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HIGH-PRECISION SR AND ND ISOTOPE MEASUREMENTS USING A DYNAMIC ZOOM LENS-EQUIPPED THERMAL IONISATION MASS SPECTROMETER

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15 Keywords

16 Nu TIMS, high precision Sr isotopic measurements, high precision Nd isotopic measurements

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18 Significant statement

High precision Sr and Nd isotopic measurements are of key importance in the field of
Earth Sciences because they are powerful tools to trace sources of materials and to date them.
Here, we report the first high-precision data for ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd (external error of 5-6
ppm for Sr and 4-5 ppm for Nd) measured using a Nu Instruments TIMS. Such precisions will
open new opportunities in fields such as geochemistry, geochronology, cosmochemistry,
archaeology or forensics.

25

26 Abstract

Techniques for the determination of radiogenic strontium (⁸⁷Sr/⁸⁶Sr) and neodymium 27 (¹⁴³Nd/¹⁴⁴Nd) isotope ratios by Thermal Ionisation Mass Spectrometry (TIMS) are presented in 28 this study. We have developed a 5 lines acquisition routine for both elements, taking advantage 29 of the 16 Faraday cups available on the Nu Instruments TIMS in conjunction with an efficient 30 31 zoom lens system. This allows increased flexibility regarding the number of lines in a 32 multidynamic acquisition routine whilst maintaining optimal peak alignment and peak shape for every measurement line despite the fact that the detectors are not movable. The long-term 33 reproducibility obtained for our Sr (NBS 987) and Nd (Rennes-Ames) standard solutions gives 34 a $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}}$ of 0.7102467 ± 0.0000043 (6.0 ppm, 2 s.d., n = 38) and a $({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{multidyn}}$ 35 of 0.5119537 ± 0.0000022 (4.2 ppm, 2 s.d., n = 31), respectively. We also report 36 (⁸⁷Sr/⁸⁶Sr)_{multidyn} and (¹⁴³Nd/¹⁴⁴Nd)_{multidyn} for a set of terrestrial rock standards (including 5 37 38 basalts (BCR-2, BHVO-2, BIR-1, Be-N and BR-24), one rhyolite (RGM-1) and one andesite 39 (AGV-2)) with the same, or greater, level of precision as for the pure standards solutions. This level of precision is 2 to 3 times better than the literature data for Sr isotope ratios, and 40 comparable to the latest high precision data reported for Nd isotope ratios. This is the first paper 41 42 reporting such high precisions for radiogenic Sr and Nd data generated using a TIMS from Nu 43 Instruments.

- 44 1. Introduction
- 45

Isotope geochemistry has been widely used to probe the evolution and heterogeneity of the 46 terrestrial mantle (e.g., White 2015). Among the different tools available, radiogenic isotopes 47 48 are of particular interest because (i) they are not directly fractionated by magmatic processes and thus are good source tracers, and (ii) they give information about the timing of processes 49 via their parent-to-daughter decay ratios being time-integrated over the entire history of the 50 Earth. A large number of isotope systems are available, but the most extensively used are the 51 incompatible lithophile element systems: ⁸⁷Rb-⁸⁷Sr (half-life of 49.23 Ga), ¹⁴⁷Sm-¹⁴³Nd (half-52 life of 106 Ga), ¹⁷⁶Lu-¹⁷⁶Hf (half-life of 3.86 Ga), ¹³⁸La-¹³⁸Ce (half-life of 292.5 Ga), ²³⁸U-²⁰⁶Pb 53 (half-life of 4.47 Ga), ²³⁵U-²⁰⁷Pb (half-life of 0.71 Ga), ²³²Th-²⁰⁸Pb (half-life of 14.05 Ga). 54

The ⁸⁷Rb-⁸⁷Sr and ¹⁴⁷Sm-¹⁴³Nd systems were the first used. A major advantage of these 55 systems is that Rb is more incompatible than Sr while Sm is less incompatible than Nd during 56 57 partial melting of the mantle. This results in a crust enriched in incompatible elements (high Rb/Sr and low Sm/Nd) and an upper mantle depleted in incompatible elements (low Rb/Sr and 58 high Sm/Nd) after melt extraction. Pioneering work in the 1970s defined the ⁸⁷Sr/⁸⁶Sr and 59 60 ¹⁴³Nd/¹⁴⁴Nd mantle array (De Paolo and Wasserburg, 1979), and since then traditional 61 radiogenic (Sr-Nd-Pb) isotope compositions measured in oceanic island basalts (OIBs) around the world have refined the original mantle array to 5 end-member mantle components: DMM 62 (for depleted MORB mantle), HIMU (corresponding to a reservoir with high ²³⁸U/²⁰⁴Pb and 63 often associated with recycling of oceanic crust; Chauvel et al. 1992), EM1 and EM2 (for 64 enriched mantle 1 and 2, which are reservoirs characterized by variable Rb/Sr and low Sm/Nd) 65 and PREMA (for prevalent mantle) also called FOZO or C. Despite this, the exact number of 66 end-member compositions and their nature are still highly debated. Indeed, establishing subtle 67 differences depends on improved precision and accuracy of isotopic measurements. 68

Improvement in analytical techniques over the last years has led to better precisions for 69 70 isotope measurements: differences of a few parts per million (ppm) can now be detected 71 compared to precisions of the order of tens or hundreds of ppm in the late 1970s. This has 72 allowed the definition of for example distinct parallel trends between EM1 and EM2 mantle end-members in the Ce-Nd isotope space or in the Hf-Nd isotope space (e.g., Doucelance et al. 73 74 2021; Béguelin et al. 2021), leading to a better constraint on the nature and the age of the 75 recycled material responsible for the extended mantle heterogeneity. Another example of the utility of high precision measurements for radiogenic isotope systems comes from Abouchami 76 et al. (2005) who used high precision Pb isotope data to report, for the first time, different trends 77 78 between the two chains of Hawaiian volcanoes Loa and Kea, with only very little compositional overlap in their Pb isotope features. This has allowed to better constrain the structure and 79 geometry of the plumes ascending to the surface. Similar fine structures could be found in the 80 Sr-Nd isotopic space with the improvement in precision of Sr and Nd isotope data as reported 81 82 in our study. Aside from mantle geochemistry, the improvements in analytical protocol have greatly advanced the field of geochronology. For example, the latest high-precision Sm-Nd 83 geochronology data allow for the resolution of ages to a precision of \pm 1.0 Ma on very small 84 samples (1-10 ng of Nd; e.g., Starr et al., 2020). 85

86 In this paper, we demonstrate that the latest generation of thermal ionisation mass 87 spectrometers (TIMS) from Nu Instruments allows precisions of a few ppm to be reached, by taking advantage of the presence of a large number of detectors accompanied by an efficient zoom lens system. As mentioned above, this will have important implications in the field of mantle geochemistry, but not only. Indeed, the Sr and Nd systematics are also powerful tools in fields such as cosmochemistry, archaeology, ocean chemistry or paleoclimatic studies, to only cite a few. Improving the precision on measurements should help establishing small differences in sources or in temporal variations, or it could be a key tool to distinguish minor changes in geological and environmental processes.

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- 97 2. Chemical procedures
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a. Sample digestion

Complete digestion of between 50 mg and 100 mg of rock powder was accomplished using
a 3:1 mixture of 28N HF and 16N HNO₃ acids on a hotplate at ~ 120°C for at least two days.
The samples were then dried down and redissolved two times with 5 ml of 6N HCl followed
by 5ml of 2N HCl to decompose fluorides. The set of rock standards analysed in the course of
this study comprises 5 basalts (BCR-2, BHVO-2, BIR-1, Be-N and BR-24), one rhyolite (RGMand one andesite (AGV-2) to encompass a wide range of geological matrices.

