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Rapid decomposition of geological samples by ammonium bifluoride (NH₄HF₂) for combined Hf-Nd-Sr isotope analyses

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Abstract

RATIONALE

Complete decomposition of silicate rock matrices is crucial in determining their isotopic compositions, but acid dissolution in high-pressure steel-jacketed bomb, which has been the only powerful, effective technique thus far, is time-consuming and expensive. Rock dissolution using ammonium bifluoride (ABF) is a viable alternative, which is described here.

METHODS

Geological reference materials (GRMs) were digested using ABF in closed Teflon™ beakers at temperatures of 220/230 °C in convection oven and subsequently treated with HNO₃. Hf-Sr-Nd were separated and purified using ion exchange chemistry columns calibrated for 50-2 mg samples. Isotopic composition of Sr-Nd were measured by Thermal Ionization Mass Spectrometry, while that of Hf by Multi Collector Inductively Coupled Plasma Mass Spectrometry, both with normal 10¹¹ Ω and gain calibrated 10¹³ Ω amplifiers.

RESULTS

Total procedural blanks of our protocol are 0.5 ng for Sr, 0.2 ng for Nd and <25 pg for Hf. Test runs with GRMs, ranging in composition from basic to felsic and dissolved in ABF gave accurate ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios as compared to those obtained with the bomb dissolution technique. Reproducibilities were comparable, on the order of 10-20 ppm. Our technique allows combined Hf-Sr-Nd isotope analyses of low mass (50-2 mg) samples.

CONCLUSIONS

The ABF digestion is an alternative technique to high-pressure bomb dissolution in matrix decomposition for accurate and reproducible Hf-Nd-Sr isotope analyses of geological samples within reasonable time (3-4 days), with high sample throughput and for low costs in geochemistry and environmental sciences.

Keywords: ammonium bifluoride; rock digestion; column chemistry; Hf-Nd-Sr isotopes

57 **1. Introduction**

58 Complete mineral decomposition is crucial in determining the elemental and isotopic
59 composition of geological samples. Full recovery of trace and rare earth elements (REEs),
60 including Zr and Hf, is relatively hard to achieve for some silicate rocks containing large
61 amounts of strongly refractory heavy minerals like zircon, rutile and garnet. Various
62 techniques were developed for this purpose, including microwave-assisted acid digestion¹⁻³,
63 sintering and fusion⁴⁻⁸, and high pressure dissolution in PicoTrace[®] systems^{3,9} or in steel-
64 jacketed Parr[™] bombs¹⁰⁻¹⁴. Fusion and high-pressure bomb dissolutions allow full recoveries
65 of Zr and Hf, while microwave acid digestion and pressure digestion in PicoTrace systems
66 were shown to fail^{3,15,16}. Nevertheless, fusion and pressurized vessel digestions have their
67 drawbacks. Fusion is often neglected due to high blank levels and high yield of total dissolved
68 solids, which may compromise mass spectrometry^{4,8}. High-pressure bomb dissolution, which
69 uses distilled HF-HNO₃ and HCl acids, is demonstrated to be very efficient in decomposing
70 silicate rocks having high refractory mineral content^{13,14}. However, it is time-consuming,
71 expensive, often leads to the formation of insoluble fluorides and associated sample
72 throughput is relatively low^{11,13,14}.

73 Fluoride-bearing salts offer an alternative to sample decomposition and converting metal
74 oxides to fluorides¹⁷. Both ammonium fluoride (NH₄F) and ammonium acid fluorides
75 (NH₄F·xHF with x=1, 1.5 or 2) were found to be effective in breaking down solid inorganic
76 matrices and refractory mineral separates¹⁸⁻²¹. Ammonium bifluoride (ABF, NH₄F·HF or
77 NH₄HF₂) dissolution at elevated temperature has recently been introduced and systematically
78 investigated in decomposition of geological samples²²⁻²⁴ and demonstrated to be successful in
79 breaking down granodiorites with excellent recoveries of Zr and Hf²².

80 ABF is a colorless, water-soluble substance with melting and boiling points of ~126.5 and
81 238 °C¹⁷. Hydrofluoric acid (HF) vapors are being produced during thermal decomposition of
82 ABF starting from ~120 °C²³, and making it effective in breaking down Si-O bonds during
83 fluorination. Major advantages of using ABF over steel-jacketed bomb dissolution include 1)
84 safety issues, as the direct use of corrosive and toxic HF can be avoided, 2) cheaper and more
85 rapid dissolution chemistry and 3) much higher sample throughput. Although ABF has
86 successfully been used in decomposing geological materials for elemental analysis by
87 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)^{22,23,25}, its applicability has never
88 been demonstrated in isotopic analysis. Using five well-characterized United States
89 Geological Survey (USGS) geological reference materials (GRMs) from mafic to felsic
90 compositions, this study provides evidence that successful, low-blank level Hf and Nd-Sr
91 isotopic analyses of small amounts (50 to 5 mg) of geological samples with a variable range
92 of zircon contents are feasible after elemental separations by the column chemistry setup
93 presented in this study.

94 **2. Methods**

95 **2.1. Reagents, lab wares and materials**

96 All chemical separations in this study were performed in clean room environment (PicoTrace,
97 class 100) at the Department of Lithospheric Research, University of Vienna, Austria. Milli-Q
98 water (18.2 MΩ cm at 25 °C) produced by a Millipore water purification system was used for
99 all sample chemical preparations. Concentrated hydrochloric acid (HCl) was twice purified
100 using a Savillex[™] DST-1000 Teflon sub-boiling distillation system, while concentrated,
101 suprapure nitric acid (HNO₃) was purchased from Sigma-Aldrich. Trace metal grade
102 ammonium bifluoride (NH₄HF₂; also called ammonium hydrogen fluoride) salt was acquired
103 from Carl Roth GmbH + Co. KG (Roti[®] Metic, 99.999%, R5363.1) and Sigma-Aldrich
104 (99.999%, 455830-25G). To ensure exact acid molarities for column chemistry titration was
105 done using a Titrette instrument, with 0.1 M NaOH and methyl orange. All labware, including
106

107 Savillex PFA beakers, used for digestion and elemental separations were pre-cleaned in 6 M
108 HCl for at least one week and an additional week in 30% HNO₃ (dilution of conc. HNO₃ by
109 volume), both at 120 °C on hotplate. Detailed information on columns used in ion exchange
110 chemistry is provided in the supporting information file and shown in Figure S1.
111 International isotope standards NBS 987, La Jolla and JMC-475 were used to monitor mass
112 spectrometer conditions and for normalization purposes during Sr, Nd and Hf isotope
113 measurements (see section 2.4 below). During Hf isotope analysis a plasma standard solution
114 purchased from Alfa Aesar (Johnson Matthey Company, stock nr. 13843, 1003±5 µg ml⁻¹,
115 Specpure) was also measured alongside JMC-475, appropriately diluted to 100 ppb
116 concentration. International rock reference materials used in this study cover a wide range of
117 compositions from mafic to felsic. These GRMs included AGV-2 (andesite), BCR-2 (basalt),
118 GSP-2 (granodiorite), RGM-2 (rhyolite) and STM-2 (syenite), all obtained from the USGS.

119

120 **2.2. Sample digestion**

121 Powders of 50 and 5 mg of the GRMs were weighed into pre-cleaned, 7 ml Savillex PFA
122 beakers. For AGV-2 and GSP-2, 10 and 2 mg samples were also tested. The amount of ABF
123 added to the samples was set to attain a ~5-6:1 ABF:sample mass ratio^{22,23}. Capped vials were
124 then heated to 220 °C or 230 °C for 24 hours^{22,23} in convection oven (Mettler GmbH). This
125 longer digestion period was applied to ensure full sample decomposition, but heating for a
126 much shorter (3-6 hours) time is potentially sufficient^{22,23}. Oven and beaker temperatures
127 were checked using an infrared thermometer (Eventek ET300) after 3 hours of heating and at
128 the end of the cycle, and temperatures were found to match the nominal temperatures within ±
129 2-5 °C. After cooling, 2 ml concentrated (65%) HNO₃ was added to the saltcakes (Figure 1),
130 and left on a hotplate for 1 hour at 160 °C in closed beakers^{22,23}. These sample solutions were
131 subsequently evaporated to dryness. Finally, evaporated samples were taken up in 1:1 ml
132 concentrated HNO₃/MQ water and heated to 120 °C on a hotplate for 6 hours. The final clear
133 solutions obtained (Figure 1) were dried down again, treated with 6 M HCl for 1 hour on a
134 hotplate at 120 °C and evaporated to dryness before column chemistry.

135

136 **2.3. Column chemistry**

137 Details of column calibrations and ion exchange chemistry procedures for elemental
138 separations/purifications can be found in the supporting information file.

