Ruthenium isotopic fractionation in primitive achondrites: Clues to the early stages of planetesimal melting

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1 ABSTRACT

2 Primitive achondrites derive from the residual mantle of incompletely differentiated planetes-3 imals, from which partial silicate and metallic melts were extracted. As such, primitive 4 achondrites are uniquely useful to examine the early stages of planetesimal melting and dif-5 ferentiation. To better understand the nature of this early melting and melt segregation as well 6 as the nature of the melts involved, we obtained mass-dependent Ru isotopic compositions of 7 17 primitive achondrites, including winonaites, acapulcoite-lodranites, ureilites, brachinites, 8 and two ungrouped samples. Most primitive achondrites with subchondritic Ru concentrations 9 are characterized by heavy Ru isotopic compositions relative to chondrites, likely reflecting 10 the extraction of isotopically light partial metallic melts. While the segregation of early-11 formed S-rich partial Fe-Ni-S melts likely had no effect on the Ru isotope compositions, ex-12 traction of S-free partial metallic melts at higher temperatures after removal of the early formed S-rich partial melts provides a viable mechanism for producing the observed Ru iso-13 14 topic fractionation and fractionated highly siderophile element ratios among primitive achon-15 drites. Together, these observations indicate that differentiation of primitive achondrite parent 16 bodies involved the segregation of distinct partial metallic melts over a range of temperatures, 17 and that these melts ultimately formed a partial core with fractionated and light Ru isotopic 18 composition. This contrasts with the unfractionated Ru isotope signatures previously estimat-19 ed for bulk iron meteorite cores, which therefore indicates quantitative metal segregation dur-20 ing core formation in the iron meteorite parent bodies. The less efficient metal segregation in 21 primitive achondrite parent bodies most likely reflects lower initial amounts of heat-producing 22 ²⁶Al due to later accretion or impact disruption of the parent bodies during differentiation.

23

1. Introduction

25 The chemical differentiation of planetary bodies involves the segregation of metal and sili-26 cate melts. In terrestrial planets and also in many meteorite parent bodies, this process result-27 ed in efficient metal - silicate separation and the formation of a metallic core overlain by a silicate mantle and crust. For instance, 'magmatic' iron meteorites are thought to derive from 28 29 the cores of differentiated protoplanets (Scott and Wasson, 1975), whereas differentiated 30 achondrites, such as eucrites and angrites, sample the silicate portion of such bodies (Mittle-31 fehldt, 2014). However, there are also planetary bodies that in spite of melting and melt mi-32 gration remained incompletely differentiated, such as the parent bodies of primitive achon-33 drites. The term primitive achondrites was initially used to describe meteorites with overall 34 bulk chondritic chemical composition but textural evidence for melting, and has more recently 35 been extended to generally encompass meteorites from incompletely differentiated parent 36 bodies, including meteorites with non-chondritic compositions (Weisberg et al., 2006). More 37 specifically, primitive achondrites are thought to represent melting residues that have lost par-38 tial silicate and Fe-Ni-S melts to varying degrees (Day et al., 2012; Keil, 2014; Dhaliwal et 39 al., 2017; Keil and McCoy, 2018; Collinet and Grove, 2020a,b). According to this definition, 40 primitive achondrites include winonaites, acapulcoite-lodranites, ureilites, brachinites and 41 brachinite-like meteorites, and several ungrouped achondrites (Weisberg et al., 2006). Owing 42 to the high degree of melting inferred for ureilites and brachinites, both are sometimes also 43 classified as differentiated achondrites (Mittlefehldt, 2014), but because of their incompletely 44 differentiated nature are considered as primitive achondrites in this study.

A common feature of primitive achondrites is that the temperatures reached inside their parent bodies (~960 to ~1300 °C) were sufficiently high for partial melting of metal and silicates but remained too low for complete melting and differentiation. The distinct groups of primitive achondrites seem to differ, however, in the extent of melting and melt segregation. 49 Whereas most winonaites provide evidence for only minimal partial silicate melting (Benedix 50 et al., 1998; Benedix et al., 2005; Floss et al., 2008; Hunt et al., 2017), the acapulcoitelodranite parent body is thought to have undergone slightly larger but still small degrees of 51 52 partial melting (Mittlefehldt et al., 1996; McCoy et al., 1997a,b; Dhaliwal et al., 2017). By contrast, ureilites and brachinite-clan meteorites provide evidence for more extensive partial 53 54 melting (~20–30%), which for the ureilites occurred under reducing (Goodrich, 1992; Mittle-55 fehldt et al., 1998; Warren et al., 2006; Goodrich et al., 2007), and for the brachinites under 56 more oxidizing conditions (Day et al., 2012; Keil, 2014; Day et al., 2019). Taken together, primitive achondrites provide a record of partial melting and melt extraction during the onset 57 58 of planetesimal melting and differentiation under various conditions. Such information cannot 59 easily be retrieved from fully differentiated meteorites, where later global melting has largely 60 obliterated the signatures of earlier melting processes. This makes primitive achondrites 61 uniquely useful for studying the initial melting and chemical differentiation of planetesimals.