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b. Separation of strontium and neodymium

110 The Sr and Nd chemical separations were achieved in a two-step chromatographic procedure adapted from the one published in Chauvel et al. (2011). The first step, common to 111 both elements, corresponds to a cation-exchange chromatography in HCl on a BioRad PolyPrep 112 column filled with 2 ml of AG50W-X8 resin (200-400 mesh). This step allows the removal of 113 major elements, while collecting the Sr fraction in 3.5N HCl and the LREE fraction in 6N HCl. 114 From there, the Sr fraction was further purified using a small (~ 3 mm diameter) homemade 115 shrink fit Teflon column filled with ~ 0.4 mL of Sr-spec resin (50-100 μ m). Rubidium, and its 116 117 interfering ⁸⁷Rb isotope, was removed using 3N HNO₃ and Sr was collected in ultrapure Milli-Q® water (18.2 MΩ.cm). On the other hand, the LREE fraction was further purified using a 118 119 plastic column (~ 7 mm diameter) filled with ~ 1 mL of Ln-spec resin (50-100 μ m). During this 120 step, the Nd fraction is collected in 0.25N HCl, allowing to separate it from Sm, the main interfering species when measuring ¹⁴³Nd/¹⁴⁴Nd. Our chemical procedures give a total 121 procedural blank of ~ 100 pg for Sr and ~ 25 pg for Nd. 122

Following the Sr and Nd chemical separations, we systematically analysed an aliquot of 5% of each processed sample on an Agilent 8900 triple quadrupole ICP-MS at the Institut de Physique du Globe de Paris. This allows for the determination of the Sr and Nd recoveries, but also to ensure that no residual trace of Rb and Sm is present in the Sr and Nd fractions that will be loaded on filaments. Strontium and Nd recoveries were > 75% and > 85% respectively, giving on average more than 20 μ g Sr and more than 1.5 μ g Nd subsequently available for analysis, with typically Rb/Sr < 1×10⁻⁵ and Sm/Nd < 6×10⁻⁵, for all the rock standards.

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132 3. Strontium and neodymium isotope measurements by Nu TIMS

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a. Generalities

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Strontium and neodymium isotopes are generally measured in static mode (on both 136 137 TIMS and MC-ICPMS), with all the ion beams acquired simultaneously. This configuration is 138 easier to set up on a mass spectrometer, does not necessitate a large number of detectors, and 139 provide isotopic results precise enough when looking at variability between samples of the order of tens of ppm of more. However, when higher precision data is required, isotope 140 measurements in a dynamic mode allow to better compensate for the relative deterioration of 141 the Faraday detectors and their change in efficiency with time, and thus return more accurate 142 143 isotopic results (e.g., Avanzinelli et al. 2005, Henshall et al. 2018, Fukai et al. 2017).

144 A Nu TIMS was installed at the Institut de Physique du Globe de Paris early 2020 (Serial No. 010) to perform high-precision Sr and Nd isotope measurements, in addition to other 145 isotope systems such as Ca and W isotopes for instance. The instrument is equipped with 16 146 147 fixed Faraday detectors, that can be dynamically connected to amplifiers with different feedback resistors (10¹⁰, 10¹¹, 10¹² and 10¹³ Ω). The fixed Faraday detectors system is 148 compensated by the presence of a zoom-lens system located between the magnet and the 149 detector array (Fig. 1a). This zoom-lens system is made of two lenses: quad 1 primarily focuses 150 the individual beams, while quad 2 controls the dispersion of the beams relative to each other. 151 The large number of detectors, in conjunction with an efficient zoom lens system, allows 152 significant flexibility regarding the number of lines in a multidynamic acquisition routine whilst 153 maintaining optimal peak alignment and peak shape for every measurement line despite the fact 154 that the detectors are not movable. In practice, the natural dispersion of the Nu TIMS is such 155 that the Re isotopes will align in adjacent collectors without the need for any quadratic field 156 157 being applied to the zoom lens system. As we go lower in mass (as for Nd and Sr isotopes compared to Re), the distance between the isotopes increases (Fig. 1a-1), because lighter 158 elements will be separated more as they pass through the magnetic sector. Applying the correct 159 set of voltages to the zoom lens system (quad 1 and quad 2 values in Table 1, referring to the 160 161 electrostatic field applied across each lens stack) will create a continuous electrostatic field which then effectively acts to demagnify the mass separation at the detectors by deflecting the 162 isotopes increasingly when moving farther away from the central point of the lens stack (Fig. 163 1a-2 and 1a-3). This allows for the alignment of the isotopes into the adjacent collectors whilst 164 maintaining good peak shapes (Fig. 1b). Optimal alignment is now achieved electrostatically 165 and not mechanically, allowing a robust and reproducible alignment within milliseconds and 166 167 insuring robust conditions for multidynamic measurements. The benefit of a multidynamic acquisition routine is a better correction for cup efficiencies compared to static measurements, 168 169 a better constraint on the oxide corrections when running in negative mode (for W isotopes for instance) and a better external reproducibility. Note that for Sr and Nd isotope analyses, all the 170 Faraday cups used were connected to amplifiers with a $10^{11} \Omega$ feedback resistor, and a 30 min 171 172 gain calibration was performed every morning.

174 Strontium isotopic measurements were performed using roughly 300 ng of Sr loaded on 175 previously outgassed zone-refined Re single filaments. About 0.7 µl of TaF₅ activator and 1 µl of sample in 0.5N HNO₃ were loaded onto the filament, in between two Parafilm strips 176 separated by ~ 3 mm, at ~ 0.75 A. The role of the Parafilm strips was to prevent the sample and 177 178 the activator spreading on the filament during the loading, so that a small spot could be obtained. 179 The activator and the sample were left to dry down between each step. The Parafilm strips were then burnt off at ~ 1.6 A and the filament glowed briefly to dull red at ~ 2.0 A. Rubidium 180 interferences were monitored on the TIMS using ⁸⁵Rb, but even in the case of residual rubidium, 181 it was burnt off from the filament before the strontium was properly emitted. The sample 182 filament was slowly heated until a stable 88 Sr⁺ beam of ~ 12-13 V was obtained and typically 183 measured for 6-7 h (corresponding to ~ 200 cycles, with a total acquisition time of 80 s per 184 cycle). The run length was variable and depended on when the sample was consumed. This 185 translated into 'raw' ⁸⁶Sr/⁸⁸Sr typically close to 0.1204 at the start of an analysis and lower than 186 0.1185 (and sometimes even down to 0.1180) when the analysis stopped. Baselines were 187 188 measured for 3 min every 20 cycles and peaks were recentred every 40 cycles.

Strontium isotopes were measured using a 5 lines acquisition routine (Table 1a). The 189 ⁸⁷Sr/⁸⁶Sr and ⁸⁴Sr/⁸⁶Sr acquired in each line were corrected for instrumental mass fractionation 190 with the exponential law using the ⁸⁶Sr/⁸⁸Sr acquired in the same line and assuming (⁸⁶Sr/⁸⁸Sr)_{ref} 191 = 0.1194. A multi-static ⁸⁷Sr/⁸⁶Sr (hereafter (⁸⁷Sr/⁸⁶Sr)_{multistat}) and a multi-static ⁸⁴Sr/⁸⁶Sr 192 (hereafter (⁸⁴Sr/⁸⁶Sr)_{multistat}) can then be obtained by averaging the 5 static ⁸⁷Sr/⁸⁶Sr acquired in 193 the 5 lines and the 4 static ⁸⁴Sr/⁸⁶Sr acquired in the first 4 lines, respectively. A dynamic ⁸⁷Sr/⁸⁶Sr 194 195 is obtained by combining the measurements from two different magnetic field positions (e.g., 196 lines 1 -2, Table 1a), following:

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$$\left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_{1-2} = \sqrt{\left(\frac{{}^{87}Sr_{H9}}{{}^{86}Sr_{H7}}\right)_1} \times \left(\frac{{}^{87}Sr_{H7}}{{}^{88}Sr_{H9}}\right)_2} \times \left(\frac{{}^{88}Sr}{{}^{86}Sr}\right)_{ref}$$
(1)

198 We can note that a correction for time-drift is applied for dynamic ratios (Garçon et al. 2018), 199 and although the drift correction code may not be identical to Garçon et al. (2018), a similar effect can be seen. This time drift correction is utilized to minimize effects associated with a 200 201 growing or changing signal emission between magnet positions. It does so by adding an extra 202 measurement line at the start of each block and comparing this measurement to the following for a correction back to a set time and intensity. A multi-dynamic ⁸⁷Sr/⁸⁶Sr (hereafter 203 (⁸⁷Sr/⁸⁶Sr)_{multidyn}) can then be obtained by averaging the 4 dynamic ⁸⁷Sr/⁸⁶Sr. As mentioned 204 earlier, we favoured dynamic measurements because they allow for the effective correction of 205 potential differences in cup efficiencies and amplifier gains between Faraday detectors. Using 206 the analytical conditions described above (very long and high intensity analysis), we obtained 207 internal precision for an individual Sr analysis typically better than 2 x 10⁻⁶ (2 se) on 208 (87Sr/86Sr)_{multidyn} (Fig.2). In comparison, a 2 hours analysis (corresponding to more 209 210 'conventional' Sr isotope studies but with much higher intensities) gives an internal precision typically around 2.5 x 10⁻⁶ (2 se) on (⁸⁷Sr/⁸⁶Sr)_{multidyn} (Fig.2). Finally, assuming that our analyses 211 are made with a ⁸⁸Sr signal 4 to 10 times higher than 'conventional' Sr isotopes studies, we can 212 213 estimate the internal precisions that would be obtained for 2 hours runs at low signal (1-3V on ⁸⁸Sr); these would be ~ 5-8 x 10⁻⁶ (Fig. 2). Such values are comparable to the internal precisions 214

obtained in similar conditions and using other TIMS (e.g., Carpentier et al. 2014) or another Nu
TIMS (e.g., Fourny et al. 2016, 2019).

