1	Spurious molybdenum isotope anomalies resulting
2	from non-exponential mass fractionation
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29 Abstract

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31 Mass-independent (nucleosynthetic) Mo isotope anomalies are uniquely useful for 32 constraining genetic relationships among meteoritic and planetary materials and, by 33 extension, the origin and nature of Earth's late-stage building blocks. The meaningful 34 interpretation of such data, however, critically depends on the accurate correction of any 35 natural and analytical mass-dependent isotope fractionation, which is commonly 36 assumed to follow the 'exponential law'. Here, using new high-precision Mo isotope data 37 for a diverse set of terrestrial samples, we show that mass-dependent Mo isotope 38 fractionation in nature typically does not adhere to this law, but is instead dominated by 39 equilibrium and Rayleigh processes. We demonstrate that even moderate degrees of 40 such non-exponential fractionation (*i.e.*, mass-dependent isotope fractionation deviating 41 from the exponential law) can result in significant spurious mass-independent Mo isotope 42 anomalies that, when misinterpreted as nucleosynthetic anomalies, can lead to 43 erroneous conclusions, particularly with respect to Earth's accretion history. 44 Consequently, assessing the magnitude and origin of mass-dependent fractionation will 45 be essential for future efforts to precisely determine the mass-independent Mo isotope 46 composition of bulk silicate Earth and to identify potential nucleosynthetic isotope 47 anomalies in terrestrial rocks.

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50 **1. Introduction**

51 Nucleosynthetic isotope anomalies are mass-independent isotope variations resulting 52 from the heterogeneous distribution of presolar matter, which makes them a formidable 53 cosmochemical tool for constraining genetic relationships between meteoritic and 54 planetary materials (e.g., Dauphas and Schauble, 2016). An element that has proven 55 uniquely powerful in this regard is molybdenum (Mo), because (i) it is relatively abundant 56 in almost all types of Solar System materials, (ii) there are large nucleosynthetic isotope 57 variations among bulk meteorites, and (iii) it can clearly distinguish between different 58 nucleosynthetic processes (e.g., Burkhardt et al., 2011; Budde et al., 2019). Most 59 significantly, Mo isotope systematics have revealed a fundamental difference between 60 'non-carbonaceous' (*i.e.*, ordinary/enstatite chondrite-related) and 'carbonaceous' (*i.e.*, 61 carbonaceous chondrite-related) meteorites (Budde et al., 2016), and that this so-called 62 NC-CC dichotomy most likely reflects a spatial separation of two genetically distinct 63 reservoirs in the protoplanetary disk, which has far-reaching implications for the 64 formation and early evolution of the Solar System (Bermingham et al., 2020; Kleine et al., 2020; Kruijer et al., 2020; Warren, 2011). 65

66 Furthermore, Mo isotopes can provide critical insights into Earth's accretion history 67 and, by extension, into the origin of its habitability and the general dynamics of planet 68 formation. Due to its moderately siderophile character, most of the Mo delivered to Earth 69 was partitioned into its core, meaning that the Mo in the present-day bulk silicate Earth 70 (BSE) derives almost exclusively from the late stages of accretion (i.e., during or after 71 the giant Moon-forming impact and the cessation of core formation). Hence, the Mo 72 isotope signature of BSE holds valuable information on the integrated composition, and 73 thus on the origin, of the material accreted to Earth during the last ~10–20% of its growth 74 history (Dauphas, 2017). As a result of >4 billion years of geological activity and 75 convective stirring, the Earth's mantle is generally assumed to be well homogenized with 76 respect to such nucleosynthetic anomalies. However, growing evidence for the existence 77 of primordial mantle domains (e.g., Bennett et al., 2007; Touboul et al., 2012), combined 78 with the recent discovery of nucleosynthetic Ru isotope anomalies in some Archaean 79 rocks (Fischer-Gödde et al., 2020), suggests that some heterogeneities might have 80 existed during Earth's early formative period and even been preserved until today. Such 81 anomalous portions of the mantle might, for example, lack certain late-accreted 82 components, potentially leading to small nucleosynthetic Mo isotope variations, which 83 could have been recorded in some ancient or (modern) deep mantle-derived rocks. The 84 discovery of such isotopic anomalies, relative to the BSE composition, would allow 85 identifying specific building blocks of the Earth as well as better assessing the extent to 86 which the nature of its accreted material changed over time.

87 However, both the precise determination of the mass-independent Mo isotope 88 composition of BSE (*i.e.*, with respect to nucleosynthetic isotope variations) and the 89 reliable identification of potential nucleosynthetic anomalies in terrestrial rocks require 90 highly precise and accurate data. State-of-the-art techniques for multicollector 91 inductively-coupled plasma mass spectrometry (MC-ICP-MS; Budde et al., 2016; Poole 92 et al., 2017) and negative thermal ionization mass spectrometry (N-TIMS; Nagai and 93 Yokoyama, 2016; Worsham et al., 2016; Yobregat et al., 2022) are capable of 94 determining Mo isotope ratios with the required uncertainty of <10 ppm. At this level of 95 precision, however, certain complications regarding the accuracy of the data can become 96 significant; most notably, the effects of mass-dependent isotope fractionation. This is 97 because, in order to isolate the genuine mass-independent anomalies from the 98 measured data, it is essential to fully eliminate any natural and analytical mass 99 fractionation. For this, the data are internally normalized to a given isotope ratio, where 100 it is commonly assumed that all mass-dependent fractionation is accurately described by 101 the 'exponential law': $r_{2/1} = R_{2/1} \times (m_2/m_1)^{\beta}$, where *r* and *R* are the measured and true, 102 respectively, abundance ratio of isotopes 2 and 1, m is the isotopic mass, and β is the 103 fractionation factor (Russell et al., 1978). While this empirical law has in general proven 104 to be adequate for correcting isotope fractionation in the mass spectrometer, processes 105 in the laboratory and especially in nature can follow different mass fractionation laws. In 106 such cases, the conventional 'internal normalization' using the exponential law can 107 create significant spurious mass-independent anomalies, as has been demonstrated for 108 several elements (Mg, Davis et al., 2015; Ca, Ti, Zhang et al., 2014).