62 Metal-silicate fractionation during melting may result in mass-dependent isotopic varia-63 tions between melt and residue, which in turn may help assessing the nature and conditions of 64 the melting process (e.g., Shahar et al., 2011; Hin et al., 2013; Bourdon et al., 2018). For 65 primitive achondrites, the investigation of isotopic fractionations of highly siderophile ele-66 ments (HSEs) are particularly promising, because the HSEs fractionate considerably between 67 metallic components with different S contents (Rankenburg et al., 2008; Hayden et al., 2011; 68 Day et al., 2012; Horstmann et al., 2014; Dhaliwal et al., 2017). As such, isotopic fractiona-69 tion of HSEs might be expected in primitive achondrites depending on the degree of metal 70 melting and segregation. Prior studies focused on Pt and Pd isotopic fractionations in ureilites 71 (Creech et al., 2017a,b), but so far, no systematic study on the entire range of primitive 72 achondrites has been conducted, and so the extent and significance of isotopic fractionation 73 during partial melting of primitive achondrite parent bodies remain unknown.

74 Here, we present mass-dependent Ru isotopic data for 17 primitive achondrites which were 75 subject to different degrees of partial melting and melt migration. The sample set includes winonaites, acapulcoite-lodranites, ureilites, brachinites, and two ungrouped primitive achon-76 77 drites. A prior study on magmatic iron meteorites has shown that the crystallization of metallic cores results in significant Ru isotopic fractionation between early- and late-crystallized 78 79 solids, most likely reflecting isotopic fractionation between S-rich metallic melt and S-poor 80 solids (Hopp et al., 2018). As such, the investigation of mass-dependent Ru isotopic variations 81 among primitive achondrites holds considerable promise for investigating the extent and na-82 ture of partial metal melting, and the separation of distinct metallic components during the 83 onset of planetesimal differentiation.

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2. Samples and analytical methods

85 2.1. Samples

86 Samples selected for this study include 15 primitive achondrites from four different groups 87 (winonaites, ureilites, acapulcoites-lodranites, brachinites) and two ungrouped primitive 88 achondrites (Table 1). All samples are cold or hot desert finds, but a previous study has shown 89 that bulk HSE abundances and inter-element ratios in this type of meteorites are not signifi-90 cantly affected by terrestrial weathering (Hyde et al., 2014). Furthermore, there is no differ-91 ence in the mass-dependent Ru isotopic signatures of chondrite falls and finds (Hopp and 92 Kleine, 2018), and so we do not expect terrestrial weathering to have altered the Ru isotopic 93 compositions of the samples of this study. Terrestrial alteration, however, may hamper the 94 identification of HSE carrier phases (i.e., metal or sulfides) in primitive achondrites (Crossley 95 et al., 2020), but this is not relevant for this study, because only bulk samples were investigat-96 ed.

Hammadah al Hambra 193 (HaH 193) is the only winonaite investigated in this study. This
sample displays no geochemical evidence for silicate melt extraction, contains up to ~27
vol.% of Fe-Ni metal, and ~3 vol.% of troilite. The Fe-Ni metal is mostly present as blebs and
veins, indicating that temperatures above the Fe-Ni-S cotectic were reached (Hunt et al.,
2017).

102 The four acapulcoite-lodranites of this study comprise two acapulcoites (Dhofar 125 and MET 01195) and two lodranites (NWA 7474 and GRA 95209). Although GRA 95209 is offi-103 104 cially classified as a lodranite, it was recently described as a transitional acapulcoite-lodranite 105 based on its composition and enrichment in HSEs (Dhaliwal et al., 2017; Keil and McCoy, 106 2017). Samples MET 01195 and GRA 95209 contain ~4 to 7 vol.% Fe-Ni metal and ~2.4 to 4 107 vol.% troilite. The major carrier of HSEs in these meteorites is Fe-Ni metal, which is enriched 108 by a factor of 20-300 relative to associated troilite grains (Dhaliwal et al., 2017). The presence 109 of metal veins and drainage networks in these samples provide evidence for local migration 110 and segregation of Fe-Ni metal and S-rich partial melts, which resulted in local depletions and 111 enrichments of these melts. Such accumulation of Fe-Ni metal has not only been observed in 112 transitional acapulcoite-lodranites, but also in one acapulcoite (MET 01195) (Dhaliwal et al., 113 2017).