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218 Neodymium isotopic measurements were performed using between 600 ng and 800 ng of Nd loaded on previously outgassed zone-refined Re double filaments. About 1 µl of sample 219 220 in 0.5N HNO₃ was loaded onto the sample filament, in between two Parafilm strips at ~ 0.75 221 A. Once dried, roughly 0.5 μ l of 1N H₃PO₄ activator was loaded on top of the sample at ~ 1.2 222 A. Then, once the activator was dried and similarly to Sr, the Parafilm strips were burnt off at 223 ~ 1.6 A and the filament glowed briefly to dull red at ~ 2.0 A. After having heated the ioniser filament to a temperature of $\sim 1900^{\circ}$ C in the source chamber, the sample filament was slowly 224 heated until a stable ${}^{142}Nd^+$ beam of ~ 6-8 V was obtained and typically measured for 7-8 h 225 (corresponding to ~ 300 cycles, with a total acquisition time of 50 s per cycle). Unlike for Sr 226 227 analyses, we did not systematically run until the Nd was totally consumed. However, if the sample was getting exhausted by the end of an analysis, it translated into 'raw' ¹⁴⁶Nd/¹⁴⁴Nd 228 typically starting at 0.7200 to finish at 0.7250 when the analysis was stopped. Baselines were 229 230 measured for 3 min every 20 cycles, and peaks were recentred every 60 cycles.

Similarly to the Sr method, Nd isotopes were measured using a 5 lines acquisition 231 232 routine (Table 1b). The method and the equations described in this paper for Nd isotope 233 measurements on the Nu TIMS are adapted from Thirlwall (1991) and Garçon et al. (2018). The ¹⁴³Nd/¹⁴⁴Nd, ¹⁴⁵Nd/¹⁴⁴Nd, ¹⁴⁸Nd/¹⁴⁴Nd and ¹⁵⁰Nd/¹⁴⁴Nd acquired in each line were corrected 234 for instrumental mass fractionation with the exponential law using the ¹⁴⁶Nd/¹⁴⁴Nd acquired in 235 the same line and assuming $({}^{146}Nd/{}^{144}Nd)_{ref} = 0.7219$. A multi-static ${}^{i}Nd/{}^{144}Nd$ (hereafter 236 $({}^{i}Nd/{}^{144}Nd)_{multistat}$, with i = 143, 145, 148 or 150) can then be obtained by averaging the 5 static 237 ⁱNd/¹⁴⁴Nd acquired in the 5 lines. Dynamic ¹⁴³Nd/¹⁴⁴Nd and ¹⁴⁵Nd/¹⁴⁴Nd are obtained by 238 combining the measurements from three different magnetic field positions (i.e. lines 1-2-3, 2-239 240 3-4 or 3-4-5, Table 1b), following for instance:

241
$$\begin{pmatrix} \frac{143}{Nd} \\ \frac{1-2-3}{1-2-3} = \sqrt{\left(\frac{143}{144}Nd_{H1}}{144}Nd_{H2}\right)_{3}} \times \left(\frac{143}{144}Nd_{Ax}}{144}Nd_{H1}\right)_{2} \times \left(\frac{m_{143}}{m_{144}}\right)^{2F_{1}}$$
(2)
242 With $F_{1} = \frac{\ln\left(\frac{\left(\frac{146}{144}Nd\right)_{ref}}{\left(\frac{146}{144}Nd_{Ax}}{144}\right)_{1}\right)}{\ln\left(\frac{m_{146}}{m_{144}}\right)}$ (3)

243 Dynamic ¹⁴⁸Nd/¹⁴⁴Nd and ¹⁵⁰Nd/¹⁴⁴Nd are obtained by combining the measurements from two 244 different magnetic field positions (i.e. lines 1-3, 2-4 or 3-5, Table 1b), following for instance:

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$$\begin{pmatrix} \frac{148Nd}{144Nd} \end{pmatrix}_{1-3} = \begin{pmatrix} \frac{148Nd_{H4}}{146Nd_{H2}} \end{pmatrix}_{1} \times \begin{pmatrix} \frac{146Nd}{144Nd} \end{pmatrix}_{ref} \times \begin{pmatrix} \frac{m_{148}}{m_{146}} \end{pmatrix}^{F_{3}}$$
(4)
246 With $F_{3} = \frac{\ln \begin{pmatrix} \begin{pmatrix} \frac{146Nd}{144Nd} \\ \frac{146Nd_{H4}}{144Nd_{H2}} \end{pmatrix}_{3} \end{pmatrix}}{\ln \begin{pmatrix} \frac{m_{146}}{m_{144}} \end{pmatrix}}$ (5)

As in the Sr procedure, a correction for time-drift is applied for dynamic ratios. A multidynamic $^{i}Nd/^{144}Nd$ (hereafter ($^{i}Nd/^{144}Nd$)_{multidyn}) can then be obtained by averaging the 3 dynamic $^{i}Nd/^{144}Nd$. Using the analytical conditions described above (very long and high intensity analysis), we obtain internal precision for an individual Nd analysis typically better than 1 x 10⁻⁶ (2 se) on ($^{143}Nd/^{144}Nd$)_{multidyn}. We do not report values for $^{142}Nd/^{144}Nd$ in this paper because the chromatographic procedure used in the course of this study was not designed to remove Pr and Ce from Nd (Table 2b).

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- 255 256

b. Reproducibility of pure standard solutions

257 We obtain $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}} = 0.7102467 \pm 0.0000043$ (6.0 ppm, 2 s.d., n = 38) for NBS 987 (Fig. 3) and $({}^{143}Nd/{}^{144}Nd)_{multidyn} = 0.5119537 \pm 0.0000022$ (4.2 ppm, 2 s.d., n = 31) for 258 259 Rennes-Ames (Fig. 4). We can note here that if we consider only the sub data corresponding to the first 60 cycles (~ 2 hours) of each NBS 987 analysis, we obtain similar values, i.e. 260 $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{multidyn}} = 0.7102456 \pm 0.0000044$ (6.2 ppm, 2 s.d., n = 38). These data are consistent 261 262 with the data reported in the literature, however the external precisions reported here on pure standard solutions are two to three times better than the most precise published data for 263 ⁸⁷Sr/⁸⁶Sr, and comparable to the most precise literature data for ¹⁴³Nd/¹⁴⁴Nd (Table 3 and Fig. 264 265 3a and 4a).

Our measurement of JNdi-1 gives $({}^{143}Nd/{}^{144}Nd)_{multidyn} = 0.5120941 \pm 0.0000022$ (4.4 ppm, 266 2 s.d., n = 9), which is slightly lower than the reference value of 0.512115 \pm 0.000007 reported 267 in Tanaka et al. (2000). However, our (143Nd/144Nd)_{multidyn} is in agreement with the high-268 precision data of 0.512099 ± 0.000005 (9.2 ppm, 2 s.d., n = 54) reported in Garçon et al. (2018). 269 270 It is also very close to the latest high-precision data reported by Pin and Gannoun (2019 a,b) of 271 0.512101 ± 0.000003 (5.9 ppm, 2 s.d., n = 12) and 0.512104 ± 0.000003 (5.9 ppm, 2 s.d., n = 15). We note that despite plotting within error of each other, the two values reported by Pin and 272 Gannoun indicate that small variations can occur for analyses run on the same instrument in the 273 274 same laboratory, even in the course of high precision isotope work.