109 For Mo, however, this potential problem has so far received little attention, despite the 110 fact that previous studies have revealed large mass-dependent isotope variations in 111 terrestrial samples (total range of >1.3 ‰/amu), which are typically interpreted to reflect 112 non-exponential (equilibrium or Rayleigh) fractionation processes (Kendall et al., 2017; 113 Willbold and Elliott, 2017). To address this issue, we obtained new high-precision Mo 114 isotope data for a diverse set of highly-fractionated terrestrial samples with the aim to 115 constrain how pronounced and widespread such non-exponential fractionation is in 116 nature and, ultimately, to assess its potential impact on internally normalized Mo isotope 117 data. As such, this study highlights the need for a careful data examination in current 118 and future studies that use nucleosynthetic Mo isotope anomalies in order to constrain 119 Earth's accretion history (e.g., Bermingham et al., 2022; Touboul et al., 2021).

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122 2. Materials and Methods

123 The samples investigated in this study include several kimberlites, continental and 124 marine sediments, and the NIST 'SRM 129c' high-sulfur steel; sample types that have a 125 high likelihood of being affected by significant mass-dependent Mo isotope fractionation 126 (e.g., Kendall et al., 2017). The kimberlites are from different occurrences in sub-Saharan 127 Africa and have been analyzed for W isotopes in a previous study (Tappe et al., 2020). 128 All continental sediments (mostly claystone and shale) derive from the Denver Basin 129 (Colorado, USA), while the marine sediments (calcareous clays) are from the Frontale 130 section at the Umbria-Marche Basin (Italy) and the Caravaca Basin (Spain). Additionally, 131 aliquots of the geological reference material 'BHVO-2' and two Mo solution standards 132 (see below) were processed (with and without sample matrix) through the entire 133 analytical protocol (with Mo amounts of $\sim 1 \mu q$, which is the typical value for most 134 samples), in order to assess the accuracy and precision of our procedures.

135 Sample preparation and digestion, the chemical separation of Mo, and the isotope 136 measurements were conducted in the Institut für Planetologie at the University of 137 Münster ('IfP') as well as in the Isotoparium at the California Institute of Technology 138 ('CIT'), and followed our previously established protocols (Budde et al., 2019). In short, 139 cleaned and powdered samples of ~0.2-1 g were digested in PFA vials on a hotplate 140 using mixtures of concentrated $HF-HNO_3(-HCIO_4)$ and $HCI-HNO_3$. Mo was then 141 separated from the sample matrix by anion exchange chromatography (using Bio-Rad 142 AG1-X8 resin), where Mo was eluted in dilute HNO₃. For the kimberlites, the extra clean-143 up step that is performed for selected samples was critical for eliminating their high Nb 144 contents. Subsequently, all Mo cuts were further purified using Eichrom TRU extraction 145 chromatography resin to remove any remaining matrix elements (e.g., Fe/Mo was 146 <1×10⁻³) and minimize isobaric interferences from Zr and Ru (Ru/Mo and Zr/Mo were 147 $<<1\times10^{-4}$). The Mo yield for the entire procedure was typically $\sim70-80\%$, and total 148 procedural blanks were ~4 ng Mo and thus negligible. Mo concentrations were 149 determined on small aliguots using a Thermo Scientific XSeries 2 (IfP) or iCAP RQ (CIT) 150 quadrupole ICP-MS.

151 The Mo isotope compositions were determined using Thermo Scientific Neptune Plus 152 MC-ICP mass spectrometers, equipped with a Cetac Aridus II (IfP) or Aridus3 (CIT) 153 desolvator and a combination of standard sampler and H skimmer (Ni) cones. The analyses were performed in low-resolution mode using analyte concentrations of ~100 154 155 ng/ml Mo and an integration time of 100×8.4 s per measurement, which consumed ~80 156 ng Mo. The mass-dependent data are reported as δ-unit (*i.e.*, parts per 1,000) deviations 157 relative to the bracketing solution standard, where $\delta^{98}Mo = [(^{98}Mo/^{95}Mo)_{sample} /$ $(^{98}Mo)^{95}Mo)_{standard} - 1] \times 10^{3}$. We have not utilized a double-spike here because the 158

159 respective laboratories were not equipped for such analyses at the time of our study; 160 however, as we will discuss in Section 4, this is inconsequential for the conclusions of 161 this study. The internally normalized data were obtained from the same measurements, 162 by correcting mass fractionation using ${}^{98}Mo/{}^{96}Mo = 1.453173$ and the exponential law, 163 as conventionally done in Mo isotope studies (e.g., Bermingham et al., 2018; Budde et 164 al., 2019; Poole et al., 2017; Yokoyama et al., 2019). These (mass-independent) data 165 are reported as ε -unit (*i.e.*, parts per 10,000) deviations relative to the bracketing solution 166 standard, where $\epsilon^{i}Mo = [(^{i}Mo/^{96}Mo)_{sample} / (^{i}Mo/^{96}Mo)_{standard} - 1] \times 10^{4} (i = 92, 94, 95, 97, 10^{4})$ 167 100).

