19.4 ± 2.8	0.4 ± 5.3	9.5 ± 2.2	-0.2 ± 2.7	10.3 ± 1.5	0.8 ± 2.7	-9.5 ± 2.2	0.8 ± 2.7	0.08 ± 0.13	T20
ANG14-287	K25	0.499	1074	61	10	2.2 ± 3.0	-8.3 ± 2.6	2.0 ± 4.0	13.7 ± 4.1	2.7 ± 5.3	5.5 ± 1.7	-1.4 ± 2.7	8.1 ± 3.1	2.6 ± 3.6	-5.5 ± 1.7	2.6 ± 3.6	-0.29 ± 0.14	120
SAF17-15	K26	0.525	1556	83	9	1.9 ± 2.8	-3.5 ± 2.3	1.7 ± 3.0	7.0 ± 2.5	2.3 ± 3.9	2.3 ± 1.5	-1.2 ± 2.0	4.5 ± 1.9	2.2 ± 2.5	-2.3 ± 1.5	2.2 ± 2.5	-0.07 ± 0.11	120
IH57	K27	0.522	795	62	9	-0.8 ± 2.1	-7.3 ± 2.0	-0.1 ± 2.4	9.6 ± 2.0	-0.1 ± 3.3	4.8 ± 1.3	0.0 ± 1.6	4.4 ± 1.6	-0.4 ± 2.1	-4.8 ± 1.3	-0.4 ± 2.1	-0.32 ± 0.09	120
NAM18-01	K20	1.063	354	60	5	-2.0 ± 3.0	-12.6 ± 4.0	-2.3 ± 4.9	14.0 ± 3.7 21.1 ± 3.6	-3.0 ± 0.5	0.5 ± 2.7 0.6 + 3.2	-09 + 37	5.0 ± 5.1	-2.7 ± 4.1	-0.5 ± 2.7	-2.7 ± 4.1	-0.15 ± 0.10	T20
SAF18-58	K30	0.523	1554	79	10	18 + 38	-74 + 30	15 + 34	119 + 21	21 + 45	49 + 20	-10 + 23	69 + 23	20 + 31	-49 + 20	20 + 31	-0.25 + 0.12	T20
GEOLOGICAL R	EFERENCE M	ATERIALS																
JG-1	DI35	0.899	1149	81	10	0.1 ± 4.1	-3.4 ± 3.1	0.3 ± 4.1	5.0 ± 3.5	0.4 ± 5.5	2.3 ± 2.1	-0.2 ± 2.7	2.6 ± 3.0	0.3 ± 3.6	-2.3 ± 2.1	0.3 ± 3.6	-0.13 ± 0.14	T20
JA-2	DI36	1.507	1540	88	10	1.4 ± 3.6	-4.0 ± 3.3	1.6 ± 4.5	7.5 ± 4.1	2.1 ± 6.1	2.7 ± 2.2	-1.1 ± 3.0	4.6 ± 3.3	2.0 ± 4.0	-2.7 ± 2.2	2.0 ± 4.0	-0.19 ± 0.16	T20
JB-2	JB202	0.494	156	60	3	2.9 ± 8.6	-17.6 ± 9.0	2.1 ± 11.2	26.3 ± 8.8	2.9 ± 14.9	11.7 ± 6.0	-1.4 ± 7.4	14.7 ± 6.2	2.9 ± 8.7	-11.7 ± 6.0	2.9 ± 8.7	-0.13 ± 0.36	T20
JB-2	JB204	0.526	163	60	3	-1.9 ± 8.6	-21.0 ± 9.0	-1.2 ± 11.2	26.4 ± 8.8	-1.5 ± 14.9	14.0 ± 6.0	0.8 ± 7.4	12.1 ± 6.2	-1.9 ± 8.7	-14.0 ± 6.0	-1.9 ± 8.7	-0.44 ± 0.36	T20
JB-2	JB205	0.522	165	65	3	0.5 ± 8.6	-16.5 ± 9.0	0.4 ± 11.2	22.6 ± 8.8	0.6 ± 14.9	11.0 ± 6.0	-0.3 ± 7.4	11.7 ± 6.2	0.7 ± 8.7	-11.0 ± 6.0	0.7 ± 8.7	-0.08 ± 0.36	120
DTS 2b	DTS39	3.323	35	49	1	4.5 ± 12.3	-22.0 ± 12.0	2.2 ± 15.5	32.3 ± 13.0	3.0 ± 20.6	14.7 ± 8.0	-1.5 ± 10.3	10.3 ± 9.0	1.7 ± 12.0	-14.7 ± 8.0	1.7 ± 12.0	0.09 ± 0.36	this P16