The seven ureilites of this study are all desert finds, three of which (DaG 319, Dhofar 115 1519, NWA 7630) have previously been investigated for their elemental HSE systematics (Budde et al., 2015; Rankenburg et al., 2008). These samples have variable, chondritic to subchondritic Ru concentrations. In ureilites, the HSEs are hosted in various metallic phases, the most abundant of which is metal along silicate grain boundaries (~1-3 vol.%). Besides this grain boundary metal, spherules consisting of cohenite, metal, and sulfides can be found enclosed in silicates (Goodrich et al., 2013).

121 Two of the three brachinites of this study were previously investigated for their elemental 122 HSE systematics (NWA 3151, NWA 4882) and display chondritic to subchondritic Ru con-123 centrations (Day et al., 2012; Crossely et al., 2020). The most abundant HSE carrier in brachinites is troilite (up to 6 vol.%) followed by metal grains (up to ~2 vol.%) (Keil, 2014; 124 125 Crossley et al., 2020). However, the HSE inventory of these samples is typically controlled by 126 metal grains, which are characterized by much higher HSE concentrations than troilite (Day et 127 al., 2012). Interestingly, NWA 4882 contains only minor amounts of Fe-Ni metal, so that the 128 main HSE carrier in this sample is pyrite, the dominant sulfide phase of this sample (Crossley 129 et al., 2020). The initial metal content of NWA 4882, and the relationship between metal and 130 pyrite in this sample are unclear (Crossley et al., 2020).

131 Of the two ungrouped achondrites of this study, NWA 6112 has petrographic and miner-132 alogical properties as well as O isotopic compositions similar to brachinite clan meteorites 133 (Hasegawa et al., 2019), and may derive from the same or a similar parent body (Day et al., 134 2019). The other ungrouped primitive achondrite NWA 8548 of this study displays O isotopic 135 affinities to CR chondrites (Greenwood et al., 2017) and contains abundant metal and sulfide. 136 The nucleosynthetic Mo and Ru isotope anomalies of this sample are similar to other carbo-137 naceous meteorites, indicating that NWA 8548, unlike all other samples of this study, derives 138 from the carbonaceous (CC) meteorite reservoir, i.e., the outer solar system (Hopp et al., 139 2020).

140 2.2. Sample preparation

The samples (1 – 5 g) were cut using a diamond saw, cleaned with SiC abrasives and deionized water in an ultrasonic bath, and crushed to fine powders in an agate mortar. About 0.3 to 1 g of each sample powder was digested using reverse *aqua regia* inside sealed Carius tubes at 220 °C for 2 days (Shirey and Walker, 1995; Hopp et al., 2016). Bulk meteorites dis-

145 play variable nucleosynthetic Ru isotope anomalies that result predominantly from the hetero-146 geneous distribution of s-process Ru among meteorites (Chen et al., 2010; Fischer-Gödde et 147 al., 2015; Fischer-Gödde and Kleine, 2017; Bermingham et al., 2018). Determining mass-148 dependent Ru isotopic fractionations, therefore, requires additional measurements of the nu-149 cleosynthetic Ru isotope anomaly for each sample. For most primitive achondrites of this 150 study, nucleosynthetic Ru isotopic compositions have been reported by Hopp et al. (2020), 151 and for three ureilites the Ru isotope anomalies were determined as part of this study. To this 152 end, nucleosynthetic isotope anomalies and mass-dependent isotopic signatures were meas-153 ured either on aliquots of the same sample solutions or on a different digestion of the same 154 bulk powder. For the former, aliquots were therefore only spiked after Carius tube digestion 155 (and not as usually done before). We have previously shown that for chondrites that contain 156 presolar grains it is essential that the spiked and unspiked analyses are made on aliquots of the 157 same digestion (Hopp and Kleine, 2018), because the Ru isotope anomalies may vary between 158 different Carius tube digestions (Fischer-Gödde et al., 2015). However, this is not a problem 159 for equilibrated chondrites (petrologic types 5-6) or primitive achondrites, because thermal 160 metamorphism and melting on their parent bodies destroyed all presolar grains. Note that 161 Goderis et al. (2015) found variable nucleosynthetic Os isotope anomalies in ureilites digested 162 inside Carius tubes, but this variability was interpreted to reflect nucleosynthetic Os isotope 163 variability inside the ureilite parent body, and not incomplete digestion of presolar phases