139

140 **2.4. Mass spectrometry**

141 **2.4.1. TIMS measurements**

142 Strontium and neodymium isotope analyses were performed at the Department of
143 Lithospheric Research, University of Vienna using a Thermo-Finnigan Triton TI multi-
144 collector instrument in static mode. Pure element fractions were analyzed using a Re double
145 filament assembly. Measurements were done at ~6 V (⁸⁸Sr) and 1-2 V (¹⁴⁴Nd), with 4 sec on-
146 peak integration and 3 sec idle time. One analysis block comprised ten cycles and the isotopic
147 ratios were obtained from 80 blocks, to get the best precision. Nevertheless, the measurement
148 of 20 blocks is in general sufficient saving time and cost of analyses. Mass fractionation
149 during measurement was corrected for ⁸⁶Sr/⁸⁸Sr = 0.1194, and ¹⁴⁶Nd/¹⁴⁴Nd = 0.721903,
150 respectively. A mean ⁸⁷Sr/⁸⁶Sr ratio of 0.710258±0.000013 (2SD, n=41) was determined for
151 the isotopic standard NBS987 (or SRM987) (ref. value: ⁸⁷Sr/⁸⁶Sr=0.710248)²⁶ and a mean
152 ¹⁴³Nd/¹⁴⁴Nd ratio of 0.511844±0.000009 (2SD, n=25) for the La Jolla (ref. value: ¹⁴³Nd/¹⁴⁴Nd
153 = 0.511858)²⁷ isotopic standard during the analysis periods. These mean ratios were used to
154 normalize Sr and Nd isotopic ratios to the reference values of NBS987 and La Jolla.
155 Uncertainties of isotopic ratios represent 2 standard errors of the mean (2SE).

156

157 **2.4.2. MC-ICP-MS analysis**

158 A subset of Hf isotope analyses were performed at the NAWI Central Laboratory for Water,
159 Minerals and Rocks, a joint lab facility of the NAWI Graz Geocenter located at the Institute
160 of Applied Geosciences of Graz University of Technology (Graz, Austria). However, the
161 majority of the Hf isotope measurements were performed at the Isotope Climatology and
162 Environmental Research Centre, Institute for Nuclear Research (Debrecen, Hungary). Dried
163 samples from column #2 (Figure S1) were dissolved in 0.1 ml 0.1 M HNO₃ overnight and
164 diluted to a sample volume of 2 to 3 ml prior to analysis for appropriate concentrations and
165 ~15 min analysis time. At both laboratories, Hf isotope analyses were performed in dry-
166 plasma mode. A Nu Plasma II MC-ICP-MS equipped with a Nu Instruments DSN100
167 desolvating system and a MicroMist U-series glass nebulizer was used in Graz, while the
168 analyses were done on a Thermo Neptune Plus MC-ICP-MS equipped with an Aridus 3
169 desolvation nebulizer in Debrecen (nominal flow rates of 100 µl/min in both cases). A
170 Faraday gain calibration was made prior to the tuning of both instruments and thus prior to
171 GRM measurements. In Graz, all masses were measured using 10¹¹ Ω amplifiers, while in
172 Debrecen 10¹³ Ω amplifiers were used for ¹⁷⁵Lu, ¹⁷⁴Hf and ¹⁷²Yb. Details of the gain
173 calibration protocol for the 10¹³ Ω current amplifiers are given in the supporting information
174 file.

175 A wash out cycle of 3 to 10 min in duration of 1% HNO₃ occurred between individual
176 measurements. The overall sensitivity for Hf was measured to be between 200 and 370 V/ppm
177 Hf with the Nu Plasma II and 474 to 913 V/ppm Hf for the Thermo Neptune Plus system. Hf
178 isotopes (¹⁷⁴Hf, ¹⁷⁶Hf, ¹⁷⁷Hf, ¹⁷⁸Hf, ¹⁷⁹Hf, and ¹⁸⁰Hf) and one of each interfering element
179 (¹⁸²W, ¹⁷²Yb, ¹⁷⁵Lu) were measured simultaneously using the Faraday cup configuration
180 shown in Table 1. Analyses comprised 20 blocks each with 5 cycles with an integration time
181 of 8 sec. Baselines were measured at mid-masses at the beginning of each block for 30 sec.
182 All GRMs were analyzed during one single analytical session in order to avoid inter-session
183 analytical variability.

184 An exponential mass bias correction for Hf (βHf) is applied using ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325²⁸⁻³¹.
185 ¹⁷⁶Lu and ¹⁷⁶Yb interference corrections on ¹⁷⁶Hf were made using recommended values of
186 ¹⁷⁶Lu/¹⁷⁵Lu = 0.026549 and ¹⁷⁶Yb/¹⁷²Yb = 0.58862³⁰, with mass bias factors βYb = βLu = βHf.
187 Final, interference-corrected Hf isotope ratios and reported errors represent the mean and 2
188 standard error of the mean (2SE) values.

189 Mean ¹⁷⁶Hf/¹⁷⁷Hf isotopic composition of the JMC-475 standard measured during analytical
190 sessions in Graz were 0.282177±0.000047 (2SD, n=6, 100 ppb solution) and
191 0.282170±0.000136 (2SD, n=13, 10 ppb) versus the preferred value of 0.282163±0.000009³¹.
192 Repeat analyses on JMC-475 in Debrecen yield a mean value of 0.282140±0.000035 (2SD,
193 n=32, 10 ppb). During the Hf isotopic measurements five GRMs were analyzed in between at
194 least two isotopic measurements of JMC-475. The measured ¹⁷⁶Hf/¹⁷⁷Hf isotopic ratios of
195 GRMs were then normalized to JMC-475 using the mean of bracketing analyses of JMC-475
196 and its “true” ¹⁷⁶Hf/¹⁷⁷Hf isotopic ratio of 0.282163 (Blichert-Toft et al., 1997).

197 The Hf plasma standard solution of Alfa Aesar (JMC 13843) was analyzed twice in Graz and
198 gave ¹⁷⁶Hf/¹⁷⁷Hf isotopic ratios of 0.282223±0.000010 and 0.282219±0.000034, being in
199 excellent agreement with 0.282228±0.000005 of JMC 14375 (same standard solution with
200 different Hf concentration) reported by Choi et al.³².

201

202 **2.4.3. Reference values of GRMs used to test accuracy**

203 Accuracy of the isotopic compositions obtained with the closed vessel ABF digestion of
204 GRMs and the column chemistry setup detailed above was tested using Sr, Nd and Hf isotope
205 ratios of the same USGS GRMs published by Weis et al.^{33,34}, except for BCR-2, which is
206 from Jweda et al.³⁵. These studies were chosen because of the especially careful analytical

207 protocols used (e.g. high pressure bomb dissolution before Hf isotopic analyses)³⁶ and the
208 systematic multi-isotopic characterizations of numerous USGS GRMs.
209 Beyond these publications, isotopic ratios of GRMs published in the literature were taken
210 from the GEOREM database³⁶, as of September 2020, and shown in figures after filtering.
211 First, values without quoted uncertainties were omitted. Second, isotopic ratios being outside
212 the 3σ range of the calculated mean of the remaining data were detected as outliers (normality
213 was tested using QQ plots). Third, new mean \pm 2 SD values were calculated from the filtered
214 datasets (shown in Figures 2-3), named filtered GEOREM mean (fGm \pm 2SD).
215

216 3. Results and discussion

217 3.1. Procedural blanks

218 Total procedural blanks (i.e. including chemistry) of Sr and Nd were measured using spiked
219 blanks and found to be 0.5 ng for Sr and 0.2 ng for Nd using ABF purchased from Sigma-
220 Aldrich. Strontium blank/sample ratios were found to be in the range of 0.094-0.013 % for the
221 5 mg sub-samples of GRMs (Table S5), while for the 50 mg batches these ratios were ten
222 times lower (0.009-0.001 %). Nd blank/sample ratios ranged between 0.211-0.020 % (5 mg)
223 and 0.021-0.002 % (50 mg).

224 Total procedural blanks were estimated to be <25 pg for Hf as determined for ABFs from Carl
225 Roth and Sigma-Aldrich (more details in the supporting information file). Hf blank/sample
226 ratios are calculated to be between 0.293 and 0.002 %, with median and mean values of 0.019
227 and 0.052 % for the reference materials investigated. Obviously, the smallest batch (2 mg)
228 was affected by the highest blank contribution (0.293 %). In general, blank effects on Hf-Nd-
229 Sr isotope ratios of typical 5-50 mg samples are negligible.
230