BHVO-2	BHV15-21	0.503	108	68	20	-41 + 40	-17.8 + 5.2	-31 + 70	196 + 62	-40 + 93	11.7 ± 2.0	20 + 47	78 + 41	-40 + 54	-11.8 + 3.5	-40 + 54	_	B18
SRM 129c	N9C01	0.301	225	75	5	-10 + 92	-151 + 23	-17 + 66	17.9 + 8.3	-22 + 88	10.0 + 1.5	11 + 44	93 + 73	-0.8 + 7.5	-10.0 + 1.5	-0.8 + 7.5	-	B18
SRM 129c	N9C02	0.333	249	74	5	53 + 40	-105 + 50	28 + 85	178 + 92	38 + 114	70 + 33	-19 + 57	117 + 52	47 + 61	-70 + 33	47 + 61	-	B18
SRM 129c	N9C03	0.339	254	58	5	5.4 ± 5.5	-17.2 ± 4.6	4.2 ± 8.1	28.6 ± 8.8	5.7 ± 10.8	11.4 ± 3.1	-2.9 ± 5.4	16.6 ± 6.6	5.2 ± 7.3	-11.4 ± 3.1	5.2 ± 7.3	-	B18
SRM 129c	N9C04	0.316	237	64	5	5.9 ± 8.0	-9.9 ± 5.1	4.5 ± 6.3	19.3 ± 5.0	6.1 ± 8.4	6.6 ± 3.4	-3.0 ± 4.2	12.1 ± 4.6	5.5 ± 5.7	-6.6 ± 3.4	5.5 ± 5.7	-	B18
SRM 129c	N9C05	0.304	227	74	5	1.9 ± 8.3	-17.5 ± 6.1	1.4 ± 8.8	25.2 ± 8.4	2.0 ± 11.7	11.6 ± 4.1	-1.0 ± 5.8	13.8 ± 7.1	2.2 ± 8.2	-11.6 ± 4.1	2.2 ± 8.2	-	B18
DIFFERENT OPE	RATORS/LAB	ORATORI	ES (selecte	ed)														
SRM 129c	#1-20				20	1.0 ± 1.8	-14.0 ± 1.8	1.0 ± 2.1	20.0 ± 1.6	0.0 ± 2.7	10.0 ± 1.1	0.0 ± 1.4	-	-	-	-	-	C16
SRM 129c	BW09				5	0.6 ± 5.4	-4.8 ± 3.3	0.5 ± 5.3	7.0 ± 5.4	1.0 ± 7.3	3.0 ± 2.5	-0.5 ± 3.7	-	-	-	-	-	K17a
BCR-2	-				10	-0.3 ± 2.9	-1.1 ± 3.2	-0.6 ± 4.1	0.7 ± 3.3	-U.3 ± 5.5	0.5 ± 2.2	0.2 ± 2.8	-	-	-	-	-	K1/D
BCR-2	-				22	0.0 ± 9.0	-9.0 ± 4.0	0.0 ± 0.5	13.0 ± 10.0	1.0 ± 14.1	0.0 ± 5.0	-0.5 ± 7.1	-	-	-	-	-	H15 K16
BHVO-2	_				18	-06 + 23	-61 + 28	-03 + 42	78 + 43	-04 + 58	4.5 1 2.2	02 + 29		_	_	_	_	K17b
JB-2	_				16	05 + 25	-118 + 23	07 + 30	166 + 25	10 + 39	78 + 15	-05 + 20	84 + 19	06 + 24	-78 + 15	06 + 24	-	A19
AGV-2	-				12	0.2 ± 3.4	-8.3 ± 3.2	0.1 ± 4.9	11.3 ± 4.9	-0.3 ± 6.5	5.8 ± 2.1	0.1 ± 3.2		_	· - · ·	_	-	K15
La Palma basalt	LP1 (weak)				7	0.9 ± 5.1	-16.1 ± 2.0	0.2 ± 6.4	21.8 ± 8.1	0.3 ± 8.6	10.7 ± 1.3	-0.2 ± 4.3	-	-	-	-	-	T19
SOLUTION STAN	IDARDS					= 0	= 0		= 0		= 0		= 0		= 0			
Special Alesar (IIP)	(IGL)A				40	-15 + 15	-18 + 15		= U 14 + 16		= U 12 + 10		=0		-12 + 10			- thie