After digestion, the sample solutions were transferred into 50 ml centrifuge tubes and centrifuged for 20 minutes to separate and remove un-dissolved silicates. Following centrifugation, the solution was split into spiked (~35%) and unspiked (~65%) aliquots and transferred into separate 60 ml Savillex PFA beakers. The spiked aliquots were mixed with appropriate amounts of a 98 Ru- 101 Ru double spike and equilibrated for 24 hours in 6 M HCl at 120 °C. This procedure has been tested using iron meteorites (Hopp et al., 2018) and chondrites (Hopp 170

and Kleine, 2018) and has been shown to result in accurate and reproducible Ru isotopic data.

171 All labware for unspiked and spiked aliquots were always kept strictly separate.

172 2.3. Chemical separation of Ru

173 The chemical separation of Ru from both the spiked and unspiked aliquots followed the 174 methods outlined in Hopp and Kleine (2018) and is only briefly repeated here. After diges-175 tion, all sample solutions were dried at 100 °C on a hot plate and re-dissolved twice with 10 176 ml of 6 M HCl. This procedure ensures complete removal of HNO3 from the sample solu-177 tions. After conversion into chloride form, the samples were re-dissolved in 10 to 50 ml of 0.2 178 M HCl and loaded onto cation exchange columns filled with 10 ml pre-cleaned BioRad AG 179 50W-X8 (100-200 mesh) resin (Fischer-Gödde et al., 2015). On these columns, the bulk of 180 the HSE was eluted in a total volume of 14 ml 0.2 M HCl, while the major elements (i.e., Fe 181 and Ni) remain adsorbed on the resin. The HSE fractions were dried on a hotplate at 110 °C 182 and re-dissolved in 1 ml 0.2 M HCl + 10% Br₂, before loading onto columns filled with 0.25 183 ml BioRad Macro-Prep DEAE resin. Ruthenium and Mo were eluted in 6 ml of the same so-184 lution, whereas Pd is quantitatively adsorbed on the resin as a bromine complex and is subse-185 quently eluted using 6 M HCl. The Ru fractions were dried and re-dissolved three times using 186 10 ml 1 M HF. To remove remaining Zr and Mo, the Ru fractions were dissolved in 7 ml 1 M 187 HF and were loaded onto anion exchange columns filled with 2 ml of pre-cleaned BioRad AG 188 1-X8 (100-200 mesh) resin (Burkhardt et al., 2011). Ruthenium is then eluted in 14 ml 1 M 189 HF, whereas Zr and Mo remain adsorbed onto the resin. The final Ru fractions were dried and 190 re-dissolved in 0.5 ml 0.28 M HNO₃. This procedure results in pure Ru fractions with Mo/Ru 191 <0.0005, Zr/Ru <0.005 and Pd/Ru <0.001, all of which are sufficiently low to allow for reliable correction of interferences on ⁹⁶Ru, ⁹⁸Ru, ¹⁰⁰Ru, ¹⁰²Ru and ¹⁰⁴Ru. Finally, the overall Ru 192 yield of the chemical separation varies between ~60 and ~90%. The Ru blank is 49 ± 33 pg 193

Ru (1 s.d.; n=5) and hence insignificant, given that more than 70 ng Ru was analyzed for eachsample.