231 3.2. Isotopic compositions of GRMs

232 The five USGS GRMs have published reference values and thus could be used to test the
233 accuracy of measured isotope ratios of ABF digested GRM samples. All five $^{87}\text{Sr}/^{86}\text{Sr}$
234 isotopic ratios of AGV-2 were found to be in good agreement ($\Delta^{87}\text{Sr}/^{86}\text{Sr}_{\text{sa-ref}}$: -20 to 5 ppm,
235 see Table 2, Figure 2A) with the preferred value of 0.703981 ± 0.000009 ³³ and the filtered
236 GEOREM mean value (fGm \pm 2SD: 0.703985 ± 0.000020). The sample mean and 2SD (sm \pm
237 2SD: 0.703975 ± 0.000020), calculated from our five measurements, overlap with both the
238 Weis et al.³³ and fGm \pm 2SD values. The 2SD value of 0.000020 indicate a relatively high
239 reproducibility. The mean Sr isotope ratio of BCR-2 (sm \pm 2SD: 0.705009 ± 0.000020) agrees
240 within uncertainty with both the reference value of 0.705000 ± 0.000011 of Jweda et al.³⁵
241 ($\Delta^{87}\text{Sr}/^{86}\text{Sr}_{\text{sa-ref}}$: -2 to 22 ppm, Table 2, Figure 2B) and the preferred value of
242 0.705013 ± 0.000010 of Weis et al.³³. It exactly matches the filtered GEOREM mean (fGm \pm
243 2SD) of 0.705009 ± 0.000042 . For GSP-2, the measured ratios and especially the sample mean
244 (sm \pm 2SD: 0.765154 ± 0.000105 , Table 2) correspond with the preferred value of
245 0.765144 ± 0.000075 ³³. These values are in the upper 2SD range of the filtered GEOREM
246 mean (fGm \pm 2SD: 0.765097 ± 0.000165 , Figure 3A). In general, our data display a relatively
247 larger scatter, clearly indicated by the high 2SD value of 0.000105. The poor reproducibility
248 of GSP-2 is not unique to this study, it can be observed in both the Weis et al.³³ and
249 GEOREM datasets and demonstrate that GSP-2 should be avoided as a GRM for Sr isotopic
250 studies. Measurements of RGM-2 gave by -49 to -33 ppm ($\Delta^{87}\text{Sr}/^{86}\text{Sr}_{\text{sa-ref}}$, Table 2, Figure 3B)
251 less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the reference value of Weis et al.³³ given for RGM-1
252 (obtained from the same rock body as RGM-2). Also, our sm \pm 2SD value of
253 0.704169 ± 0.000022 is lower than the fGm \pm 2SD value of 0.704224 ± 0.000024 . The reason
254 for this discrepancy is as yet unclear. Measured Sr isotope ratios of STM-2 and the calculated
255 sm \pm 2SD value of 0.703704 ± 0.000010 were found to be in excellent agreement with the
256 preferred mean value of 0.703701 ± 0.000006 of Weis et al.³³ (Figure 3C).

257 Five determinations of the Nd isotopic compositions of AGV-2 form a very tight group
258 around the $sm \pm 2SD$ value of 0.512789 ± 0.000004 (Table 2, Figure 2C), independent of
259 sample volume and digestion temperature. Our $sm \pm 2SD$ value matches extremely well the
260 preferred value of 0.512791 ± 0.000013 ³³ measured by TIMS and the $fGm \pm 2SD$ value of
261 0.512784 ± 0.000023 . The very low 2SD value of the sample mean (0.000004) imply that these
262 measurements are highly reproducible. The same is observed for BCR-2, for which the
263 measured $^{143}Nd/^{144}Nd$ ratios were within 10 ppm ($\Delta^{143}Nd/^{144}Nd_{sa-ref}$, Table 2) to the reference
264 value of 0.512637 ± 0.000013 of Jweda et al.³⁵ (Figure 2D), and displayed small scatter around
265 $sm \pm 2SD$ (0.512632 ± 0.000011). This sample mean and the filtered GEOREM average (fGm
266 $\pm 2SD$: 0.512632 ± 0.000024) were found to be identical. Measurements of GSP-2 also proved
267 to be excellent both in terms of accuracy ($\Delta^{143}Nd/^{144}Nd_{sa-ref}$: -13 to 2 ppm, Table 2) and
268 reproducibility ($sm \pm 2SD$: 0.511371 ± 0.000014), when compared to the mean value of
269 0.511374 ± 0.000003 of Weis et al.³³ or $fGm \pm 2SD$ (0.511367 ± 0.000023 , Figure 3D). The
270 $^{143}Nd/^{144}Nd$ ratios of sub-samples (50 and 5 mg) of RGM-2 agree within uncertainty with the
271 preferred value of 0.512802 ± 0.000015 ³³ and yield an $sm \pm 2SD$ value of 0.512792 ± 0.000006
272 overlapping $fGm \pm 2SD$ (0.512794 ± 0.000018 , Figure 3E). Two aliquots of STM-2 gave
273 isotopic ratios ($\Delta^{143}Nd/^{144}Nd_{sa-ref}$: 1 ppm, Table 2) and an average ($sm \pm 2SD$:
274 0.512914 ± 0.000004 , Figure 3F), which are indistinguishable from the preferred value of
275 0.512913 ± 0.000009 ³³. While the measured Nd isotopic ratios of both RGM-2 and STM2 were
276 found to be excellent in terms of accuracy, the high reproducibilities are based on only two
277 separate digestions/aliquots and thus potential underestimations.
278 The Hf isotopic compositions of all sub-samples of AGV-2 obtained at both decomposition
279 temperatures, together with the $sm \pm 2SD$ value (0.282985 ± 0.000013), overlap with the
280 preferred value of 0.282984 ± 0.000009 of Weis et al.³⁴ (Figure 2E), with $\Delta^{176}Hf/^{177}Hf_{sa-ref}$ well
281 within 10 ppm (Table 2). These Hf isotope ratios were found to be at the higher end of values
282 in the GEOREM database ($fGm \pm 2SD$: 0.282975 ± 0.000019 , Figure 2E), with a generally
283 good reproducibility. Measured $^{176}Hf/^{177}Hf$ ratios of BCR-2 decomposed at 220 and 230 °C
284 match well the suggested value of 0.282869 ± 0.000011 of Jweda et al.³⁵ (Figure 2F), with the
285 higher digestion temperature digestions being closer to the preferred value ($\Delta^{176}Hf/^{177}Hf_{sa-ref}$:
286 8 and 5 ppm, Table 2) and the filtered GEOREM mean (0.282869 ± 0.000023). For GSP-2, all
287 but one measured ratios were found to be in excellent agreement ($\Delta^{176}Hf/^{177}Hf_{sa-ref}$: -5 to 8
288 ppm, one value is 19 ppm, Table 2) with the preferred value of 0.281949 ± 0.000008 ³⁴. Our sm
289 $\pm 2SD$ value (0.281952 ± 0.000016) closely corresponds with that of Weis et al.³⁴ and is within
290 uncertainty in agreement with $fGm \pm 2SD$ (0.281940 ± 0.000033 , Figure 3G). Reproducibility
291 of our analyses on GSP-2 is fair, but slightly worse than that of Weis et al.³⁴ (Table 2). Except
292 for one offset value of STM-2 (5 mg, 230 °C, $\Delta^{176}Hf/^{177}Hf_{sa-ref}$: 20 ppm, Table 2), the Hf
293 isotope ratios of both the RGM-2 and STM-2 GRMs correspond within error with the
294 preferred values of 0.283017 ± 0.000013 and 0.283021 ± 0.000005 of Weis et al.³⁴ (Figure
295 3H,I). Our $sm \pm 2SD$ values of 0.283024 ± 0.000011 of RGM-2 and 0.283022 ± 0.000023 of
296 STM-2 agree well with those of Weis et al.³⁴, albeit with lower reproducibilities.

297

298 **3.3. Protocol advantages/disadvantages and potential applications**

299 The reference method for decomposing geological samples with high concentration of
300 refractory heavy minerals (zircon, garnet, etc.), such as granites/granodiorites, for trace/rare
301 earth element and especially Hf isotopic analyses is the steel-jacketed, high-pressure bomb
302 dissolution. However, this method has some disadvantages including digestion time, which
303 may take ~ 1-2 weeks^{11,13} and the extra efforts put in loading/unloading the bombs, low
304 sample throughput and high costs of steel-jacketed ParrTM bombs. For studies involving
305 numerous samples of magmatic/metamorphic or sedimentary rocks, the bomb dissolution
306 method is time-consuming and expensive. In such cases the ABF decomposition can be a

307 viable alternative as 1) it is a low-cost method, 2) the digestion time is reduced to 3 to 4 days,
308 and 3) the number of samples to be digested at the same time depends on oven capacity, but
309 may well exceed 50. While the use of ABF eliminates the need to handle toxic, concentrated
310 HF, ABF itself is hazardous and has to be treated with caution. Since HF vapor and ammonia
311 are released upon decomposition of ABF, the convection oven must be vented to an exhaust
312 system or be placed directly under a fume hood.

313 As demonstrated in section 3.2, the majority of measured Hf-Nd-Sr isotope ratios of USGS
314 GRMs match well the preferred values. One exception is the Sr isotopic ratios of RGM-2 with
315 less radiogenic ratios (Figure 3B). Decomposition temperatures (220 and 230 °C) do not
316 significantly affect the final ratios. The presented data therefore demonstrate that accurate
317 isotopic ratios can be obtained using the ABF digestion method, which thus is a viable
318 alternative to high-pressure (Parr) bomb dissolution. In terms of reproducibility, the ABF
319 technique is comparable to the Parr-bomb dissolution method^{33,34}, but does not offer an
320 improvement in external precision. This, however, was not the goal of the present study and
321 further measurements are clearly required to better assess reproducibility. Based on the tests
322 with 50, 10, 5, 2 and 1 mg samples performed, we suggest that the ABF method, together with
323 the described column chemistry procedure, can reliably be used for the isotopic analyses even
324 of very small (2-10 mg) samples.

325
326

327 **4. Conclusions**

328 Isotopic analyses of five USGS GRMs, dissolved in oven using ABF at oven temperatures of
329 220 and 230 °C, were done in this study to test the method's feasibility in combined Hf-Nd-Sr
330 isotopic analyses of rock samples. The described ion exchange chemistry procedures resulted
331 in low total chemistry blanks for Sr, Nd and Hf, and the mass spectrometry measurements
332 provided accurate and reproducible Hf-Nd-Sr isotopic ratios as demonstrated by the USGS
333 GRMs investigated, covering a mafic to felsic compositional range. The preferred closed
334 vessel ABF digestion method deploys a temperature in the range of 220–230 °C, slightly
335 below the boiling point (238 °C) of ABF. Method advantages over Parr-bomb dissolution
336 include low costs and high sample throughput, without compromising accuracy and external
337 precision.