NIST SRM 3163	(IGE)				5	-2.0 ± 3.0	-1.0 ± 3.0		1.0 ± 3.0		-1.0 ± 2.0		0.0 ± 3.0		-1.2 1 1.0			K12
					-													
INTERCEPTS (µi	W at vield=10	9%)																
(calculated)					43	-0.7 ± 2.3	3.7 ± 4.2		-6.4 ± 5.7		-2.4 ± 2.8		-2.4 ± 3.3		2.4 ± 2.8			this

W_{sing}: the total amount of W initially present in a sample before the ion exchange chromatography (determined by isotope dilution); n: number of measurements. Unless stated otherwise, the denominator in the µW notation is the same as in the normalization ratio [e.g., µ¹²⁴W (64) represents µ¹²⁵¹⁴W (internally normalized to ¹⁸⁶W/¹⁵⁴W].

^ Measured in different analytical sessions, run alternately with the IfP standard at 50 ng/ml W; see Section 2.2 for details

* Corrected (internally) for the analytical ¹⁵³W effect using the slopes for a pure ¹⁶³W deficit (m') provided in Table S2, where $\mu W_{out} = \mu W_{max} - m \times \mu W_{max}$. $\mu^{150} M_{V} (63)_{out} = \mu^{150} W_{V} (63)_{max} - 2 \times \mu^{140} W_{V} (63)_{max}$ $\mu^{150} M_{V} (64)_{out} = \mu^{150} W_{V} (63)_{max} - (-1) \times \mu^{150} W_{V} (63)_{max}$ $\mu^{150} M_{V} (64)_{out} = \mu^{150} W_{V} (63)_{max} - (-1) \times \mu^{150} W_{V} (63)_{max}$ $\mu^{150} W_{V} (64)_{out} = -1)^{150} W_{V} (63)_{max} - (-1) \times \mu^{150} W_{V} (63)_{max}$ $\mu^{150} W_{V} (64)_{out} = -1)^{150} W_{V} (63)_{max} - (-1) \times \mu^{150} W_{V} (63)_{max}$ $\mu^{150} W_{V} (64)_{out} = -1)^{150} W_{V} (63)_{max} - (-1) \times \mu^{150} W_{V} (63)_{max}$ Uncertainties include all propagated uncertainties induced by the correction, where $\sigma(\mu W_{out})^2 = \sigma(\mu W_{max})^2 + m^2 \times \sigma(\mu W_{max})^2$.

Uncertainties include all propagated u A19: Archer et al. (2019a) B15: Budde et al. (2015) B18: Budde et al. (2015) B18: Budde et al. (2015) H15: Holds et al. (2015) H15: Holds et al. (2015) K15: Knuijer et al. (2012) K17: Knuijer et al. (2017a) K17: Knuijer et al. (2017a) T19: Tusch et al. (2019)