196 2.4. Mass spectrometry and data reduction

197 All Ru isotope measurements were performed using the ThermoScientific Neptune Plus 198 MC-ICPMS at the Institut für Planetologie in Münster. To avoid any cross contamination, 199 different introduction systems, nebulizers, and cones were used for the measurement of spiked 200 and unspiked samples. All samples and standards were dissolved in 0.28 M HNO₃ and the 201 solutions were introduced into the mass spectrometer using an CETAC Aridus II desolvating 202 system combined with a 70 µl/min ESI PFA nebulizer for spiked samples and a Savillex C-203 Flow nebulizer with a 50 µl/min uptake rate for unspiked samples. The formation of oxides, measured as CeO/Ce, was reduced to <1% through the addition of N₂ to the sample gas. All 204 205 solutions were measured at concentrations of ~100 ppb Ru using conventional Ni H cones. Ion beams were simultaneously collected in static mode for all seven stable Ru isotopes (⁹⁶Ru, 206 ⁹⁸Ru, ⁹⁹Ru, ¹⁰⁰Ru, ¹⁰¹Ru, ¹⁰²Ru, ¹⁰⁴Ru) together with ⁹⁷Mo and ¹⁰⁵Pd as interference monitors. 207 Ruthenium masses were measured using Faraday cups connected to $10^{11} \Omega$ feedback resistors, 208 and the ion beams at 97 Mo and 105 Pd were collected using $10^{12} \Omega$ feedback resistors. Spiked 209 210 sample measurements comprised 50×8.2 s integrations of the ion beams and consumed ~70 211 ng Ru. Measurements of unspiked samples comprised 100×8.2 s integration and consumed 212 ~100 ng Ru for a single measurement. The baselines were measured on peak with 40×4.2 s 213 integrations on a solution blank prior each measurement. The unspiked sample analyses were 214 bracketed by measurements of an in-house Ru solution standard (Alfa Aesar Ru), and ion 215 beam intensities of samples and standards were matched to within better than 10%. Mass bias was corrected by internal normalization to 99 Ru/ 101 Ru = 0.7451 (Chen et al., 2010) using the 216 217 exponential law. The internally normalized Ru isotopic compositions are reported in the ε - notation, i.e., the parts-per-10,000 deviation of the ¹⁰⁰Ru/¹⁰¹Ru ratio from the average value
obtained for the bracketing standards.

The mass-dependent Ru isotopic data are reported as permil deviations relative to the composition of an Alfa Aesar standard solution (RuCl₃; Lot # 61300952) as follows:

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$$\delta^{102/99} Ru = ({}^{102/99} Ru_{sample} / {}^{102/99} Ru_{standard} - 1) \times 10^3$$
(1)

Data reduction and calculation of $\delta^{102/99}$ Ru values was performed off-line as described in Hopp et al. (2016), using either the 'double spike toolbox' (Rudge et al., 2009) or the geometrical approach described in Siebert et al. (2001). The four isotopes used in the inversion are 98 Ru, 99 Ru, 101 Ru, and 102 Ru. Both data reduction schemes were used and yielded identical results. The data reduction provides the natural fractionation factor α , from which the massdependent Ru isotopic composition of a sample is calculated as follows:

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$$\delta^{102/99} Ru_{meas.} = -1000 \times (\alpha_{sample} - \alpha_{standard}) \times \ln(m_{102}/m_{99})$$
(2)

where m_{102} and m_{99} are the atomic weights of 102 Ru and 99 Ru, and $\alpha_{standard}$ is the mean composition measured for the spiked Alfa Aesar standard solution in each analytical session.

The external reproducibility of the Ru stable isotope measurements was estimated to be $\pm 0.05\%$ (2 s.d.; n=20) for $\delta^{102/99}$ Ru, based on repeated measurements of spiked Ru standard solutions, Ru doped geochemical reference materials (BHVO-2, BCR-2, UB-N) (Hopp et al., 2016), and by seven replicate digestions of an Allende (CV3) chondrite powder (Hopp and Kleine, 2018).

3. Results

238 *3.1. Ruthenium concentrations*

The Ru concentration data for primitive achondrites obtained by isotope dilution are summarized in Table 1. Several samples of this study have previously been analyzed for Ru (and

241 other HSE) concentrations and, in general, the results of these studies are in good agreement. 242 A direct comparison of these data is difficult, however, because the HSE concentrations dis-243 play substantial intra-sample heterogeneity. This most likely reflects the heterogeneous distri-244 bution of metal, the predominant host of HSEs in primitive achondrites, at the sampling scale 245 (Keil, 2014, Keil and McCoy, 2018). This problem is exacerbated by the small sample sizes 246 of a few tens of milligrams used in most prior studies. Note that although we used larger sam-247 ples sizes (Table 1), the Ru concentrations may still not be representative for the true bulk 248 rock.