168 Of note, the two bracketing solution standards Alfa Aesar (prepared from Puratronic 169 Mo powder, lot# C24P28; IfP) and NIST SRM 3134 (lot# 130418; CIT) used in the course 170 of this study have virtually identical ε^i Mo (mass-independent) compositions (Table 1), 171 meaning that both subsets of ε^i Mo data are directly comparable. However, our cross-172 calibration also reveals that they display very different degrees of mass-dependent 173 fractionation; for consistency, all δ^{98} Mo values are thus reported relative to the commonly 174 used SRM 3134.

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177 **3. Results**

178 The Mo concentration and isotope data for the samples investigated in this study are 179 summarized in Table 1. Their Mo concentrations vary typically between about 0.3 and 7 180 μ g/g, while kimberlite 'K18' and sediment 'KT17' are characterized by exceptionally high 181 values of 58 and 13 μ g/g, respectively. The samples show substantial variations in the 182 internally normalized isotope data (using the exponential law) that are mostly resolved 183 from the solution standards. Their magnitude generally decreases in the order ϵ^{92} Mo > 184 $\epsilon^{94,100}$ Mo > ϵ^{95} Mo > ϵ^{97} Mo, where the anomaly in ϵ^{97} Mo is often in the opposite direction 185 to the other ϵ^{i} Mo (Fig. 1). The ϵ^{92} Mo range from about -0.4 to +1.0, and the samples 186 broadly follow a single correlation line in diagrams of ε^{i} Mo versus ε^{j} Mo (Fig. 2). Similarly, 187 the samples show large and mostly resolved mass-dependent isotope variations with 188 measured δ^{98} Mo between about -3.3‰ (sediment 'KT03') and +0.9‰ (kimberlite 'K23'), 189 corresponding to a total range of ~1.4 ‰/amu.

190 Interestingly, the degree of mass-dependent isotope fractionation is strongly 191 correlated with the apparent mass-independent anomalies, as demonstrated in Fig. 3. 192 Using the measured δ^{98} Mo, the samples define a regression line that does not pass 193 through the origin but intercepts the *x*-axis (ϵ^{92} Mo = 0) at a δ^{98} Mo of -0.65±0.08 ‰ (95% 194 CI, n=20). Of note, the processed aliquots of the geological reference material BHVO-2 195 and the solution standards ('DI33', 'CT45', 'K31') show no ϵ^{i} Mo anomalies, but an almost

196 identical shift toward negative δ^{98} Mo with an average deviation of -0.63±0.20 ‰ (95%) 197 CI, n=6) from their accepted/true value (-0.07‰ for BHVO-2, Willbold et al. (2016); ≡0‰ 198 for the solution standards). After correction for this systematic offset (Section 4.1), the 199 δ^{98} Mo range from about -0.9 to +1.5 ‰ for the kimberlites and about -2.6 to +0.1 ‰ for 200 the sediments. These values generally fall within the range previously observed for 201 igneous and sedimentary samples (Kendall et al., 2017; Willbold and Elliott, 2017); 202 except for sediment 'KT03' (δ^{98} Mo = -2.6‰) that, to our knowledge, represents the 203 lightest Mo isotope compositions for natural samples measured to date.

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206 **4. Discussion**

207 *4.1.* Origin of Mo isotope variations

208 Mass-dependent isotope fractionation can occur (i) during natural/geologic 209 processes, (ii) during the chemical separation procedure, and (iii) in the mass 210 spectrometer. The fact that the aliguots of BHVO-2 and the solution standards (with and 211 without sample matrix) processed here show a consistent shift toward negative δ^{98} Mo 212 with an average deviation of -0.63±0.20 ‰ from their initial composition (see Section 3), 213 demonstrates that significant mass fractionation was induced in the laboratory. Given the 214 standard-sample bracketing applied here, any instrumental mass bias should be 215 eliminated provided that solution standard and samples match closely in terms of 216 concentration and purity (e.g., Albarède et al., 2004), which was ensured in this study. 217 Nonetheless, with this technique small matrix effects can still arise from unidentified 218 impurities in the analyzed sample solutions. In such a case it is expected that the 219 measured δ^{98} Mo would inversely correlate with the Mo amount, because of a decreasing 220 impurity-to-Mo ratio with increasing amount of Mo (e.g., Murphy et al., 2016); this is, 221 however, not observed (Fig. S1). Since the Mo yield of our chromatographic separation 222 was <90%, another potential explanation is that the non-quantitative recovery of Mo was 223 accompanied by mass-dependent fractionation, as has been documented for numerous 224 elements including Mo (e.g., Anbar et al., 2001; Siebert et al., 2001). For instance, 225 Siebert et al. (2001) observed that the isotopic composition of the eluted Mo 226 progressively changes from light to heavy, when anion exchange resin and dilute HNO₃ 227 are used (comparable to our protocol). In such a case, an incomplete elution of Mo can 228 result in negative δ^{98} Mo of the collected Mo cuts, which is generally consistent with the 229 data in this study. The δ^{98} Mo obtained here, however, do not scale with the Mo yield of 230 the chemical separation procedure (Fig. S1), as would be expected. Consequently, it 231 remains unclear at what point exactly this analytical fractionation was induced. Of note, 232 Pietruszka and Reznik (2008) observed in experiments that Mo added to solutions that were passed through anion exchange chromatography appeared isotopically light (δ^{98} Mo: -0.9 to -2.1 ‰). The authors attributed this to the presence of resin-derived organics in the analyzed solutions, changing the mass bias behavior relative to that of the unprocessed solution used for standard-sample bracketing. This so-called 'column matrix effect' is thus a combined chromatographic and instrumental effect and, given the overlap in the analytical protocols, a likely explanation for the offset observed here.