338

339 **Data Availability statement**

340 The data that supports the findings of this study are published in the main text and the
341 supplementary material of this article and openly available in the PANGAEA Data Repository
342 at <https://doi.pangaea.de/10.1594/PANGAEA.924619>.

343

344 **Conflict of interest**

345 There are no conflicts to declare.

346

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TABLES

Table 1. Faraday cup and amplifier configurations for Hf isotopic measurements by Nu Plasma II and Neptune Plus MC-ICP-MS instruments

Nu Plasma II

Cup	H5	H3	H2	H1	Axial	L1	L2	L3	L5
Isotope	¹⁸² W	¹⁸⁰ Hf	¹⁷⁹ Hf	¹⁷⁸ Hf	¹⁷⁷ Hf	¹⁷⁶ (Hf+Lu+Yb)	¹⁷⁵ Lu	¹⁷⁴ Hf	¹⁷² Yb

463 All masses measured with 10¹¹ Ohm amplifiers

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465 Neptune Plus

Cup	H3	H2	H1	Center	L1	L2	L3	L5
Isotope	¹⁸⁰ Hf	¹⁷⁹ Hf	¹⁷⁸ Hf	¹⁷⁷ Hf	¹⁷⁶ (Hf+Lu+Yb)	¹⁷⁵ Lu	¹⁷⁴ Hf	¹⁷² Yb

466 Masses 175, 174 and 172 measured with 10¹³ Ohm amplifiers, the rest using 10¹¹ Ohm amplifiers

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Table 2. Sr-Nd-Hf isotopic compositions of USGS GRMs

GRM name	Type	Amount dissolved (mg)	Digestion temperature (°C)	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE/2SD ^a	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE/2SD	$^{176}\text{Hf}/^{177}\text{Hf}$	2SE/2SD	Mass spectrometer ^b	$\Delta^{87}\text{Sr}/^{86}\text{Sr}_{\text{sa-ref}}$ (ppm) ^c	$\Delta^{143}\text{Nd}/^{144}\text{Nd}_{\text{sa-ref}}$ (ppm) ^d	$\Delta^{176}\text{Hf}/^{177}\text{Hf}_{\text{sa-ref}}$ (ppm) ^e
AGV-2	andesite	50	230	0.703968	0.000004	0.512791	0.000003	0.282994	0.000006	Thermo Neptune Plus	-13	0	10
AGV-2 rpt 1 ^f	andesite	50	230					0.282986	0.000006	Thermo Neptune Plus			2
AGV-2 rpt 2 ^g	andesite	50	230					0.282975	0.000004	Thermo Neptune Plus			-9
AGV-2	andesite	5	230	0.703961	0.000006	0.512786	0.000004	0.282982	0.000012	Thermo Neptune Plus	-20	-5	-2
AGV-2	andesite	10	220	0.703979	0.000004	0.512788	0.000004	0.282993	0.000010	Thermo Neptune Plus	-2	-3	9
AGV-2 rpt 1	andesite	10	220					0.282985	0.000008	Thermo Neptune Plus			1
AGV-2	andesite	5	220	0.703979	0.000004	0.512791	0.000004	0.282981	0.000008	Thermo Neptune Plus	-2	0	-3
AGV-2	andesite	2	220					0.282986	0.000141	Thermo Neptune Plus			2
AGV-2	andesite	1	220	0.703986	0.000004	0.512788	0.000010			-	5	-3	
Mean^h				0.703975	0.000020	0.512789	0.000004	0.282985	0.000013				
BCR-2	basalt	50	230	0.705004	0.000004	0.512632	0.000003	0.282874	0.000007	Thermo Neptune Plus	4	-5	5
BCR-2	basalt	5	230	0.704998	0.000004	0.512638	0.000004	0.282877	0.000009	Thermo Neptune Plus	-2	1	8
BCR-2	basalt	50	220	0.705022	0.000004			0.282883	0.000011	Nu Plasma II	22		14
BCR-2 rpt 2	basalt	50	220	0.705011	0.000005	0.512627	0.000003	0.282893	0.000006	Nu Plasma II	11	-10	24
Mean				0.705009	0.000020	0.512632	0.000011	0.282882	0.000016				
GSP-2	granodiorite	50	230	0.765144	0.000004	0.511376	0.000003	0.281947	0.000012	Thermo Neptune Plus	0	2	-2
GSP-2 rpt 2	granodiorite	50	230					0.281950	0.000003	Thermo Neptune Plus			1
GSP-2	granodiorite	50	220	0.765180	0.000004	0.511361	0.000003	0.281944	0.000005	Nu Plasma II	36	-13	-5
GSP-2	granodiorite	5	230	0.765205	0.000011	0.511373	0.000004	0.281968	0.000009	Thermo Neptune Plus	61	-1	19
GSP-2 rpt 1	granodiorite	5	230					0.281948	0.000005	Thermo Neptune Plus			-1
GSP-2	granodiorite	10	220	0.765085	0.000004	0.511374	0.000003	0.281957	0.000004	Thermo Neptune Plus	-59	0	8

GSP-2 rpt 1	granodiorite	10	220					0.281953	0.000003	Thermo Neptune Plus				4
Mean				0.765154	0.000105	0.511371	0.000014	0.281952	0.000016					
RGM-2	rhyolite	50	230	0.704161	0.000004	0.512794	0.000003	0.283028	0.000006	Thermo Neptune Plus	-49	-8		11
RGM-2	rhyolite	5	230	0.704177	0.000005	0.512790	0.000004	0.283020	0.000012	Thermo Neptune Plus	-33	-12		3
Mean				0.704169	0.000022	0.512792	0.000006	0.283024	0.000011					
STM-2	syenite	50	230	0.703701	0.000004	0.512914	0.000004	0.283012	0.000007	Thermo Neptune Plus	0	1		-9
STM-2 rpt 1	syenite	50	230					0.283024	0.000006	Thermo Neptune Plus				3
STM-2 rpt 2	syenite	50	230					0.283020	0.000002	Thermo Neptune Plus				-1
STM-2	syenite	5	230	0.703708	0.000009	0.512914	0.000004	0.283041	0.000006	Thermo Neptune Plus	7	1		20
STM-2 rpt 1	syenite	5	230					0.283016	0.000006	Thermo Neptune Plus				-5
Mean				0.703704	0.000010	0.512914	0.000004*	0.283022	0.000023					
<i>Reference values^d</i>														
AGV-2	andesite			0.703981	0.000009	0.512791	0.000013	0.282984	0.000009					
BCR-2	basalt			0.705000	0.000011	0.512637	0.000013	0.282869	0.000011					
GSP-2	granodiorite			0.765144	0.000075	0.511374	0.000003	0.281949	0.000008					
RGM-1	rhyolite			0.704210	0.000014	0.512802	0.000015	0.283017	0.000013					
STM-2	syenite			0.703701	0.000006	0.512913	0.000009	0.283021	0.000005					
<i>Filtered GEOREM mean values^d</i>														
AGV-2	andesite			0.703985	0.000020	0.512784	0.000023	0.282975	0.000019					
BCR-2	basalt			0.705009	0.000042	0.512632	0.000024	0.282869	0.000023					
GSP-2	granodiorite			0.765097	0.000145	0.511367	0.000023	0.281940	0.000033					
RGM-2	rhyolite			0.704224	0.000024	0.512794	0.000018	0.283019	0.000003					
STM-2	syenite			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.					

^aUncertainties of measured isotopic ratios are 2 standard errors of the mean, while uncertainties of mean values are 2 standard deviations on the average of replicate analyses

^bMass spectrometer used for Hf isotopic measurements (Sr-Nd isotopic compositions were measured using a Thermo Triton Plus TIMS)

$$^c \Delta^{87\text{Sr}/^{86}\text{Sr}}_{\text{sa-ref}} (\text{ppm}) = [(^{87\text{Sr}}/^{86}\text{Sr})_{\text{sample}} - ^{87\text{Sr}}/^{86}\text{Sr}_{\text{reference}}] - 1] \times 1000000$$

$$^d \Delta^{143\text{Nd}/^{144}\text{Nd}}_{\text{sa-ref}} (\text{ppm}) = [(^{143\text{Nd}}/^{144}\text{Nd})_{\text{sample}} / ^{143\text{Nd}}/^{144}\text{Nd}_{\text{reference}} - 1] \times 1000000$$

$$^e \Delta^{176\text{Hf}/^{177}\text{Hf}}_{\text{sa-ref}} (\text{ppm}) = [(^{176\text{Hf}}/^{177}\text{Hf})_{\text{sample}} / ^{176\text{Hf}}/^{177}\text{Hf}_{\text{reference}} - 1] \times 1000000$$

^f"Rpt 1" means a replicate isotopic analysis on the same solution during the same analytical session

^g"Rpt 2" means a replicate isotopic measurement on the same solution during a separate (later) analytical session

Isotopic ratios measured on different aliquots (1, 2, 5, 10, 50 mg) are from separate digestions (solutions), likewise those with the same aliquot size, but dissolved at different temperatures (220 or 230 °C)