249 The range of Ru concentrations obtained for the primitive achondrites of this study is con-250 sistent with the range reported in prior studies for the same or similar samples. For instance, 251 for the two acapulcoites (Dhofar 125, MET 01195) and the lodranite NWA 7474 we obtained 252 near chondritic Ru concentrations (Fischer-Gödde et al., 2010; Horan et al., 2003), whereas 253 the transitional acapulcoite-lodranite GRA 95209 is highly enriched in Ru (~2480 ppb). These 254 results are in good agreement with those of a prior study on the same samples (Dhaliwal et al., 255 2017). Likewise, a Ru concentration of 903 ng/g for the winonaite HaH 193 is in the range of 256 chondritic Ru concentrations, consistent with the inferred minimal melt loss from winonaites 257 (Hunt et al., 2017). The ureilites of this study have Ru contents between 70 to 460 ng/g, which 258 is consistent with the range of concentrations observed in prior studies (Rankenburg et al., 259 2008; Budde et al., 2015). For the ureilite DaG 319, Rankenburg et al. (2008) reported slight-260 ly higher Ru concentrations (317 and 342 ng/g) than determined in this study (249 ng/g Ru), 261 and this discrepancy most likely reflects the heterogeneous distribution of HSE-rich carriers 262 in this polymict sample. For ureilite Dhofar 1519, the Ru concentrations obtained in this study 263 (461 ng/g) and by Budde et al. (2015) (494 ng/g) are in reasonably good agreement. Further-264 more, Ru concentrations between 189 and 868 ng/g for brachinites and 1683 ng/g for NWA 265 6112, which is similar to brachinite-like meteorites, are consistent with the range of Ru con266 centrations reported for brachinite clan meteorites (Day et al., 2012). The Ru concentration of 267 NWA 4882 determined in this study (189 ng/g) is in excellent agreement with a recently re-268 ported value of 191 ng/g for this sample (Crossley et al., 2020). Finally, the Ru concentration 269 of 536 ng/g for NWA 8548, which is the only carbonaceous achondrite investigated in this 270 study (Hopp et al., 2020), falls within the range of Ru concentrations for carbonaceous chon-271 drites (Fischer-Gödde et al., 2010; Horan et al., 2003).

272 3.2. Mass-dependent Ru isotopic compositions

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273 The primitive achondrites of this study exhibit variable nucleosynthetic Ru isotope anoma-274 lies (Table 2), which arise from the heterogeneous distribution of presolar components at the 275 bulk meteorite scale (Hopp et al., 2020). Obtaining the true mass-dependent Ru isotopic com-276 position for these samples, therefore, requires correction for the nucleosynthetic isotope 277 anomalies because the double spike inversion assumes a purely mass-dependent origin (fol-278 lowing the exponential law) for the isotopic difference between samples and standard. Previ-279 ous studies used a linear correlation of modeled nucleosynthetic isotope anomalies (i.e., ϵ^{100} Ru) and the measured $\delta^{102/99}$ Ru for the correction (Hopp et al., 2018; Hopp and Kleine, 280 281 2018):

$$\delta^{102/99} Ru_{\text{corr.}} = \delta^{102/99} Ru_{\text{meas.}} - (-0.092) \times \epsilon^{100} Ru$$
(3)

~ 102/00

283 This correction method is valid only if the nucleosynthetic Ru isotope anomalies are pre-284 dominantly caused by variation in s-process nuclides. Although prior studies have shown that 285 this is the case for almost all meteorites, the Ru isotope anomalies of some primitive achondrites, and especially of brachinites (Hopp et al., 2020), may also reflect the heterogeneous 286 287 distribution of p- and/or r-process Ru nuclides. We have, therefore, also applied a different 288 correction approach, in which the measured unspiked isotopic compositions corrected for 289 mass-dependent fractionation by internal normalization is used in the double spike inversion

instead of the Alfa Aesar standard (Hopp et al., 2016). In this case, the difference between the 290 291 isotopic compositions determined from the double spike measurements and the internally-292 normalized, unspiked measurements are solely mass-dependent. For both correction methods 293 uncertainties of unspiked and spiked measurements are propagated and a 20% uncertainty was 294 assumed on the modeled slope for the correlation with *s*-process variations (equation 3). Both correction methods result in indistinguishable corrected $\delta^{102/99}$ Ru values to within <0.02 % 295 296 (Table 1; Fig. 1), demonstrating that both methods are valid and provide accurate mass-297 dependent Ru isotopic compositions.

The corrected $\delta^{102/99}$ Ru values of the primitive achondrites reveal that many of them are enriched in heavy Ru isotopes relative to chondrites (Fig. 2; Table 1). These samples also tend to have subchondritic Ru concentrations (Fig. 3). By contrast, the $\delta^{102/99}$ Ru of some primitive achondrites overlaps with the chondritic value (Fig. 2, 3), and these samples typically have chondritic or superchondritic Ru abundances, although the $\delta^{102/99}$ Ru values of two ureilites (NWA 6378, NWA 6399) are not resolved from the chondritic value despite their subchondritic Ru concentrations.