239 Importantly and independent of its exact origin, the mass-dependent analytical 240 fractionation described above is roughly constant and seems to vary neither with the 241 yield nor the amount of Mo processed. This is further supported by the analyzed 242 kimberlite and sediment samples, which have much larger variations in δ^{98} Mo (incl. 243 positive values), yield, and Mo amount (Fig. S1), but plot along a well-defined ϵ^{92} Mo-244 δ^{98} Mo regression line that is shifted by -0.65±0.08 ‰ relative to the (unprocessed) SRM 245 3134 (Fig. 3). Of note, the samples display little scatter around this regression line, where 246 the deviation is also independent of yield and Mo amount (Fig. S1). These observations 247 indicate that these samples (i) have natural mass fractionation effects that are distinct 248 from the analytical fractionation with respect to magnitude/direction as well as 249 mechanism (see Section 4.2 for discussion), and (ii) experienced the same analytical 250 fractionation as the processed standard materials. Based on the above findings, it can 251 be assumed that the offset observed for the BHVO-2 and solutions standards is 252 representative and that the analytical fractionation for the samples can thus be accurately corrected within the associated uncertainties, where $\delta^{98}Mo_{corr.} = \delta^{98}Mo_{meas.} + (0.63\pm0.20)$. 253 254 For the following discussion, we will use the values thus obtained, because they provide 255 the best representation of the natural mass-dependent effects in the kimberlite and 256 sediment samples, which is supported by the fact that the regression line for the 257 corrected δ^{98} Mo passes exactly through the current estimate for the BSE composition 258 (Fig. 3).

259 As a result of the internal normalization applied here, any Mo isotope fractionation 260 following the exponential law is cancelled out. Therefore, residual eⁱMo variations reflect 261 mass-dependent fractionation that does not adhere to this law or, alternatively, mass-262 independent isotope anomalies. The latter can potentially have a nucleosynthetic 263 (Dauphas et al., 2002) or a nuclear field shift (NFS; Fujii et al., 2006) origin; however, a 264 close inspection of the Mo isotope patterns reveals that the investigated samples 265 generally display a U-shaped pattern, which is very distinct from that for the NFS effect 266 and the characteristic W-shaped pattern of nucleosynthetic anomalies (Fig. 4a). This is 267 more clearly demonstrated in diagrams of ε^{i} Mo versus ε^{j} Mo, showing the data relative to 268 the distinct correlations lines defined by non-carbonaceous ('NC') and carbonaceous 269 ('CC') materials, which reflect genuine nucleosynthetic isotope variations; *i.e.*, variable

270 deficits in Mo nuclides produced in the slow neutron capture process ('s-process') (e.g., 271 Budde et al., 2019). In the ϵ^{95} Mo $-\epsilon^{94}$ Mo diagram (Fig. 2a), which is typically used to 272 illustrate this NC-CC dichotomy, the samples investigated here generally scatter around 273 the current BSE estimate, supporting the previous conclusion that the BSE plots in 274 between the NC- and CC-lines and that its Mo isotope composition, therefore, represents 275 a mixture of inner (NC) and outer (CC) Solar System materials (Budde et al., 2019). 276 However, many samples show clearly resolved deviations from the BSE value and some 277 even overlap, within uncertainties, with the NC-line (near the position of enstatite 278 chondrites). Taken at face value, this would be the first evidence for the preservation of 279 nucleosynthetic Mo isotope anomalies in terrestrial rocks, which would in turn have far-280 reaching implications for Earth's accretion history. The other $\epsilon^{i}Mo - \epsilon^{j}Mo$ diagrams (Fig. 281 2b-e), however, reveal fundamental inconsistencies with such an interpretation, as the 282 samples plot at varying positions relative to the NC- and CC-lines and many even clearly 283 beyond them. The latter is noteworthy because all known bulk Solar System materials 284 (meteoritic and planetary) plot on or in between the NC/CC-lines, meaning that it is 285 implausible that building blocks with such mass-independent Mo isotope compositions 286 existed. It can, therefore, essentially be ruled out that the ε^{i} Mo variations obtained here 287 have a mass-independent (nucleosynthetic or NFS) origin.

288 Consequently, these apparent anomalies most likely result from an inadequate 289 correction of mass-dependent Mo isotope fractionation, which is supported by several 290 lines of evidence. Various fractionation laws have been derived in the past (empirically 291 and theoretically) in order to describe natural and analytical mass-dependent effects, 292 where the most important are the exponential, equilibrium, Rayleigh, power, and linear 293 fractionation laws. Except for the latter, these can be represented by the 'generalized 294 power law' (GPL): $(r_{2/1}/R_{2/1}) = (r_{3/1}/R_{3/1})^{\theta}$ with $\theta = (m_2^n - m_1^n) / (m_3^n - m_1^n)$, where the 295 differences between the individual laws are reflected by distinct values for n, which is a 296 free parameter for the mass fractionation exponent (Maréchal et al., 1999). We note that, 297 as a first-order approximation, the exponential law also describes kinetic isotope 298 fractionation $(n \rightarrow 0)$; the reader is referred to Dauphas and Schauble (2016) for details. 299 The differences between these laws are best illustrated when plotting their predicted 300 effects as deviations from the conventionally used exponential law. As demonstrated in 301 Fig. 5a, non-exponential Mo isotope fractionation results (when internally normalizing to ⁹⁸Mo/⁹⁶Mo using the exponential law) in characteristic U-shaped isotope patterns, where 302 the anomaly in ϵ^{92} Mo is largest and that in ϵ^{97} Mo is smallest (and in the opposite 303 304 direction), as observed for the samples investigated here. Of note, these systematics are also evident from the $\epsilon^{i}Mo - \epsilon^{j}Mo$ diagrams (Fig. 2), where the samples generally follow 305 306 the slopes for the predicted effects of non-exponential isotope fractionation.