Also, as seen in Figure 3b, there is no resolvable difference between (⁸⁷Sr/⁸⁶Sr)_{multidyn} and 275 (⁸⁷Sr/⁸⁶Sr)_{multistat}, which is expected when the drift in the mass bias is corrected properly and the 276 277 Faraday cups show little evidence for deterioration (the detectors have been used for less than a year in the course of this study). Similarly to ⁸⁷Sr/⁸⁶Sr, there seems to be no significant offset 278 between $(^{143}Nd/^{144}Nd)_{multidyn}$ and $(^{143}Nd/^{144}Nd)_{multistat}$, the difference between the two ratios 279 being on average ~ 2 ppm, i.e. within error (Fig. 4b). It is also important to note that for the Nd 280 281 systematics, the multidynamic method yields more reproducible data than the multistatic 282 method, translating into a smaller error on the mean ratio (± 0.0000022 versus ± 0.0000040 on the ¹⁴³Nd/¹⁴⁴Nd, 2 s.d., n = 31). For the Sr systematics, both methods seem to give comparable 283 reproducibility at the moment (± 0.0000043 versus ± 0.0000041 on the ⁸⁷Sr/⁸⁶Sr, 2 s.d., n=38). 284 One thing worth to note here is that, as shown in Figure 4b, the ¹⁴³Nd/¹⁴⁴Nd seems to decrease 285 with time (for both (¹⁴³Nd/¹⁴⁴Nd)_{multidyn} and (¹⁴³Nd/¹⁴⁴Nd)_{multistat}). The origin of this drift is not 286 287 clear to us yet, but we believe it could be several things, from how the beam behaves (growing 288 or dying), how it fractionates (i.e. reverse fractionation occurring; e.g., Garçon et al. 2018) to 289 the gain or the bucket efficiency. Thus, if we can see a 4 ppm change between running the analysis using a standard or reverse cup configuration (see below), maybe the same could be
seen between a growing and dying signal. Alternatively, a good indication of bucket efficiency
would be to monitor how the ¹⁴³Nd/¹⁴⁴Nd static ratios behave individually when the gain is
stable over a time period. However, we could not see one (¹⁴³Nd/¹⁴⁴Nd)_{stat} being systematically
and significantly lower than the others. Overall, it is difficult to say what causes this change
given it is a very small change.

296 Furthermore, we have compared two reverse methods (Table 1b and 1c) for Nd isotope measurements on the pure standard solution Rennes-Ames and have noticed the 297 (143Nd/144Nd)multidyn obtained with each method were within errors of each other. Thus, in 298 February 2021, we obtained a $(^{143}Nd/^{144}Nd)_{multidyn}$ of 0.5119535 ± 0.0000013 (2.5 ppm, 2 s.d., 299 n = 7) with the cup configuration reported in table 1b, which is within error of 300 $(^{143}Nd/^{144}Nd)_{multidyn} = 0.5119514 \pm 0.0000018$ (3.5 ppm, 2 s.d., n = 5) obtained with the reverse 301 method reported in table 1c. The relative difference between those two values is of ~ 4 ppm. 302 Similarly, we obtained the same relative difference of ~ 4 ppm for $(^{143}Nd/^{144}Nd)_{multidyn}$ between 303 the two Nd reverse methods in June 2021, with the cup configuration reported in table 1b giving 304 305 0.5119500 ± 0.0000004 and the set-up reported in Table 1c giving 0.5119481 ± 0.0000007 . Overall, although the method reported in Table 1b seems to give a slightly higher 306 (¹⁴³Nd/¹⁴⁴Nd)_{multidyn}, this is not significant compared to the external reproducibility (2 s.d.) of 307 4-5 ppm reported in this study for (¹⁴³Nd/¹⁴⁴Nd)_{multidyn}. The cup configuration reported in Table 308 309 1b was the one finally used during this study.

310 Finally, the data obtained in this study for stable isotopes, i.e. 84 Sr/ 86 Sr = 0.0564902 ± 0.0000018 (31.9 ppm, 2 s.d., n = 38) for NBS 987, and ¹⁴⁵Nd/¹⁴⁴Nd = 0.3484004 ± 0.0000013 311 (3.7 ppm, 2 s.d., n = 31), ¹⁴⁸Nd/¹⁴⁴Nd = 0.2415798 ± 0.0000019 (8.0 ppm, 2 s.d., n = 31) and 312 150 Nd/ 144 Nd = 0.2364508 ± 0.0000056 (23.5 ppm, 2 s.d., n = 31) for Rennes-Ames, are 313 consistent with previous studies (Table 3). The precisions reported here on those ratios are 314 315 comparable to the latest high-precision isotope data reported in Burkhardt et al. (2019) for the 316 Sr standard solution NBS 987 and Pin and Gannoun (2019) for the Nd standard solution 317 Rennes-Ames (Fig. 5).

- 318
- 319 *c. Precision*

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In this section, we compare the actual errors of our analyses on the Nu TIMS with the theoretical uncertainties expected from Johnson-Nyquist noise and counting statistics, these processes being considered as the two main contributors to the observed internal uncertainty for a given analysis. The reader is referred to the supplementary section of Luu et al. (2019) for more details about the theoretical uncertainty model and the calculations, but the important details are summarized below.

Johnson-Nyquist noise ($\sigma_{Johnson}$), the phenomenon of thermally-generated voltage noise in the feedback resistor, has a standard deviation given by $\sigma_{Johnson} = \sqrt{\frac{4RkT}{t}}$, where R is the feedback resistor of the amplifier connected to the Faraday cup (here $10^{11} \Omega$ for all cups measuring Sr and Nd isotopes), k is the Boltzmann constant (= 1.38×10^{-23} J/K), T is the

amplifier housing temperature (= 307 K) and t is the total integration time (= integration time 331 332 per static measurement \times total number of cycles). Note that we include this noise in our uncertainty model for completeness, but it is insignificant compared to the shot noise. Counting 333 statistics (σ_{counting}), or shot noise, describes the statistics of the arrival of ions at the detector as 334 a Poisson distribution. It is given by $\sigma_{counting} = \sqrt{\frac{V_m Re}{t}}$, where V_m is the mean amplifier output 335 voltage over the total integration time t, and e is the elementary charge (= 1.60×10^{-19} C). 336 Combining these errors by adding in quadrature the total absolute error on each isotope gives 337 $\sigma_{abs}^{x} = \sqrt{\sigma_{Johnson}^{2} + \sigma_{counting}^{2}}$, and the total relative error can be written as $\sigma_{rel}^{x} = \frac{\sigma_{abs}^{x}}{v_{m}^{x}}$, with 338 339 x = 86, 87 or 88 for Sr isotopes for instance. From there, the 2 s.e. relative error on the (⁸⁷Sr/⁸⁶Sr)_{multidyn} is derived by the quintuple jump type error propagation calculation as: 340 $2se_{rel}^{multidyn} = 2 \times \frac{1}{2n} \sqrt{n \times (\sigma_{rel}^{\chi})^2 + n \times (\sigma_{rel}^{Z})^2 + (4n-2) \times (\sigma_{rel}^{\gamma})^2}, \text{ where n correspond}$ 341 to the number of static measurements -1 (so n = 4 in our case). Finally, the 2 s.e. absolute error 342 on the $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}}$ is calculated as: $2se_{abs}^{multidyn} = 2se_{rel}^{multidyn} \times \frac{A_{87}}{A_{86}}$, where A₈₇ and A₈₆ 343 correspond to the relative abundances of ⁸⁷Sr (7.00%) and ⁸⁶Sr (9.86%) isotopes, respectively. 344 The reader is referred to the supplementary information of this paper for more details about 345 these equations and the error propagation calculations. 346

347 The results of that model are plotted in Figure 6, for the case of Sr systematics. We chose to plot the typical internal precisions (2 s.e.) for (⁸⁷Sr/⁸⁶Sr)_{multidyn} against 1/sqrt(number of ions 348 detected) because this latter parameter reflects the total integration time, while accounting for 349 350 the different average total intensities of the dataset. On figure 6a, we can clearly see that the 351 data fall below the model, for both the geostandards and the pure standard solution NBS 987. This is unexpected and may not look correct at first glance. However, we used a Monte Carlo 352 353 simulation for the quintuple-jump uncertainty on the ratio and it agrees well with the error propagation model described above, so we are confident that the discrepancy between the actual 354 and the theoretical errors is not due to a mistake in the algebra of propagating the errors. 355