4. Discussion

306 *4.1. Comparison of mass-dependent Ru isotope variations among meteorites*

Mass-dependent dependent isotope variations among meteorites may reflect a multitude of processes before and after accretion of their parent bodies. For instance, condensation and evaporation processes in the solar nebula may lead to isotopic fractionation and, ultimately, to distinct mass-dependent isotopic compositions among bulk meteorites (Dauphas et al., 2015; Hellmann et al., 2020). Mass-dependent isotope variations may also be induced by processes on the parent bodies, such as impact-induced volatilization or magma degassing (e.g., Moynier et al., 2010; Hin et al., 2017; Young et al., 2019), fractional crystallization of melts (Hopp et al., 2018; Bonnand and Halliday, 2018; Ni et al., 2020), and fractionation between co-existing melts and residual solids during partial melting (Creech et al., 2017a,b). Thus, before discussing the origin of mass-dependent Ru isotope variations among primitive chondrites in more detail, we first compare them to Ru isotope fractionations reported for other groups of meteorites in prior studies.

319 Enstatite, ordinary, and carbonaceous chondrites have uniform mass-dependent Ru isotopic 320 compositions, indicating that processes within the solar nebula, even under very different re-321 dox conditions, did not result in significant Ru isotopic fractionation (Hopp and Kleine, 2018). This observation together with the estimated chondritic $\delta^{102/99}$ Ru for the bulk cores of 322 323 the IIAB, IID, IIIAB, and IVA iron meteorite parent bodies (Hopp et al., 2018) reveals that 324 significant Ru isotopic fractionation among most bulk planetary bodies is not expected. The 325 heavy Ru isotopic composition of primitive achondrites, therefore, does not seem to be inher-326 ited from their precursor material, but more likely is the result of processes on their parent 327 bodies.

The only bulk object that has an estimated non-chondritic and heavy initial $\delta^{102/99}$ Ru is the 328 329 IVB iron meteorite parent body, which may reflect oxidative evaporation prior to core crystal-330 lization (Walker et al., 2008; Hopp et al., 2018). However, whereas the IVB iron meteorites 331 are among the most strongly volatile-depleted materials known, primitive achondrites are 332 thought to derive from volatile-undepleted parent bodies (Day et al., 2012; Day et al., 2019; Collinet and Grove, 2020a). Thus, the heavy $\delta^{102/99}$ Ru values of primitive achondrites do not 333 334 seem to be related to Ru loss during oxidative evaporation of the precursor material or degas-335 sing from metallic magmas. Moynier et al. (2010) observed increasingly heavier Zn isotopic 336 compositions with decreasing Zn content for ureilites and argued that this reflects impact-337 induced volatilization of Zn and associated diffusion-limited Zn isotopic fractionation. However, the ureilites investigated in the present study show no clear correlation between $\delta^{102/99}$ Ru and Ru concentration (Fig. 3). This observation combined with the much more refractory character of Ru compared to Zn suggests that the rather uniform and heavy Ru isotopic compositions of primitive achondrites are not the result of impact volatilization and associated loss of Ru.

343 Hopp et al. (2018) have shown that solidification of the metallic cores of iron meteorite 344 parent bodies resulted in increasingly heavier Ru isotopic compositions with progressive frac-345 tional crystallization. This most likely reflects the extraction of isotopically light Ru into the 346 crystallizing solids, which, as crystallization proceeded, led to an increasingly heavier isotopic 347 composition of the remaining melt and late-crystallized solids. Sulphur is incompatible in 348 solid metal and, therefore, became enriched in the remaining melt during crystallization. As 349 such, the iron meteorite data suggest that S-poor solid metal is isotopically light for Ru com-350 pared to co-existing S-rich metallic melt (Hopp et al., 2018). The Ru isotopic data for iron 351 meteorites, therefore, suggest that Ru partitioning among metallic melts and remaining solid 352 metal and sulfide components may lead to Ru isotopic fractionation. Such processes were also 353 important in the evolution of primitive achondrites (e.g., Day et al., 2012; Dhaliwal et al., 2017), suggesting that their heavy $\delta^{102/99}$ Ru is related to melting of metal and melt segregation 354 355 during the partial differentiation of their parent bodies.