307 Furthermore, as would be expected for an inadequate correction of mass 308 fractionation, the ε^{i} Mo anomalies are strongly correlated with the degree of mass-309 dependent isotope fractionation (F). As illustrated in Fig. 5b, this also allows constraints 310 to be placed on the underlying mechanism of mass fractionation, where the data 311 obtained here are generally consistent with the predicted effects of the equilibrium and 312 Rayleigh laws. This observation is in line with previous studies on mass-dependent Mo 313 isotope fractionation in magmatic and sedimentary settings, which is often attributed to 314 equilibrium or Rayleigh fractionation processes during sample formation or subsequent 315 alteration/diagenesis (Kendall et al., 2017; and references therein). The heavy signature 316 $(\delta^{98}Mo = +0.75\%)$ of the SRM 129c could have been inherited from its raw material or 317 induced by non-exponential mass fractionation during its industrial production process. 318 We note that, given their different formation histories, there is no reason to assume that 319 the fractionation mechanism is the same for all samples here; however, they show little 320 excess scatter (MSWD = 1.3) around a best-fit line with a slope corresponding to an n-321 value of -0.90, which is close to the fractionation exponent for canonical (high-322 temperature) equilibrium fractionation (n=-1; Fig. 5b). Regardless of the exact origin, the 323 investigated samples clearly show large mass-dependent isotope variations that cannot 324 be described by the exponential law, resulting in significant spurious mass-independent 325 anomalies (after the conventional internal normalization) that have no significance for 326 constraining Earth's accretion history.

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4.2. Implications for Mo isotope analyses

329 The results obtained here by combining mass-dependent and mass-independent data 330 have some important implications for the determination of Mo isotope compositions in 331 general. First, the processed aliguots of the solution standards (with and without sample 332 matrix) experienced significant mass-dependent fractionation of ~0.6‰ during the 333 analytical procedure (consistent with the systematic δ^{98} Mo offset for the other samples; 334 Fig. 3), but show no anomalies in the internally normalized (ϵ^i Mo) data. This strongly 335 suggests that this analytical (chemistry-induced and/or instrumental) fractionation does 336 indeed follow the exponential law and, therefore, represents (at least for the protocol 337 applied here) most likely a kinetic rather than an equilibrium effect (cf. Anbar et al., 2001). 338 This is noteworthy, as it means that the non-quantitative recovery of Mo during its 339 chemical separation does not induce noticeable eⁱMo anomalies when using the 340 exponential law for the internal normalization. Similarly, the Alfa Aesar and NIST SRM 341 3134 solution standards used at the IfP and CIT, respectively, show a significant 342 difference in mass-dependent fractionation (~0.2 %/amu), but have virtually identical 343 ϵ^{i} Mo compositions (Table 1). This implies that the observed difference most likely results

from kinetic isotope fractionation, and enables a direct comparison of the obtained massindependent Mo isotope data. We note, however, that there is no *a priori* reason that this should always be the case, because those high-purity solution standards are typically made from Mo ores, which primarily represent molybdenites that can show substantial, often non-exponential, mass fractionation effects (Breillat et al., 2016).

349 Second, the $\epsilon^{i}Mo - \epsilon^{i}Mo$ diagrams reveal that the best-fit lines for the samples analyzed 350 here do not pass through the origin, which is the composition of the solution standards 351 (Fig. 2). This small offset (that is also observed for the BSE estimate from Budde et al., 352 2019) cannot be explained by (non-exponential) mass fractionation, suggesting that it 353 might represent a mass-independent effect instead. The overall ϵ^i Mo variations observed 354 here are clearly inconsistent with a nuclear field shift effect, as both define very distinct 355 correlation lines that are often nearly perpendicular (Fig. 2). However, the systematic 356 offset of terrestrial rock samples from the solution standards (as evident from the non-357 zero intercepts of the best-fit lines) is best described by a slight deficit for ϵ^{100} Mo and slight excesses for the other ϵ^{i} Mo values (with ϵ^{92} Mo > $\epsilon^{95,97}$ Mo > ϵ^{94} Mo), which is 358 359 characteristic of the NFS effect. Indeed, the intersection points of the best-fit lines and 360 the theoretical NFS lines in Fig. 2 self-consistently define a Mo isotope composition that 361 is consistent with a small NFS effect on the order of a few ppm (Fig. 4b). The available 362 data is, unfortunately, not sufficient to evaluate whether this observation is significant 363 and can indeed be attributed to a NFS effect, in which case it also remains unclear 364 whether it reflects a roughly constant effect in the samples induced by the chemical 365 separation procedure or whether it is a characteristic signature of the solution standards. 366 The latter could potentially have been inherited from their raw material or induced during 367 its (industrial) processing, which can cause exotic isotope effects in metal/steel samples 368 (e.g., SRM 129c) and solution standards made thereof (e.g., Akram and Schönbächler, 369 2016; Budde et al., 2019; Steele et al., 2011; Zhang et al., 2012). We note that in both 370 scenarios there is probably no noticeable impact on the conclusions from Budde et al. 371 (2019) regarding the CC contribution to BSE's Mo (see below). This is because all 372 terrestrial samples and most of those defining the NC- and CC-lines have been 373 processed through the same analytical protocol and measured relative to the same 374 solution standard. A potential small NFS effect, therefore, is expected to be rather 375 invariable for this sample set, and would thus not significantly affect the BSE's position 376 relative to the NC/CC-lines. Regardless, in line with previous findings (Fujii et al., 2006), 377 the above demonstrates that assessing the extent of potential (natural or analytical) 378 mass-independent isotope fractionation by the NFS effect will probably be important for 379 obtaining Mo isotope data with high accuracy and for ensuring comparability between 380 different protocols / data sets.