356 We then investigated the effect of the time-drift correction. As mentioned earlier, a correction for time-drift is applied for dynamic ratios. This is because the use of a time-drift correction in 357 a dynamic routine helps reducing possible fractionation changes between measurement lines, 358 359 which could cause a bias on the final ratio as suggested in Garçon et al. (2018) and observed by Roth et al. (2014). We note that although the drift correction code may not be identical to 360 Garçon et al. (2018), a similar effect can be seen. If the time-drift correction is ignored, it 361 appears that the data are now consistent with the model (Fig. 6b): the typical uncertainties 362 363 reported in Table 3 for both pure standard solution NBS987 and terrestrial rock standards are now very close to the modelled errors, showing that (i) there is no effect of the matrix on the 364 precision of an analysis, and that (ii) the Nu TIMS is performing at the best of its capabilities. 365 We can note that the (⁸⁷Sr/⁸⁶Sr)_{multidyn} with and without time drift correction are differing by 366 less than 4 ppm (Table 4), which is not significant compared to the 6 ppm external 367 reproducibility we report. Thus, all the data reported in this paper have been processed using a 368 time drift correction. 369

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4. Results for terrestrial rock standards

The (⁸⁷Sr/⁸⁶Sr)_{multidyn} and (¹⁴³Nd/¹⁴⁴Nd)_{multidyn} obtained for rock standards in this study are 374 reported in Table 3. All the results obtained by our method are in agreement with published 375 data (Fig. 7 and 8). For instance, we obtained $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}} = 0.7034750 \pm 0.0000023$ (3.3) 376 ppm, 2 s.d., n = 4) and $({}^{143}Nd/{}^{144}Nd)_{multidyn} = 0.5129662 \pm 0.0000025$ (4.8 ppm, 2 s.d., n = 4) 377 for BHVO-2, and $({}^{87}Sr/{}^{86}Sr)_{multidyn} = 0.7039814 \pm 0.0000059$ (8.3 ppm, 2 s.d., n = 4) and 378 379 $(^{143}Nd/^{144}Nd)_{multidyn} = 0.5127702 \pm 0.0000033$ (6.4 ppm, 2 s.d., n = 3) for AGV-2. We should note that the variability in ¹⁴³Nd/¹⁴⁴Nd for JNdi-1 between different studies (see section 3.b) 380 has to be taken into account when comparing the ¹⁴³Nd/¹⁴⁴Nd in the literature for terrestrial 381 382 standards. The important thing to note here is that, for both systems, the precisions reported in this study are much better than most previous studies (Fig. 7 and 8), with an external 383 reproducibility of typically 5-6 ppm (2 s.d.) for ⁸⁷Sr/⁸⁶Sr and 4-5 ppm (2 s.d.) for ¹⁴³Nd/¹⁴⁴Nd. 384 We can also note that, although our chemistry protocol does not remove ¹⁴¹Pr nor ¹⁴⁰Ce (with 385 typically $2 < {}^{141}Pr^{+/146}Nd^+ < 4$ and ${}^{140}Ce^{+/146}Nd^+ < 1$ for rock standards at the start of an 386 387 analysis), this does not seem to affect the accuracy of the ¹⁴³Nd/¹⁴⁴Nd.

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390 5. Implications

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The level of precision reached for Sr and Nd systematics in this study opens new perspectives in the field of Earth Sciences, but not only.

Indeed, the extent of the application of radiogenic isotopes is not restricted to Earth 394 Sciences. In archaeology, ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd represent a powerful tool as source tracers. 395 For instance, small differences in isotope ratios can be decisive in discriminating sources at the 396 origin of raw materials that have been used for making prehistoric artefacts, and this 397 information can be precious to understand patterns of migrations and/or interactions between 398 prehistoric societies. However, few data have been produced with good precision (e.g., Weisler 399 400 et al. 2016, Hermann et al. 2017) and thereby most studies have limited conclusions given the 401 geochemical similarity of sources and some unclear geological complications regarding the source of Sr (e.g., Thomsen and Andreasen, 2019). 402

In cosmochemistry, small isotopic anomalies, commonly down to the ppm level, are 403 present among solar system materials at a planetary scale, and so, being able to detect them 404 405 provide important constraints on planetary bodies relationships and the dynamical evolution of 406 the solar system. Considering Sr isotopes, the level of analytical precision of most studies (~ 8-10 ppm, 2 s.e.; e.g., Hans et al. 2013, Henshall et al. 2018) did not allow identification of mass-407 independent variations in ⁸⁴Sr/⁸⁶Sr between enstatite chondrites, ordinary chondrites, eucrites, 408 409 Moon, Mars and the Earth; only carbonaceous chondrites showed small resolvable positive anomalies in ⁸⁴Sr, between 40 and 60 ppm relative to NBS 987 (e.g., Moynier et al. 2012). The 410 411 latest study of bulk planetary materials by Burkhardt et al. (2019) has modified this picture, 412 reporting ordinary and enstatite chondrites, as well as Moon, with small resolvable negative

413 anomalies in ⁸⁴Sr, on the order of -10 to -20 ppm relative to NBS 987. This demonstrates that 414 improving analytical precision is key to better resolve small isotopic variability, and thus why 415 the level of precision reached for ⁸⁴Sr/⁸⁶Sr in this study (2 s.e. of ~ 5 ppm, Fig. 5a) is useful. 416 The same reasoning could be true for other systematics, e.g. mass-independent variations in 417 40 Ca.

418 High precision data such as those reported in this study also opens new chronology 419 perspectives. Even if most of the uncertainty on ages comes from the poor determination of the parent/daughter ratio, enhanced precision on the isotopic ratio translates into a smaller 420 propagated uncertainty on the age determined from Rb-Sr or Sm-Nd isochrons (Fig. 9). We 421 should be able to obtain Rb-Sr or Sm-Nd isochrons for much younger rocks, with greater 422 423 resolution between previously indistinguishable suites. We should also be able to obtain 424 isochrons for phases with lower Rb/Sr or Sm/Nd, for which the excesses in the decay products of ⁸⁷Rb and ¹⁴³Sm will be small but now detectable with our improved analytical precisions on 425 ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd. For example, recently, Baxter et al. (2017) reported high-precision 426 427 Sm-Nd dating of individual growth zones within single garnet crystals in eclogites and other metamorphic rocks, and highlighted multistage processes occurring in subduction. 428

429 In mantle geochemistry, small scale mantle heterogeneities, such as those discovered when Pb isotopes started being measured with high precision (e.g., Abouchami et al. 2005), might be 430 431 discovered for volcanic rocks in both Sr and Nd isotopic spaces. Indeed, before the study by Abouchami et al. (2005), the two chains of Hawaiian volcanoes Loa and Kea were thought to 432 have overlapping radiogenic isotope features (for Pb, Sr and Nd systematics). However, the 433 434 high precision Pb isotope data reported for the first time in Abouchami et al. (2005) thanks to a Pb triple-spike technique have allowed to differentiate the Loa and Kea trends, with only a 435 436 very little compositional overlap. Similar discoveries could be expected with the improvement 437 in precision of Sr and Nd isotope data as reported in our study.

Finally, the preservation in the Earth's deep interior of early-formed material, either 438 recycled from the surface reservoirs or residual from the early mantle differentiation, has 439 recently been evidenced by the detection of small variability in ¹⁸²W (Mundl et al. 2017, Rizo 440 et al. 2016) and ¹⁴²Nd (Peters et al. 2018), the decay products of the short-lived ¹⁸²Hf (half-life 441 of 8.9 Myr) and ¹⁴⁶Sm (half-life of 103 Myr), respectively. The total range of variations among 442 modern ocean island basalts does not exceed 15 ppm in $^{142}Nd/^{144}Nd$ and 25 ppm for $^{182}W/^{184}W$. 443 These small variabilities have become detectable thanks to the high analytical precisions 444 recently reached with dynamic measurements on the TIMS, i.e. ± 4 ppm on $^{182}W/^{184}W$ (2 s.d.; 445 Mundl et al. 2017) and \pm 4.4 ppm on ¹⁴²Nd/¹⁴⁴Nd (2 s.d., in Peters et al. 2018). These recent 446 447 discoveries are very exciting and we are currently developing analytical methods for high precision ¹⁸²W and ¹⁴²Nd isotope measurements on our Nu TIMS at IPGP, in order to expand 448 449 the currently limited dataset available.