^hMean values are calculated from all the available isotopic ratios for the respective GRM, independent of digestion temperature (220 or 230 °C) and aliquot size, and called sample mean (sm ± 2SD)

ⁱReference values of GRMs are from Weis et al.^{33,34} except for BCR-2, which is from Jweda et al.³⁵, uncertainties are 2SD

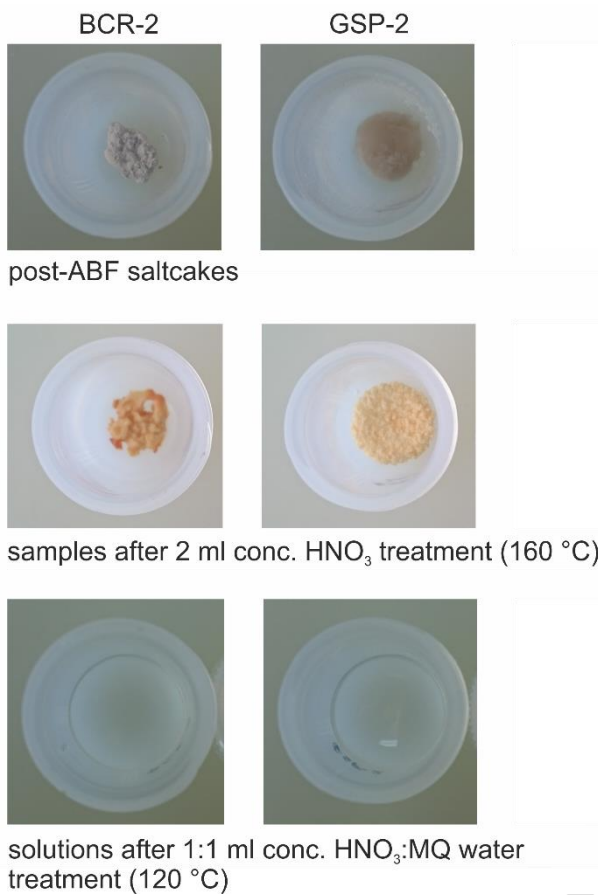
Reference isotopic ratios are normalized to NBS-987 (SRM-987), La Jolla and JMC-475 isotope standards, likewise the isotopic ratios measured in this study

^jAverage values of GRMS are based on the GEOREM database and were calculated after filtering the available data as detailed in section 2.4.3. Uncertainties are 2SD

Note that a mean value was not calculated for STM-2 due to limited data.

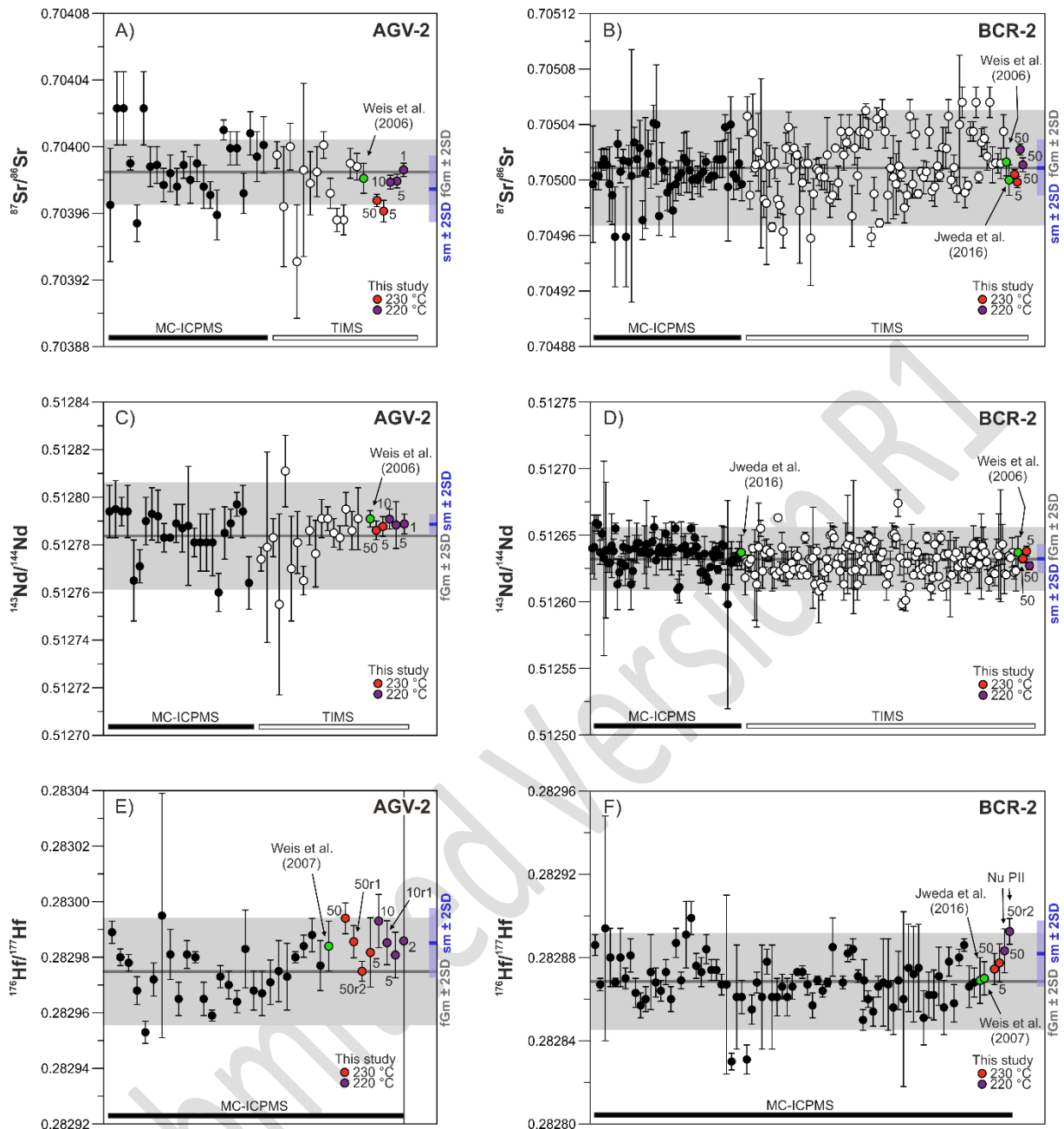
*Since the 2SD value is close to zero after rounding (6 digits), the error on the individual measurements are given here instead of calculated 2SD

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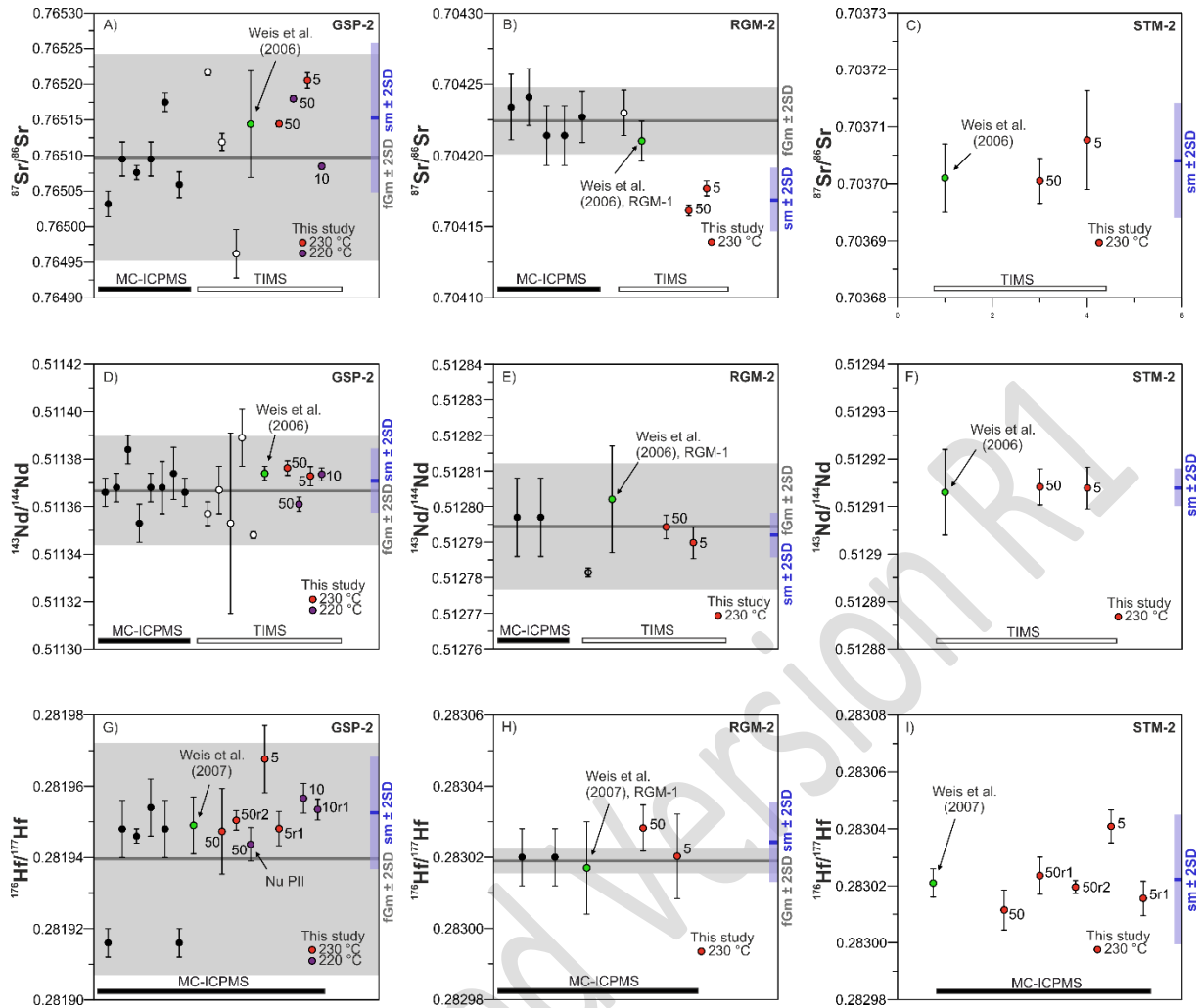
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FIGURE 1. Images of three stages of the ABF digestion procedure illustrated using rock reference materials BCR-2 (basalt) and GSP-2 (granodiorite).