381 Finally and most importantly, our data is testament to widespread non-exponential 382 mass fractionation and the first empirical evidence for its potential to create substantial 383 spurious mass-independent Mo isotope anomalies. The fact that mass fractionation in 384 all samples investigated here does not follow the exponential law strongly supports the 385 previous theoretical, experimental, and empirical considerations (Kendall et al., 2017; 386 Willbold and Elliott, 2017), concluding that equilibrium and Rayleigh (and not kinetic) 387 processes are the dominant mechanisms of mass-dependent Mo isotope fractionation in 388 natural systems. Depending on the degree of this non-exponential fractionation, using 389 the exponential law for the internal normalization can then have fundamental effects on 390 the evaluation of the measured Mo isotope data, if inappropriately interpreted as 391 nucleosynthetic isotope anomalies. For example, in case of the largest degree of 392 fractionation observed here (-0.9 %/amu), this can result in spurious anomalies of up to 393 ~1.0 ε -unit (in ε^{92} Mo), which is on the same order of magnitude as genuine 394 nucleosynthetic anomalies in bulk meteorites (ϵ^{92} Mo $\approx 0-3$; Budde et al., 2019). Further, 395 in the ϵ^{95} Mo $-\epsilon^{94}$ Mo diagram (Fig. 2a), an inadequate correction of mass-dependent 396 fractionation can lead to a significant apparent excess or deficit in s-process Mo nuclides 397 and, in extreme cases, to samples overlapping with the NC- or CC-lines, respectively (as 398 observed here for sediment 'KT03'). Of note, even a moderate degree of non-exponential fractionation of ~0.2 ‰/amu, can already result in deviations from the true $\epsilon^{92,94,100}$ Mo 399 400 that exceed typical analytical uncertainties (Fig. 6a), which could, for instance, lead to 401 the erroneous identification of isotopically anomalous domains in the silicate Earth. And 402 even if the effects are smaller than the associated uncertainties (i.e., on the order of 403 several ppm), this can have significant consequences, as demonstrated in Fig. 6b. This 404 figure illustrates the effect of non-exponential fractionation on the Δ^{95} Mo parameter, 405 which represents a measure of the position relative to the NC/CC-lines in the ϵ^{95} Mo-406 ϵ^{94} Mo diagram (Fig. 2a) that can be used to calculate the fraction of CC-derived Mo in a 407 given sample (e.g., 46±15% for BSE; Budde et al., 2019). For instance, mass 408 fractionation of only 0.2 %/amu would cause a shift in Δ^{95} Mo that corresponds to a 409 difference of ~5 percentage points in the inferred CC-fraction, which can already have 410 significant impact on constraining the nature and origin of Earth's late-state accretion 411 materials.

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414 **5. Conclusions**

The high-precision Mo isotope data obtained in this study provide further evidence for widespread mass-dependent Mo isotope fractionation by equilibrium and Rayleigh processes in terrestrial samples, highlighting that it cannot generally be assumed that 418 natural mass fractionation effects are adequately corrected for by the conventional 419 internal normalization using the exponential law. As we demonstrate here, this can lead 420 substantial spurious mass-independent Mo isotope anomalies and, when 421 misinterpreted as nucleosynthetic anomalies, to erroneous conclusions. This is 422 particularly relevant for samples with complex geological histories including diagenetic 423 or fluid-assisted processes (e.g., marine sediments, molybdenites), but can also be 424 significant for some igneous rocks. Additionally, while most bulk meteorites show only 425 small (<0.3 %/amu) fractionation effects (Burkhardt et al., 2014), an inadequate mass 426 fractionation correction can potentially be relevant for some extraterrestrial samples, in 427 particular those with extensive condensation/evaporation or aqueous alteration effects. 428 However, this problem can be addressed by obtaining high-precision mass-dependent 429 (ideally using the double-spike technique) and mass-independent data in combination, 430 which will allow to assess the magnitude and origin of mass fractionation in a given 431 sample. Based on those results, residual effects on the internally normalized ($\epsilon^{i}Mo$) 432 values from an inappropriate mass fractionation correction can be ruled out or identified, 433 and potentially mitigated by applying a more adequate fractionation law for the internal 434 normalization. Combined, this will not only shed new light on the mechanisms of natural 435 Mo isotope fractionation in general, but also be essential for applications that require a 436 high level of accuracy, such as the precise determination of the mass-independent Mo 437 isotope composition of bulk silicate Earth (with respect to the NC and CC reservoirs) and 438 the reliable identification of potential nucleosynthetic anomalies in terrestrial rocks.