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452 6. Conclusions

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- We report high-precision Sr and Nd isotope data, with an external reproducibility on the order of 5-6 ppm (2 s.d.) for ⁸⁷Sr/⁸⁶Sr and 4-5 ppm (2 s.d.) for ¹⁴³Nd/¹⁴⁴Nd. This is the first time

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such a level of precision is reported with a TIMS from Nu Instruments. Such precisions are of 457 key importance in the field of Earth Sciences because Sr and Nd systematics are powerful tools to trace sources of materials and to date them, but they also open new opportunities in fields 458 459 such as cosmochemistry, paleoclimatic studies, archaeology, tracing of food origin or forensics.

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473 8. References

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TABLE 1: Collector configuration used for Sr (a) and Nd (b) isotope measurements on the Nu TIMS during the course of this study. Note that the 635 numbers in bold purple correspond to the mass used for the peak centering for each line. (c) Reverse configuration for Nd used to test if there is 636 any difference between methods b and c. 637

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639 a.

			Sr conf	figura	tion	H11	H9	H7	Н5	Н3	H1	L1	L3	Inte	gratic	on tim	e (s)	Quad	1 (V)	Quad 2	2 (V)			
			Line 1			88	87	86	85	84	83	82	81		1	6		27	7	-27	7			
			Line 2			89	88	87	86	85	84	83	82		1	6		28	3	-42	2			
			Line 3			90	89	88	87	86	85	84	83		1	6		33	3	-61	1			
			Line 4			91	90	89	88	87	86	85	84		1	6		34	1	-77	7			
			Line 5			92	91	90	89	88	87	86	85		1	6		36	5	-91	1			
0																								
1	b.																							
Nd	configuration	H11	H10	H9	H8	H7	H6	H5	H4	H.	3 I	H2	H1	Ax	L1	L2	L3	L4	Integra	tion time	$e(s) \in C$	Quad 1 (V)	Quad 2 (V)	•
Lin	e 1	155	154	153	152	151	150	149	148	3 14	7 1	46	145	144	143	142	141	137		10		-15	127	-
Lin	e 2	154	153	152	151	150	149	148	147	7 14	6 1	45	144	143	142	141	140	136		10		-15	134	
Lin	e 3	153	152	151	150	149	148	147	140	5 14	5 1	44	143	142	141	140	139	135		10		-17	139	
Lin	e 4	152	151	150	149	148	147	146	14	5 14	4 1	43	142	141	140	139	138	134		10		-17	145	
Lin	e 5	151	150	149	148	147	146	145	144	1 14	3 1	42	141	140	139	138	137	133		10		-17	148	
2																								
3	c.																							
	Nd Reverse	H11	H10	H9	H8	H7	H6	Н5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	Integra	tion time	(s) Q	Quad 1 (V) Qua	d 2 (V)	
	Line 1	151	150	149	148	147	146	145	144	143	142	141	140	139	138	137	133		10		-18	1	49	
	Line 2	152	151	150	149	148	147	146	145	144	143	142	141	140	139	138	134		10		-18	1	46	
	Line 3	153	152	151	150	149	148	147	146	145	144	143	142	141	140	139	135		10		-18	1	40	
	Line 4	154	153	152	151	150	149	148	147	146	145	144	143	142	141	140	136		10		-17	1	37	
	Line 5	155	154	153	152	151	150	149	148	147	146	145	144	143	142	141	137		10		-17	1	31	

645 TABLE 2: a. Potential interferences (a) in the mass region 84-88 affecting the Sr isotope results 646 and (b) in the mass region 142-150 affecting the Nd isotope results. In practice, Kr, oxides and 647 doubly charged ions constitute a major issue when using plasma source mass spectrometers, 648 but they are very rare when using a TIMS. Only interferences coming from Rb and Ce-Sm (bold 649 purple) are considered when measuring Sr and Nd isotopes on a TIMS. A good Sr and Nd 650 chemical separation prior to isotope analyses on the TIMS is mandatory.

- 651
- 652

a.

Sr	$^{84}\mathrm{Sr}^+$	$^{86}{ m Sr^{+}}$	$^{87}{ m Sr}^{+}$	$^{88}\mathrm{Sr}^{+}$	-		
Kr	$^{84}{ m Kr^{+}}$	${}^{86}{ m Kr}^+$					
Rb			87 Rb ⁺				
REE	¹⁶⁸ Yb ²⁺ ¹⁶⁸ Er ²⁺	$^{172}Yb^{2+}$	$^{174}Yb^{2+}$	¹⁷⁶ Y	b^{2+}		
				¹⁷⁶ Lu	a^{2+}		
			$^{174}{ m Hf}^{2+}$	^{176}H	f^{2+}		
Fe oxides		$^{54}\text{Fe}^{16}\text{O}_2^+$	⁵⁴ Fe ¹⁶ O ¹⁷ O	+ ⁵⁴ Fe	$16O_{18}O_{+}$		
		_		⁵⁴ Fe	$17O_{2}^{+}$		
				⁵⁶ Fe	$^{16}O_2^+$		
Zn oxides	${}^{68}Zn^{16}O^+$	68Zn18O+			-		
		$^{70}Zn^{16}O^{+}$	$^{70}Zn^{17}O^{+}$	⁷⁰ Zn	$^{18}O^{+}$		
Ga oxides		69Ga17O+	$^{69}Ga^{18}O^{+}$				
			$^{71}{\rm Ga^{16}O^{+}}$	⁷¹ Ga	$^{17}O^{+}$		
Ca dimers	$^{40}Ca^{44}Ca^{+}$	$^{40}Ca^{46}Ca^+$		⁴⁰ Ca	$^{48}Ca^+$		
	$^{42}Ca_{2}^{+}$	$^{42}Ca^{44}Ca^+$		⁴² Ca	$^{46}Ca^{+}$		
		$^{43}Ca_{2}^{+}$	$^{43}Ca^{44}Ca^+$				
				⁴⁴ Ca	2 ⁺		
b.							
Nd	¹⁴² Nd	¹⁴³ Nd ¹⁴	⁴⁴ Nd ¹⁴⁵	⁵ Nd	¹⁴⁶ Nd	¹⁴⁸ Nd	¹⁵⁰ Nd
Ce	¹⁴² Ce ⁺						
Sm		14	⁴⁴ Sm ⁺			¹⁴⁸ Sm ⁺	¹⁵⁰ Sm+
Ba oxides					$^{130}Ba^{16}O$	¹³² Ba ¹⁶ O	¹³⁴ Ba ¹⁶ O
							¹³² Ba ¹⁸ O
Ru oxides		90	${}^{5}\mathrm{Ru}^{16}\mathrm{O}_{3}^{+}$		$^{98}Ru^{16}O_3^+$	$^{100}Ru^{16}O_3^+$	102 Ru 16 O ₃ +

TABLE 3: Strontium and neodymium isotope compositions for pure standard solutions and terrestrial rocks measured in the course of this study. All the ratios are multidynamic except the 84 Sr/ 86 Sr which are multistatic. Rep = the solution was loaded a second time on a different filament.