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FIGURE 2. Strontium, neodymium and hafnium isotope ratios of two USGS GRMs (AGV-2 and BCR-2) as published in the literature and measured in this study. Literature values are from the GEOREM database³⁶ (accessed: 7 September 2020), with uncertainties as quoted in the database. Reference values are from Weis et al.^{33,34} and Jweda et al.³⁵ (green dots), while the filtered GEOREM mean (fGm ± 2SD) values are calculated as described in section 2.4.3. The so-called sample mean (sm ± 2SD) values were calculated from the isotope ratios measured in this study, and given in Table 2. Values of 220 and 230 °C denote digestion temperatures using ABF in convection oven, while those of 50, 10, 5, 2 and 1 next to the isotope ratios are the dissolved amounts of GRMs in mg. Repeat measurements denoted by ‘r1’ and ‘r2’ are specified in Table 2. Most Hf isotope ratios were measured by a Thermo Neptune Plus and some by a Nu Plasma II MC-ICP-MS. Those measured by the latter are indicated (Nu PII).



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491 **FIGURE 3.** Strontium, neodymium and hafnium isotope ratios of three USGS GRMs (GSP-
492 2, RGM-2, and STM-2) as published in the literature and measured in this study. Literature
493 values are from the GEOREM database³⁶ (accessed: 7 September 2020), with uncertainties as
494 quoted in the database. Reference values are from Weis et al.^{33,34}. The filtered GEOREM
495 mean (fGm ± 2SD) values are calculated as described in section 2.4.3. Note that fGm ± 2SD
496 could not be calculated for STM-2, for which only one published measurement was available.
497 For RGM-2, the isotopic ratios of RGM-1 (obtained from the same rock body as RGM-2)
498 published by Weis et al.^{33,34} are also shown. 220 and 230 °C denote digestion temperatures
499 using ABF convection oven and values (50, 10 and 5) next to the isotope ratios are the
500 dissolved amounts of GRMs in mg. Repeat measurements denoted by 'r1' and 'r2' are
501 specified Table 2. Most Hf isotope ratios were measured by a Thermo Neptune Plus and some
502 by a Nu Plasma II MC-ICP-MS. Those measured by the latter are indicated (Nu PII).
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Rapid Communications in Mass Spectrometry

Supporting Information for

**Rapid decomposition of geological samples by ammonium bifluoride (NH₄HF₂)
for combined Hf-Nd-Sr isotopic analysis**

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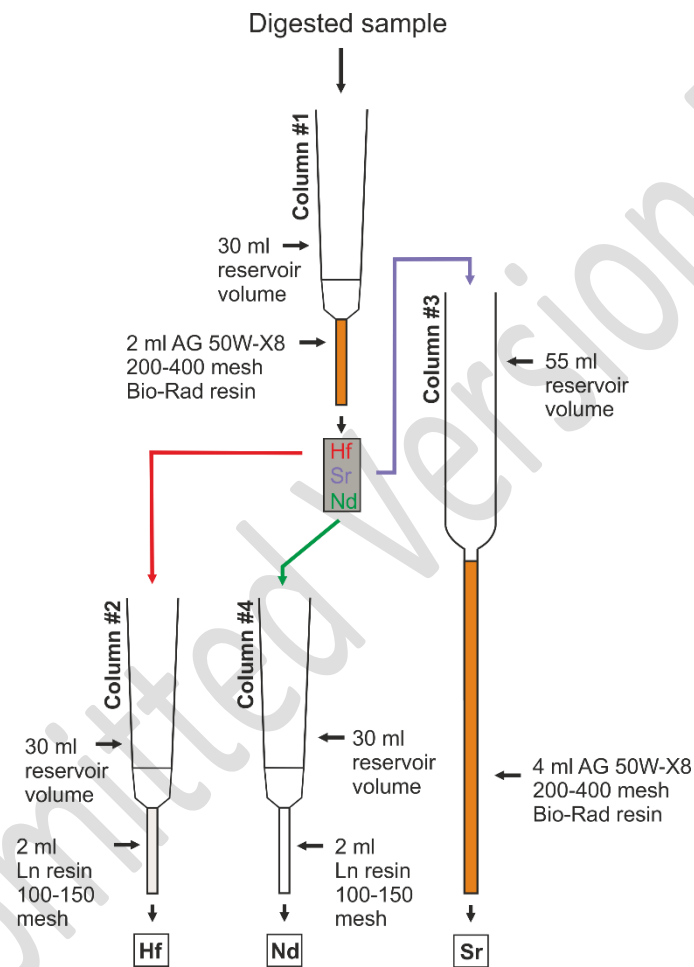
*Corresponding author: ujvari.gabor@csfk.org (email G. Újvári)

Content

- 1. Columns used for ion exchange chemistry**
- 2. Column calibrations and ion exchange chemistry**
- 3. Gain calibration of 10¹³ Ω current amplifiers**
- 4. Hf blank calculations**
- 5. Blank contributions to GRMs**

533 **1. Columns used for ion exchange chemistry**

534 Ion exchange chemistry utilized micro-columns from Triskem with reservoir (funnel) and resin
535 volumes of 30 ml and 2 ml except for Sr purification. The primary cation exchange column for
536 sequential Hf-Sr-Nd separations (column #1, Figure S1) was packed with AG W50-X8 (Bio-Rad, 200-
537 400 mesh) resin. For further purification of Hf and Nd, micro-columns (columns #2, #4) with the same
538 dimensions as column #1 were used, however for Sr cleaning larger columns (column #3) with
539 reservoir and resin volumes of 55 ml and 4 ml were utilized. Columns #2 and #3 were filled with
540 Eichrom Ln (100-150 µm mesh) and AG W50-X8 (Bio-Rad, 200-400 mesh) resins, and column #4 was
541 packed with Ln resin (100-150 µm mesh). Polyethylene frit material was set on top of the resin for
542 bed support.
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545 **FIGURE S1.** Summary of the chemical separation schemes of Hf, Sr and Nd.
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549 **2. Column calibrations and ion exchange chemistry**