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- 440

441 **Declaration of interests**

442 There are no competing interests to declare.

443

444

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- 613 **Figures captions and Tables**
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616 Fig. 1. Mo isotope patterns for selected samples showing the (apparent) massindependent anomalies, after internal normalization using the exponential law and 617 618 ⁹⁸Mo/⁹⁶Mo. The investigated samples show both negative and positive ϵ^{i} Mo anomalies. 619 but always a characteristic U-shaped pattern. Error bars are omitted for clarity; 620 'standards' represents average of processed BHVO-2 and solution standards (see 621 Section 3). 622

623 Fig. 2. Mo isotope diagrams showing the investigated samples (kimberlites, sediments, 624 SRM 129c) in the context of the NC- and CC-lines (in red and blue, respectively). Dashed 625 black lines represent predicted effects of non-exponential mass-dependent fractionation, 626 calculated after Tang and Dauphas (2012); the respective intercepts are adjusted to best 627 fit the sample data. Dotted gray lines represent theoretical effects of the nuclear field shift 628 effect (NFS; see Fig. 4). Bulk silicate Earth estimate (green diamond) as well as NC- and 629 CC-lines are based on data set from Budde et al. (2019); enstatite chondrites (red open 630 square) are shown for reference (Render et al., 2017).

- 631 **Fig. 3.** Diagram of ε^{92} Mo versus δ^{98} Mo. The measured δ^{98} Mo of the samples show a 632 systematic shift towards negative values (with $\delta^{98}Mo = -0.65\%$ at $\epsilon^{92}Mo = 0$), virtually 633
- identical to the average offset for processed BHVO-2 and solution standards (purple 634 635 triangle). Due to its kinetic nature, this analytical mass-dependent fractionation shifts 636 samples only horizontally (see Section 4). After its correction, the regression passes 637 through the bulk silicate Earth estimate (green diamond; Budde et al., 2019; Greber et 638 al., 2015). Regression calculated using the 'Model 1' of IsoplotR (v4.4); uncertainties 639 represent 95% CI. 640

641 Fig. 4. Mass-dependent and mass-independent fractionation effects on internally 642 normalized Mo isotope data, using the exponential law and ⁹⁸Mo/⁹⁶Mo, (a) Predicted 643 effects of non-exponential mass fractionation, nucleosynthetic anomalies (for NC and 644 CC materials), and the nuclear field shift effect (NFS); all patterns normalized to 645 ϵ^{94} Mo=0.8. (b) Offset of the best-fit lines in Fig. 2 (see Section 4.2 for discussion) 646 compared to a small NFS effect. The latter was calculated after Fujii et al. (2006), using 647 updated nuclear charge radii and isotope masses (Angeli and Marinova, 2013; Wang et 648 al., 2021).

- 649 650 Fig. 5. Differences between various mass fractionation laws for Mo isotopes. (a) For a 651 given degree of fractionation (F); reported as deviations from the exponential law 652 (horizontal line). Values in square brackets refer to the *n*-value in the generalized power 653 law (see Section 4.1). (b) Apparent mass-independent anomalies (here as ϵ^{92} Mo) as 654 function of the degree of mass-dependent isotope fractionation (here in ‰/amu), which 655 are inversely correlated. The best fit for the sample set (kimberlites, sediments, SRM 656 129c) is obtained for n=-0.90 in the generalized power law (see Section 4.1).
- 657
- 658 Fig. 6. Effects of non-exponential mass-dependent isotope fractionation on internally 659 normalized Mo isotope data, based on the fractionation trend (n=-0.9) observed for the 660 samples in Fig. 5b. (a) Effects in comparison to the analytical uncertainties (green band 661 represents typical values for samples analyzed here); labels mark the degree of mass-662 dependent fractionation in ‰/amu. (b) Effects on Δ^{95} Mo [= (ϵ^{95} Mo–0.596× ϵ^{94} Mo)×100]; 663 intercept of dashed line is adjusted to best fit the sample data. Horizontal lines indicate 664 inferred fraction of CC-derived Mo (see Budde et al., 2019); vertical gray bar represents 665 the total range of mass-dependent fractionation observed in natural samples (this study; Kendall et al., 2017). See Figs. 2 and 3 for further details. 666