		⁸⁷ Sr/ ⁸⁶ Sr	2se/2sd	⁸⁴ Sr/ ⁸⁶ Sr	2se/2sd	Yield	¹⁴³ Nd/ ¹⁴⁴ Nd	2se/2sd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	2se/2sd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	2se/2sd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	2se/2sd	Yield
	NDG 005	0.0100460		0.05(1000	10.106	(%)									(%)
Pure standard	NBS 987	0.7102467	4.3×10 ⁻⁶	0.0564902	1.8×10-0										
Solutions	D 4		(n = 38)		(n=38)		0.5110527	22.106	0.2494004	12 106	0.2415709	10 106	0.22(4500	5 6 10 6	
	Rennes-Ames						0.5119537	2.2×10^{-0}	0.3484004	1.3×10^{-0}	0.2415798	1.9×10^{-0}	0.2364508	5.6×10^{-0}	
Torrestrial roaks								(n-31)		(n-31)		(n-31)		(n-31)	
BHVO-2	BHVO-2 a						0.5129680	7.2×10^{-7}	0 3484000	2.2×10^{-7}	0 2415805	2 2×10-7	0 2364501	5 2×10-7	34
BII V 0-2	BHVO-2 Pam	0 7034753	1.0×10^{-6}	0.0564891	5 1×10 ⁻⁷	29	0.5129658	6.2×10^{-7}	0.3483998	1.8×10^{-7}	0.2415793	3.5×10^{-7}	0.2364491	3.5×10^{-7}	40
	BHVO-2 h	0.7034737	1.9×10^{-6}	0.0564890	4.5×10^{-7}	86	0.5129653	6.2×10^{-7}	0.3483992	2.1×10^{-7}	0.2415791	2.0×10^{-7}	0.2364487	4.3×10^{-7}	84
	BHVO-2 c	0.7034765	1.2×10^{-6}	0.0564899	5.3×10-7	75	0.5129656	6.0×10-7	0.3483997	1.7×10^{-7}	0.2415802	2.7×10^{-7}	0.2364502	3.6×10^{-7}	89
	BHVO-2 c ren	0.7034746	1.4×10^{-6}	0.0564883	4.4×10^{-7}	15	0.5129050	0.0×10	0.5405777	1./~10	0.2415002	2.3×10	0.2304302	5.0~10	07
	mean	0.7034750	2.3×10-6	0.0564891	1.3×10-6		0.5129662	2.5×10-6	0.3483996	7 2×10-7	0.2415798	1 4×10-6	0.2364495	1 5×10-6	
BCR-2	BCR-2 a	0.7050090	1.5×10^{-6}	0.0564898	5.1×10 ⁻⁷	27	0.5126183	8.5×10 ⁻⁷	0.3484002	2.9×10 ⁻⁷	0.2415858	3.7×10^{-7}	0.2364560	5.8×10 ⁻⁷	18
	BCR-2 b	0.7050103	9.9×10 ⁻⁷	0.0564873	4.5×10^{-7}	78		0.0		2.,		51,10		010/10	
	BCR-2 c	0.7050093	1.3×10^{-6}	0.0564893	4.3×10 ⁻⁷	93	0.5126142	5.1×10^{-7}	0.3483987	1.4×10^{-7}	0.2415789	1.9×10 ⁻⁷	0.2364471	2.9×10 ⁻⁷	90
	BCR-2 c rep	0.7050077	1.1×10 ⁻⁶	0.0564889	4.3×10-7										
	mean	0.7050091	2.2×10-6	0.0564893	8.4×10 ⁻⁷		0.5126162	5.7×10-6	0.3483994	2.1×10 ⁻⁶	0.2415824	9.7×10-6	0.2364515	1.3×10 ⁻⁵	
BR-24	BR-24 a	0.7050381	1.2×10-6	0.0564882	4.2×10-7	87	0.5127711	5.5×10-7	0.3483991	1.5×10-7	0.2415791	2.3×10-7	0.2364482	3.9×10-7	92
	BR-24 b	0.7050380	1.6×10-6	0.0564881	5.9×10 ⁻⁷	87	0.5127711	5.3×10 ⁻⁷	0.3483988	1.7×10 ⁻⁷	0.2415796	2.3×10-7	0.2364496	3.5×10-7	89
	BR-24 b rep	0.7050379	1.2×10 ⁻⁶	0.0564878	4.1×10 ⁻⁷										
	mean	0.7050380	1.8×10 ⁻⁷	0.0564880	4.2×10 ⁻⁷		0.5127711	2.8×10 ⁻⁸	0.3483989	4.7×10 ⁻⁷	0.2415793	7.9×10 ⁻⁷	0.2364489	2.1×10 ⁻⁶	
BIR-1	BIR-1 a	0.7031000	1.5×10-6	0.0564888	4.7×10-7	74	0.5130710	9.2×10 ⁻⁷	0.3483992	2.7×10-7	0.2415824	4.1×10 ⁻⁷	0.2364516	5.5×10-7	87
	BIR-1 b	0.7030985	1.6×10-6	0.0564892	5.6×10-7	71	0.5130734	9.5×10 ⁻⁷	0.3483992	2.6×10-7	0.2415795	3.6×10 ⁻⁷	0.2364482	5.9×10-7	86
	BIR-1 b rep	0.7030959	1.3×10-6	0.0564898	4.2×10-7										
	mean	0.7030981	4.1×10 ⁻⁶	0.0564893	1.1×10 ⁻⁶		0.5130722	3.5×10-6	0.3483992	5.7×10 ⁻⁸	0.2415810	4.0×10-6	0.2364499	4.8×10-6	
Be-N	Be-N a	0.7038004	1.6×10 ⁻⁶	0.0564873	6.0×10 ⁻⁷	75	0.5128642	6.0×10 ⁻⁷	0.3483994	1.8×10 ⁻⁷	0.2415804	2.3×10-7	0.2364517	3.9×10 ⁻⁷	91
	Be-N a rep	0.7037995	1.1×10 ⁻⁶	0.0564875	4.4×10 ⁻⁷										
	Be-N b	0.7037999	1.5×10-6	0.0564883	5.1×10 ⁻⁷	89	0.5128617	6.1×10 ⁻⁷	0.3483991	1.8×10 ⁻⁷	0.2415815	2.3×10-7	0.2364530	3.6×10-7	86
	mean	0.7037999	8.6×10 ⁻⁷	0.0564877	1.1×10 ⁻⁶		0.5128629	3.5×10-6	0.3483993	4.5×10-7	0.2415809	1.6×10 ⁻⁶	0.2364524	1.8×10 ⁻⁶	
RGM-1	RGM1-a					12									9
	RGM-1 b	0.7042043	1.4×10 ⁻⁶	0.0564873	4.4×10-7	71	0.5127778	6.9×10 ⁻⁷	0.3483999	2.1×10 ⁻⁷	0.2415802	2.6×10-7	0.2364489	4.1×10-7	91
	RGM-1 b rep	0.7041943	1.1×10 ⁻⁶	0.0564886	4.1×10 ⁻⁷										
	RGM-1 c					85									
	mean	0.7041993	1.4×10 ⁻⁵	0.0564880	1.9×10 ⁻⁶										
AGV-2	AGV-2 a	0.7039781	1.8×10 ⁻⁶	0.0564908	6.1×10 ⁻⁷	14	0.5127720	9.0×10 ⁻⁷	0.3484012	3.3×10-7	0.2415795	3.5×10 ⁻⁷	0.2364480	6.7×10-7	15
	AGV-2 b	0.7039843	9.5×10 ⁻⁷	0.0564875	3.9×10 ⁻⁷	85	0.5127688	6.2×10 ⁻⁷	0.3483987	2.0×10-7	0.2415780	2.6×10 ⁻⁷	0.2364465	4.1×10 ⁻⁷	79
	AGV-2 c	0.7039800	1.2×10 ⁻⁶	0.0564896	4.5×10-7	93	0.5127698	5.4×10 ⁻⁷	0.3483988	1.5×10-7	0.2415810	2.3×10-7	0.2364508	3.6×10 ⁻⁷	91
	AGV-2 c rep	0.7039835	1.3×10 ⁻⁶	0.0564877	4.4×10 ⁻⁷										
	mean	0.7039814	5.9×10 ⁻⁶	0.0564889	3.2×10 ⁻⁶		0.5127702	3.3×10 ⁻⁶	0.3483996	2.8×10 ⁻⁶	0.2415795	3.0×10 ⁻⁶	0.2364485	4.4×10 ⁻⁶	

660 TABLE 4: Comparison between $({}^{87}Sr/{}^{86}Sr)_{multidyn}$ when using the time drift correction, or not.

	With time drif	t correction	Without t	ime drift	Relative difference	n
			corre	ction	(ppm)	
	⁸⁷ Sr/ ⁸⁶ Sr	2sd	⁸⁷ Sr/ ⁸⁶ Sr	2sd		
NBS 987	0.7102466	4.1×10 ⁻⁶	0.7102490	5.0×10 ⁻⁶	3.4	37
BHVO-2	0.7034750	2.3×10 ⁻⁶	0.7034779	2.6×10 ⁻⁶	4.0	4
BCR-2	0.7050091	2.2×10 ⁻⁶	0.7050112	2.8×10 ⁻⁶	3.0	4
BR-24	0.7050380	1.8×10 ⁻⁷	0.7050403	1.0×10^{-6}	3.2	3
BIR-1	0.7030981	4.1×10 ⁻⁶	0.7031002	5.1×10 ⁻⁶	3.0	3
Be-N	0.7037999	8.6×10 ⁻⁷	0.7038028	2.0×10 ⁻⁶	4.1	3
AGV-2	0.7039814	5.9×10 ⁻⁶	0.7039841	5.7×10 ⁻⁶	3.7	4