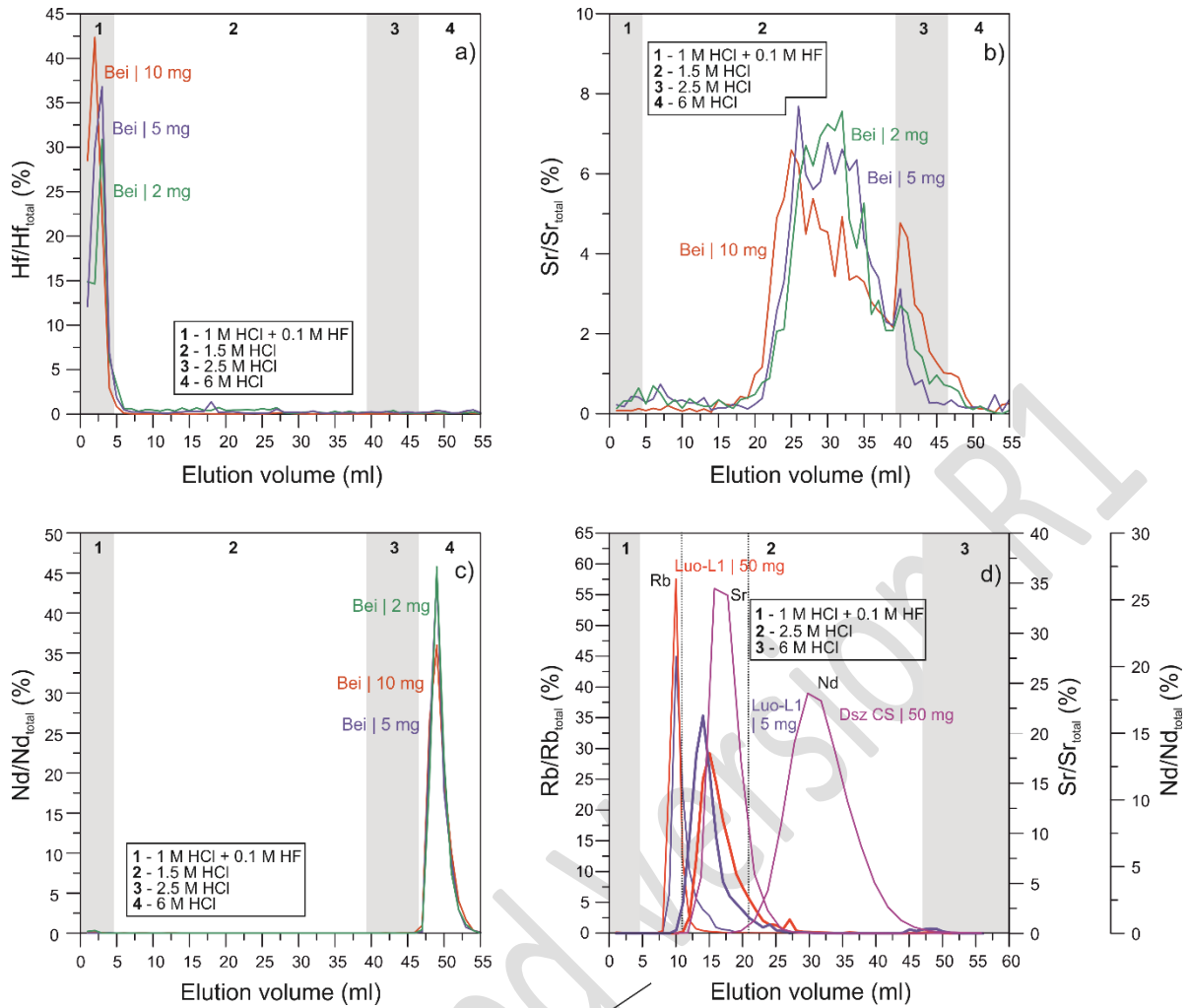
550 Ion exchange chemistry procedures outlined by Bast et al.¹ were followed in sequential separations
551 of Hf, Sr and Nd and subsequent Hf purification. These elution schemes were simplified as Rb, Sm
552 and Lu were not separated for isotope dilution concentration and isotopic composition analyses. This
553 is because we were primarily interested in the Hf-Sr-Nd isotopic compositions of dust samples in our
554 major project and these geologically very young samples did not require age corrections. Column
555 calibrations were performed using 50, 10, 5 and 2 mg loess samples from China (Bei and Luo-L1) and
556 Hungary (Dsz CS, Figure S1). Results obtained from the calibration necessitated modifications of the
557 chemistry related to Sr-Nd separations, previously published in Bast et al.¹ and Újvári et al.², due to
558 different column dimensions. For the best possible setup, we optimized the concentration and
559 amount of acids used. The first setup, shown in Figure S2a-c, resulted in excellent Hf and Nd

560 separations and recoveries (Figure S2a and c), while much less so for Sr (Figure S2b). Therefore, the
561 use of 1.5 M HCl was skipped and only 2.5 M HCl was used (Figure S2d). In this step, Rb and Sr could
562 be separated (first dotted line, Figure S2d) and we could define where to change to 6 M HCl to
563 separate Nd from Sr (second dotted line, Figure S2d). It must be noted that a perfect Rb-Sr
564 separation using this column was not necessary, as these elements were further separated and Sr
565 purified in a subsequent step (column #3, Figure S1). The column calibrations described above
566 resulted in the final setup, which is detailed below.

567 For the cation exchange chemistry (column #1, Figure S1) dried samples (after ABF digestion and
568 subsequent HNO₃ and HCl treatments) were taken up in 170 µl 6 M HCl at 140 °C on a hotplate, and
569 sequentially diluted with 780 µl MQ water and 50 µl HF to 1 M HCl – 0.1 M HF¹. Solutions were
570 transferred to a test tube, centrifuged for 30 minutes at 4500 rpm. The clean sample solutions were
571 pipetted onto the pre-cleaned and conditioned columns (#1). Hafnium and other HFSEs were
572 collected immediately after loading (Table S1), dried down at 120 °C and re-dissolved in 200 µl 0.56
573 HNO₃ – 0.3 M HF – 4% hydrogen peroxide (H₂O₂). This solution was then evaporated to dryness at 80
574 °C to oxidize organic contaminants from the resin and acids, and kept for loading onto column #2.
575 After eluting matrix elements using twice 3 ml 2.5 M HCl, Sr was collected in 10 ml 2.5 M HCl, while
576 Nd in 10 ml 6 M HCl right after Sr. Both the Sr and Nd cuts were dried at 120 °C on a hotplate, and
577 stored for further cleaning (columns #3-4).

578 Before loading onto Ln columns for further purification of Hf (column #2, Figure S1), the dried HFSE
579 cut from the primary column was taken up in 2 ml 3 M HNO₃ – 1% H₂O₂ and ultrasonicated for 30
580 minutes. After cleaning and conditioning, the often yellowish sample solutions (HFSE cut, including Hf
581 from column #1) were added to Ln columns (#2, Figure S1). Titanium was eluted using 3 M HNO₃ –
582 1% H₂O₂ until the eluate was completely colorless, usually after adding three to five times 2 ml of this
583 acid mixture. Zirconium was eluted using 24 ml 0.5 M HNO₃ – 0.06 M HF to achieve Zr/Hf<1 (Table
584 S1), and the clear cuts of Hf were collected in 3 ml 0.56 M HNO₃ – 0.3 M HF. After drying at 120 °C,
585 the clear cuts were taken up in 200 µl 0.56 M HNO₃ – 0.3 M HF – 4% H₂O₂ and dried again at 80 °C for
586 subsequent Hf isotope analysis using dry-plasma Multi Collector Inductively Coupled Plasma Mass
587 Spectrometry (MC-ICP-MS).

588 For further purification of Sr, dried samples from column #1 were taken up in 1 ml 2.5 M HCl. After
589 cleaning and conditioning with 6 M and 2.5 M HCl, sample solutions were loaded onto the columns
590 (#3) filled with AG W50-X8 (200-400 mesh, Figure S1). Subsequently, 2 and 30 ml 2.5 M HCl was
591 added to the columns before collecting Sr in 6 ml 2.5 M HCl (Table S2). Clear cuts of Sr were
592 evaporated to dryness and ready for Thermal Ionisation Mass Spectrometry (TIMS) measurements.
593 For Nd purification micro-columns packed with Ln resin were used after cleaning with 29 ml 5.9 M
594 HCl and conditioning with 5 ml and then 10 ml 0.22 M HCl. Dry Nd cuts were taken up in 150 µl 0.22
595 M HCl and loaded onto column #4 (Figure S1; Table S2). After adding twice 200 µl 0.22 M HCl, 29 ml
596 of 0.22 M HCl was used to collect Nd in a way that the collection started after ~9 to 11 minutes of
597 acid addition and lasted between 20 and 23 minutes resulting in ~15 ml clear cut solution. These Nd
598 columns were calibrated against time rather than acid volumes and therefore the column-dependent
599 collection periods are specified in minutes in Table S2. (Using volumes, i.e. having the columns run
600 empty, we have bleeding and tailing effects and these can be avoided by calibrating in time.) At the
601 end of collection, ~50 to 100 µl 2.5 M HNO₃ was added to the Nd clear cut solution to ensure Nd
602 concentration in the center of beakers for easier sample loading for TIMS analysis. The Nd clear cut
603 was dried down at 120 °C on a hotplate and stored this way for TIMS measurements.
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Final setup:
 4.5 ml 1 M HCl + 0.1 M HF - collect Hf
 2*3 ml 2.5 M HCl - remove Rb
 10 ml 2.5 M HCl - collect Sr
 10 ml 6 M HCl - collect Nd

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FIGURE S2. Elution curves for a) Hf, b) Sr and c) Nd obtained with a previous version^{1,2} and d) Rb-Sr-Nd with a modified version of chemistry using column #1. Note that the final column chemistry procedure of the primary column is different from what is presented in panel d), the final setup is listed below it. For calibration purposes loess samples from Beiguoyuan (Bei) and Luochuan (Luo-L1, both China), and Dunaszekcső (Dsz CS, Hungary) were used. Elution schemes were tested on 10, 5 and 2 mg digested samples first (a-c), and 50 and 5 mg samples afterwards (d).