669 Tab	e 1 . Summar	y of Mo	isotope	data	investigated	in this	study
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ID	Sample	Lab.	Μο (μg/g)	ε ⁹² Mo	±	ε ⁹⁴ Mo	±	ε⁰⁵Mo	±	ε ⁹⁷ Μο	±	ε ¹⁰⁰ Μο	±	Ν	δ ⁹⁸ Mo (meas.)	δ⁹⁸Mo (corr.)	F (‰/amu)
Kimberlites	S															· · · ·	· · ·
K11	LES17-02	lfP	0.84	-0.36	0.15	-0.10	0.12	0.05	0.06	0.08	0.04	-0.19	0.07	10	0.43	1.06	0.35
K14	ITA-1	lfP	4.43	-0.08	0.08	-0.05	0.04	0.04	0.04	0.02	0.05	0.02	0.06	9	-0.57	0.05	0.02
K18	NAM18-02	lfP	57.88	0.23	0.11	0.08	0.05	0.07	0.06	0.04	0.04	0.14	0.10	10	-1.49	-0.86	-0.29
K20	SAF18-57	lfP	7.39	0.16	0.10	0.10	0.04	0.11	0.04	0.08	0.05	0.03	0.03	10	-1.33	-0.70	-0.23
K22	LES17-02 (repl.)	lfP	0.79	-0.33	0.18	-0.11	0.13	0.05	0.09	0.10	0.08	-0.17	0.11	6	0.11	0.74	0.25
K23	LES17-01	lfP	0.30	-0.36	0.19	-0.04	0.19	0.05	0.09	0.11	0.13	-0.21	0.15	5	0.90	1.53	0.51
K24	LES17-03	lfP	0.20	0.36	0.16	0.10	0.24	0.14	0.14	0.02	0.21	0.12	0.08	4	-1.40	-0.77	-0.26
K25	ANG14-287	lfP	2.85	-0.19	0.09	-0.08	0.08	0.00	0.05	0.05	0.05	-0.11	0.09	8	-0.38	0.25	0.08
K26	SAF17-15	lfP	1.26	-0.02	0.24	0.01	0.17	0.09	0.12	0.09	0.08	-0.10	0.14	5	-0.39	0.24	0.08
K27	Igwisi Hills	lfP	0.38	0.12	0.21	0.09	0.09	0.11	0.02	0.10	0.03	-0.04	0.07	5	-0.76	-0.13	-0.04
K30	SAF18-58	lfP	1.23	-0.08	0.19	-0.02	0.13	0.07	0.10	0.06	0.06	-0.06	0.11	6	-0.43	0.20	0.07
Sediments	1																
KT02	Frontale	CIT	1.35	0.66	0.10	0.22	0.07	0.12	0.08	0.02	0.07	0.27	0.11	6	-1.79	-1.16	-0.39
KT03	Caravaca	CIT	1.82	1.04	0.09	0.31	0.07	0.13	0.05	-0.05	0.02	0.42	0.05	8	-3.26	-2.63	-0.88
KT17	Denver Basin	CIT	13.13	-0.06	0.09	-0.04	0.03	0.02	0.04	0.02	0.04	-0.03	0.05	9	-0.55	0.08	0.03
KT18	Denver Basin	CIT	4.24	0.18	0.09	0.02	0.07	0.06	0.04	0.03	0.03	0.11	0.05	11	-1.19	-0.56	-0.19
KT19	Denver Basin	CIT	6.59	0.18	0.11	-0.01	0.07	0.04	0.06	0.02	0.04	0.10	0.06	9	-1.09	-0.46	-0.15
KT20	Denver Basin	CIT	4.35	0.14	0.15	0.01	0.06	0.07	0.05	0.02	0.08	0.07	0.04	5	-1.35	-0.72	-0.24
KT21	Denver Basin	CIT	6.20	0.19	0.07	0.04	0.06	0.05	0.03	0.02	0.03	0.10	0.07	11	-1.10	-0.47	-0.16
KT23	Denver Basin	CIT	1.26	0.12	0.11	0.00	0.06	0.07	0.06	0.06	0.02	0.17	0.07	7	-0.90	-0.27	-0.09
Others																	
N9C02,3,4	NIST SRM 129c	lfP^	7.42	-0.29	0.07	-0.08	0.04	0.00	0.03	0.03	0.03	-0.16	0.04	35	0.10	0.73	0.24
BHV27	BHVO-2	lfP	3.81	0.01	0.10	0.00	0.09	0.05	0.05	0.05	0.03	-0.03	0.07	9	-0.89	-0.26	-0.09
BHV36	BHVO-2	CIT	3.84	-0.02	0.12	-0.03	0.10	0.02	0.06	0.03	0.03	-0.01	0.04	9	-0.60	0.03	0.01
BHV39	BHVO-2	CIT	3.66	-0.03	0.10	-0.04	0.08	0.02	0.03	0.04	0.03	0.05	0.05	11	-0.61	0.02	0.01
K31	proc. sol. std.*	lfP	_	0.05	0.14	0.05	0.07	0.08	0.04	0.04	0.05	0.00	0.09	8	-0.88	-0.26	-0.09
DI33	proc. sol. std.	IfP^	_	0.00	0.15	-0.01	0.11	0.03	0.07	0.06	0.03	0.00	0.08	10	-0.62	0.01	0.00
CT45	proc. sol. std.	CIT	_	-0.02	0.12	0.00	0.06	0.01	0.05	0.04	0.04	-0.02	0.06	11	-0.39	0.24	0.08
Δ(AA–3134) cross-calibrat.	CIT	_	-0.01	0.04	-0.01	0.03	0.00	0.02	0.00	0.02	0.04	0.02	66	-0.58	_	-0.19

The ϵ^{i} Mo were obtained by internal normalization to 98 Mo/ 96 Mo = 1.453173 using the exponential law, and are reported relative to the Alfa Aesar ('AA'; IfP) or NIST SRM 3134 ('3134'; CIT), which have virtually identical ϵ^{i} Mo compositions. All δ^{98} Mo are reported relative to SRM 3134; 'corr.' values were corrected for an analytical mass fractionation effect (Section 4.1). Reported uncertainties for the ϵ^{i} Mo values represent the 95% confidence interval of repeated measurements; for δ^{98} Mo, the external reproducibility is 0.20% for the measured (Section 3) and 0.28% for the corrected values (propagated uncertainties). N: number of analyses; F = δ^{98} Mo and δ^{98} Mo are reported values (propagated uncertainties).

674 δ⁹⁸Mo/(m⁹⁸Mo–m⁹⁵Mo).

668

675 *Kimberlite matrix (devoid of its natural Mo) doped with Mo from the Alfa Aesar solution standard before processing.

676 ^Mass-independent data previously reported in Budde et al. (2018, 2019).























Spurious molybdenum isotope anomalies resulting from non-exponential mass fractionation

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Fig. S1. Mass-dependent Mo isotope variations for samples (yellow circles) and processed standard materials (purple triangles) as function of Mo yield and amount of Mo processed. (a,b) Measured δ^{98} Mo values. (c,d) Deviation in δ^{98} Mo from the regression line displayed in Fig. 3; gray bar roughly represents the uncertainty on the regression. Uncertainties on the Mo yield and amount are estimated to be ±10 percentage points and ±5%, respectively. It is unclear whether the two samples with slightly higher deviations reflect analytical issues or mass-dependent fractionation following a different law compared to the other samples (see Fig. 5b).