FIGURE 1: a. Schematic showing where the zoom lens system allowing peak alignment while having fixed Faraday detectors sits on the Nu TIMS, and what happens to the ion beams when using or not the zoom lens system. a-1: No voltage is applied on quads 1 and 2, resulting in two ion beams diverging and being unfocused at the collector array. a-2: A voltage is applied on quad 1 only, resulting in two ion beams being focused but the natural dispersion of these ion beams does not align with the collector array. a-3: Voltages are now applied on both quads 1 and 2, resulting in two ion beams being now focused at the correct collectors.

b. Peak alignment achieved with fixed Faraday detectors for Sr and Nd isotopes when applying
adequate voltages on the zoom lens system. The isotopes ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr are collected
in H1, H5, H7 and H9 detectors, respectively (C-1). The isotopes ¹⁴²Nd, ¹⁴³Nd, ¹⁴⁴Nd, ¹⁴⁵Nd,
¹⁴⁶Nd, ¹⁴⁸Nd and ¹⁵⁰Nd are collected in L2, L1, Ax, H1, H2, H4 and H6, respectively (C-2).





FIGURE 2: Comparison between the internal errors typically obtained when running the Sr isotope analyses (i) with more than 10V of signal on ⁸⁸Sr⁺ for 6-7 hours (i.e. our standard conditions, blue dots) and (ii) with more than 10V of signal on ⁸⁸Sr⁺ for 2 hours only (orange crosses). An estimation of the internal errors obtained when running with less than 3V of signal 685 for 2 hours is also shown for comparison (black arrow).



689 **FIGURE 3**:

- 690 a. Comparison of our mean $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}}$ (blue circle) with literature data (grey circles) for 691 the pure Sr standard solution NBS 987. Note that the yellow circle corresponds to the
- 692 recommended value reported by Zhang and Hu (2020) after a compilation of the data available
- 693 in Georem. Error bars correspond to 2 sd. Literature: (a) Raczek et al. 2003, (b) Weis et al.
- 694 2006, (c) Makishima et al. 2008, (d) Aciego et al. 2009, (e) Yang et al. 2010, (f) Chauvel et al.
- 695 2011, (g) Yang et al. 2012, (h) Carpentier et al. 2014, (i) Li et al. 2014, (j) Pin et al. 2014, (k)
- 696 Mokadem et al. 2015, (l) Fourny et al. 2016, (m) Yobregat et al. 2017, (n) Di et al. 2021, (o)
- **697** Zhang and Hu 2020.
- 698 b. Comparison between $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multidyn}}$ and $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{multistat}}$ measured in the NBS 987 699 standard solution over a period of ~ 10 months on the Nu TIMS. Error bars on individual data 700 correspond to internal 2 se.
- 701



702 703

0.710240

0.710235

0.710230

Average Multidynamic:

(6.0 ppm, 2sd, n= 38)

 87 Sr/S6Sr = 0.7102467 ± 0.0000043

Average Multistatic:

(5.7 ppm, 2sd, n= 38)

⁸⁷Sr/^{S6}Sr = 0.7102465 ± 0.0000041

706 FIGURE 4:

- a. Comparison of our mean (¹⁴³Nd/¹⁴⁴Nd)_{multidyn} measured for the pure Nd standard solutions
- 708 JNDi-1 and Rennes-Ames (blue circles) with literature data (grey circles). Note that we added
- the reference Fourny et al. (2016) for comparison, given the few data available in the literature
- 710 for the Nd standard solution Rennes-Ames. Note that the yellow circle corresponds to the
- recommended value reported by Zhang and Hu (2020) after a compilation of the data available
- in Georem. Error bars correspond to 2 s.d. Literature: (a) Tanaka et al. 2000, (b) Le Fèvre and
- 713 Pin 2005, (c) Li et al. 2007, (d) Aciego et al. 2009, (e) Chu et al. 2009, (f) Li et al 2011a, (g) Li
- 714 et al 2011b, (h) Ali and Srinivasan 2011, (i) Li et al. 2014, (j) Pin et al. 2014, (k) Fourny et al.
- 715 2016, (1) Garçon et al. 2018, (m) Pin and Gannoun 2019a, (n) Pin and Gannoun 2019b, (o)
- 716 Zhang and Hu 2020, (p) Chauvel and Blichert-Toft 2001, (q) Caro et al. 2003, (r) Caro et al.
- 717 2006, (s) Weis et al. 2006, (t) Chauvel et al. 2011.
- 718 b. Comparison between $({}^{143}Nd/{}^{144}Nd)_{multidyn}$ and $({}^{143}Nd/{}^{144}Nd)_{multistat}$ measured in Rennes-Ames
- 719 over a period of ~ 8 months on the Nu TIMS. Error bars on individual data correspond to
- 720 internal 2 se.



724 FIGURE 5:

Stable Sr and Nd isotope compositions of the pure standard solutions NBS 987 (a) and Rennes-Ames (b-c) obtained in the course of this study. Error bars correspond to 2 s.e. For comparison are also plotted the latest high precision data (mean ± 2 s.d.) from Burckhardt et al. (2019) and Pin and Gannoun (2019).

729

730

FIGURE 6:

Comparison between the theoretical precision modelled on multidynamic ⁸⁷Sr/⁸⁶Sr (blue line) and the actual uncertainties obtained for our analyses of NBS 987 (purple diamonds) and geostandards (green dots), with time drift correction (a) and without time drift correction (b).

743 FIGURE 7:

Multidynamic ⁸⁷Sr/⁸⁶Sr measured for different geostandards in the course of this study (blue 744 symbols) and comparison with literature data (grey symbols). BCR-1, BHVO-1, BIR-1 and 745 746 AGV-1 are represented as circles, while BCR-2, BHVO-2 and AGV-2 are represented as 747 diamonds. Note that the data from Raczek et al. (2003) have been renormalized to 0.710248 given the different ⁸⁷Sr/⁸⁶Sr they reported for NBS 987 compared to other studies (see Figure 748 749 3a). Recommended values from Zhang and Hu (2020) are also shown for comparison (yellow 750 symbols). Literature: (a-o) same as in figure 3a. (p) Li et al. 2012, (q) Neymark et al. 2014, (r) Klaver et al. 2015, (s) Jweda et al. 2016, (t) Fourny et al. 2019, (u) Koornneef et. 2015. 751

FIGURE 8:

Multidynamic ¹⁴³Nd/¹⁴⁴Nd measured for different geostandards in the course of this study (blue symbols) and comparison with the literature. BCR-1, BHVO-1, BIR-1 and AGV-1 are represented as circles, while BCR-2, BHVO-2 and AGV-2 are represented as diamonds.
Recommended values from Zhang and Hu (2020) are also shown for comparison (yellow symbols). Literature: (a-t) same as in Figure 4a, (u) Raczek et al. 2003, (v) Mahlen et al. 2008, (w) Yang et al. 2010, (x) Li et al. 2012, (y) Klaver et al. 2015, (z) Li et al. 2015, (aa) Carpentier et al. 2014, (ab) Koornneef et al. 2015.

FIGURE 9:

a. Improvement on the uncertainty of the age determined from a Rb-Sr isochron with improvement of the precision on the 87 Sr/ 86 Sr for extraterrestrial materials (here for ~ 4.55 Ga old eucrites, Birck et al. 1978). We assumed an error of 1% on ⁸⁷Rb/⁸⁶Sr as stated in Birck et al. (1978).

b. Improvement on the uncertainty of the age determined from a Sm-Nd isochron with

- improvement of the precision on the ¹⁴³Nd/¹⁴⁴Nd for terrestrial materials (here for 2.76 Ga old
- samples from Kambalda, Chauvel et al. 1985). We assumed an error of 0.2% on the ¹⁴⁷Sm/¹⁴⁴Nd
- as estimated in Chauvel et al. (1985).