Table S1. Elution scheme for Hf-Sr-Nd separations and further Hf purification

Step	Acid	Remark
<i>Column #1 (2 ml AG W50-X8 resin, 200-400 mesh)</i>		
Cleaning	12 ml 6 M HCl 2 × backwash with 2 ml MQ water 12 ml 2 M HF 24 ml 6 M HCl 2 × backwash with 2 ml MQ water	
Conditioning	2 ml 1 M HCl – 0.1 M HF	
Load sample, collect HFSE (Hf)	1 ml 1 M HCl – 0.1 M HF	
Collect HFSE (Hf)	0.5 ml 1 M HCl – 0.1 M HF	
Collect HFSE (Hf)	3 ml 1 M HCl – 0.1 M HF	drying (120 °C), take up in 200 µl 0.56 M HNO ₃ - 0.3 M HF - 4% H ₂ O ₂ , drying (80 °C), take up in 2 ml 3 M HNO ₃ - 1% H ₂ O ₂ , ultrasonication (30 min.), load sample solution onto column #2
Elute matrix	2×3 ml 2.5 M HCl	
Collect Sr	10 ml 2.5 M HCl	drying (120 °C), take up in 1 ml 2.5 M HCl, load onto column #3
Collect LREE (Nd)	10 ml 6 M HCl	drying (120 °C), take up in 150 µl 0.22 M HCl, load onto column #4
<i>Column #2 (2 ml Ln resin, 100-150 µm)</i>		
Cleaning	12 ml 6 M HCl 12 ml 2 M HF 12 ml 6 M HCl 12 ml 2 M HF 2 ml MQ water	
Conditioning	2×2 ml 3 M HNO ₃ – 1% H ₂ O ₂	
Load HFSE (Hf) from column #1	2 ml 3 M HNO ₃ – 1% H ₂ O ₂	
Elute Ti	4-6×2 ml 3 M HNO ₃ – 1% H ₂ O ₂	repeat until colorless
Wash off H ₂ O ₂	2 ml 0.1 M HNO ₃	
Elute Zr	6×4 ml 0.5 M HNO ₃ – 0.06 HF	
Collect Hf (clear cut)	3 ml 0.56 M HNO ₃ – 0.3 M HF	drying (120 °C), take up in 200 µl 0.56 M HNO ₃ - 0.3 M HF - 4% H ₂ O ₂ , drying (80 °C), ready for MC-ICP-MS analysis

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618 **Table S2. Elution schemes of Sr and Nd purifications**

Step	Acid	Remark
<i>Column #3 (2 ml, AG 50W-X8, 200-400 mesh)</i>		
Cleaning	50 ml 6 M HCl	
Conditioning	20 ml 2.5 M HCl	
Load sample (Sr cut from column #1)	1 ml 2.5 M HCl	
Wash sample	2 ml 2.5 M HCl	
Elute matrix	30 ml 2.5 M HCl	
Collect Sr (clear cut)	6 ml 2.5 M HCl	drying (120 °C), ready for TIMS analysis
<i>Column #4 (2 ml, Ln resin 100-150 mesh)</i>		
Cleaning	29 ml 5.9 M HCl	
Conditioning	5 + 10 ml 0.22 M HCl	
Load sample (LREE - Nd cut from column #1)	150 µl 0.22 N HCl	
Wash sample	2 × 200 µl 0.22 M HCl	
Record time and add acid	29 ml 0.22 M HCl	
Collection of Nd after 9-11 min. (column dependent)		
Finish collection of Nd (clear cut) after 20-23 min. (column dependent)		add ~50-100 µl 2.5 M HNO ₃ to clear cut solutions, then evaporate to dryness (120 °C), ready for TIMS analysis

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621 **3. Gain calibration of 10¹³ Ω current amplifiers**

622 For gain calibration purposes on the Neptune Plus instrument (Debrecen, Hungary), hafnium isotope
 623 measurements of the JMC-475 Hf standard were done in four cycles, using a combination of 10¹³ Ω
 624 amplifiers, as given in Table S3. Masses of 177-180 were analyzed using 10¹¹ Ω amplifiers. Amplifier
 625 gain factors are calculated as $GF = [{}^i\text{Hf}/{}^{177}\text{Hf}_{ref}]/[{}^i\text{Hf}/{}^{177}\text{Hf}_{mbc}] \times 0.01$, where ${}^i\text{Hf}/{}^{177}\text{Hf}_{ref}$ and ${}^i\text{Hf}/{}^{177}\text{Hf}_{mbc}$
 626 are the reference and measured, mass bias corrected Hf isotope ratios of JMC-475, with $i=174$ or
 627 176. Reference values of ${}^{174}\text{Hf}/{}^{177}\text{Hf} = 0.008674 \pm 0.000032$ and ${}^{176}\text{Hf}/{}^{177}\text{Hf} = 0.282163 \pm 0.000026$ (Chu
 628 et al., 2002) were adopted for the calculations, and mean values of GFs given in Table S4 were used
 629 for subsequent Hf isotopic measurements with the 10¹³ Ω amplifiers.
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Table S3. Amplifier configuration for gain calibration

Mass	176	175	174	172
cycle 1	10 ¹¹ Ω	10 ^{13a} Ω	10 ^{13b} Ω	10 ^{13c} Ω
cycle 2	10 ^{13a} Ω	10 ^{13b} Ω	10 ^{13c} Ω	10 ¹¹ Ω
cycle 3	10 ^{13b} Ω	10 ^{13c} Ω	10 ^{13a} Ω	10 ¹¹ Ω
cycle 4	10 ^{13c} Ω	10 ^{13a} Ω	10 ^{13b} Ω	10 ¹¹ Ω

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Table S4 Calculated gain factors of 10¹³ Ω amplifiers

Cycle	Ratio	Amplifier	Gain factor
1	174/177	13b	0.01053
2	174/177	13c	0.00989
3	174/177	13a	0.01072
4	174/177	13b	0.01053
2	176/177	13a	0.01075
3	176/177	13b	0.01055
4	176/177	13c	0.00991

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634 **4. Hf blank calculations**

635 In order to estimate the total procedural chemistry Hf blank contributions, 3 batches of ammonium
 636 bifluoride (ABF) from Carl Roth (2 batches) and Sigma Aldrich (1 batch) were processed through oven
 637 digestion and column chemistry and measured by dry-plasma MC-ICP-MS (Nu Plasma II) at the TU
 638 Graz bracketed by 10 and 100 ppb Hf solutions of the international standard JMC-475.

639 Mean sensitivity for Hf (s_{Hf}) was calculated from the total Hf ion beam intensities and known Hf
 640 concentrations of the JMC-475 solutions and was found to be 303.3 ± 11.9 V/ppm (2SE, n=9). The
 641 detection limit (LOD, in V) was calculated using the measured mean background ion beam intensities
 642 (in V) on mass 176 (b_{176}) for the JMC-475 solutions and their 3 standard deviations as $LOD_{176} = b_{176} \pm 3$
 643 $SD_{b_{176}}$. Concentration LOD ($cLOD$) was calculated from the mean s_{Hf} and LOD_{176} values and was found
 644 to be 9.53 ± 0.51 ppt (2SE, n=9). Hf blanks (Hf_{blank}) are calculated as measured intensities (mass 176) of
 645 Carl Roth and Sigma Aldrich ABFs ($b_{176-ABF}$), converted in concentration ($cb_{176-ABF} = b_{176-ABF}/s_{Hf}$), minus
 646 $cLOD$ ($Hf_{blank} = cb_{176-ABF} - cLOD$). Hf blanks were estimated to be 2.03 and 14.3 ppt for the two batches
 647 of Carl Roth ABF, while it was below detection limit for Sigma-Aldrich ABF. Since 3 ml of ultrapure 2%
 648 HNO_3 was used for taking up blanks for MC-ICP-MS analyses, we calculated 24.7 pg (~25 pg) Hf blank
 649 as an upper limit using the weight of 3 ml 2% HNO_3 (3.03 g at 20 °C) and a mean Hf blank
 650 concentration of 8.17 ± 10.01 ppt of the two batches of Carl Roth ABF.

651 MC-ICP-MS analyses of the ultrapure 2% HNO_3 acid solution used for sample uptake and dilution did
 652 not result in any measurable Hf ion beam intensities. Thus, the total calculated Hf blank of <25 pg is
 653 considered to be representative for the total procedural chemistry blank.

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 656 **5. Blank contributions to GRMs**

657 Sr, Nd and Hf blank contributions to the five USGS GRMs, calculated as $Sr_{blank}/Sr_{sample[GRM]} \times 100$, are
 658 given below in Table S5.

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Table S5. Blank contributions to different batches of USGS GRMs investigated

Name	Sr conc. (ppm)	Dissolved amount (mg)	Sr in sample [GRM] (ng)	Sr blank contr. (%)	Nd conc. (ppm)	Nd in sample [GRM] (ng)	Nd blank contr. (%)	Hf conc. (ppm)	Hf in sample [GRM] (ng)	Hf blank contr. (%)
AGV-2	659.5	50	32975.0	0.00	30.49	1524.5	0.01	5.14	256.9	0.01
	659.5	10	6595.0	0.01	30.49	304.9	0.07	5.14	51.4	0.05
	659.5	5	3297.5	0.02	30.49	152.5	0.13	5.14	25.7	0.10
	659.5	2	1319.0	0.04	30.49	61.0	0.33	5.14	10.3	0.24
BCR-2	337.4	50	16870.0	0.00	28.26	1413.0	0.01	4.97	248.6	0.01
	337.4	5	1687.0	0.03	28.26	141.3	0.14	4.97	24.9	0.10
GSP-2	240.0	50	12000.0	0.00	200.00	10000.0	0.00	14.00	700.0	0.00
	240.0	10	2400.0	0.02	200.00	2000.0	0.01	14.00	140.0	0.02
	240.0	5	1200.0	0.04	200.00	1000.0	0.02	14.00	70.0	0.04
RGM-2	106.7	50	5333.2	0.01	18.92	945.8	0.02	5.97	298.7	0.01
	106.7	5	533.3	0.09	18.92	94.6	0.21	5.97	29.9	0.08
STM-2	746.5	50	37325.0	0.00	78.80	3940.0	0.01	26.27	1313.7	0.00
	746.5	5	3732.5	0.01	78.80	394.0	0.05	26.27	131.4	0.02

Sr, Nd and Hf concentrations of GRMs are from the GEOREM database

Blank contributions are calculated with 0.5 and 0.2 ng for Sr and Nd, and 25 pg for Hf

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665 **References**

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