356 *4.2. Ruthenium isotopic fractionation during partial differentiation*

The first melts to form during planetary differentiation are a Fe-Ni-S cotectic melt (940– 988 °C; Kullerud, 1963; Hsieh and Chang, 1987) and, at a slightly higher temperature, a silica- and alkali-rich silicate melt (1040–1080 °C; Collinet and Grove, 2020b). Provided that the total melt fraction was sufficiently high, these melts migrated upwards (silicate melt) and downwards (Fe-Ni-S melt), forming a mantle and core. In the parent bodies of primitive 362 achondrites, however, this process of melt migration did not proceed to completion, and so 363 depending on the extent of melting and melt migration, source regions with different degrees 364 of silicate and Fe-Ni-S melt extraction were produced. For instance, whereas brachinites and 365 ureilites derive from source regions that lost larger fractions of silicate and Fe-Ni-S melts 366 (Goodrich et al., 2007; Day et al., 2012), acapulcoites-lodranites seem to have lost smaller 367 amounts of these partial melts (McCoy et al., 1997b; Dhaliwal et al., 2017). By contrast, 368 winonaites remained largely unmolten, and so the small fractions of partial melt produced 369 could not be extracted from their parent body (Hunt et al., 2017).

370 As a highly siderophile element, Ru in primitive achondrites is quantitatively hosted in 371 metal and sulfide components (e.g., Day et al., 2012; Dhaliwal et al., 2017). The elemental 372 HSE systematics and Ru isotopic composition of primitive achondrites, therefore, reflect the 373 history of metal-sulfide fractionation during the petrogenesis of these meteorites. Prior studies 374 have shown that the elemental HSE systematics of acapulcoites-lodranites (Dhaliwal et al., 375 2017), ureilites (Rankenburg et al., 2008; Horstmann et al., 2014), and brachinites (Day et al., 376 2012) are generally consistent with the extraction and redistribution of partial Fe-Ni-S melts. 377 However, these studies also reveal that a single-stage S-rich melt segregation cannot account 378 for the complex HSE patterns of some brachinites, which instead seem to require the addi-379 tional removal of later stage S-poor metallic melts (Day et al., 2012). The presence of S-poor 380 or S-free metallic melts is also consistent with the heterogeneous distribution of Fe-Ni metal 381 and networks of S-poor metallic veins in acapulcoites-lodranites (Dhaliwal et al., 2017), and 382 with the HSE systematics of ureilites, which seem to require the presence of distinct metallic 383 melts (Rankenburg et al., 2008; Hayden et al., 2011). Together, these studies indicate that the 384 successive segregation and redistribution of S-rich and S-free partial Fe-Ni melts are the dom-385 inant processes affecting the elemental HSE systematics of primitive achondrites. Below, we

will, therefore, evaluate how these two processes may have affected the Ru isotopic composi-tion of primitive achondrites.

388 4.2.1 Modeling Ru isotopic fractionation during partial melting in the Fe-Ni-S system

389 To quantitatively assess the extent of Ru isotopic fractionation between solid and liquid 390 metal, we calculated the expected variation of $\delta^{102/99}$ Ru as a function of melt depletion. Mass 391 balance mandates that the ¹⁰²Ru/⁹⁹Ru ratio of the starting material, *R*₀, is given by:

392
$$R_0 = \frac{F[Ru]_L R_L + (1-F)[Ru]_S R_S}{[Ru]_0}$$
(4)

393 where *F* is the mass fraction of melt, and the subscripts *L* and *S* denote liquid and solid metal, 394 respectively. The Ru concentration in the solid metal, $[Ru]_S$, is given by the batch melting 395 equation:

396
$$[Ru]_{S} = \frac{D[Ru]_{0}}{F(1-D)+D}$$
(5)

where *D* is the solid–liquid partition coefficient for Ru. Substituting $[Ru]_S$ in equation 4 and introducing the isotopic fractionation factor $\alpha = R_S/R_L$ then provides the final equation with which the expected isotopic fractionation (i.e., the relative deviation of R_S from the starting composition R_0) as a function of melt depletion (i.e., *F*) can be calculated:

401
$$\frac{R_S}{R_0} = \frac{\alpha(F(1-D)+D)}{F+\alpha(1-F)D}$$
(6).

Thus, calculating the magnitude of isotopic fractionation in the residual metal in this manner requires knowledge of the partition coefficient D(Ru) and the isotope fractionation factor α . Note that the batch melting equation (eq. 5) not only applies to the partitioning of Ru between solid and liquid metal, but also to the partitioning between two immiscible metallic liquids. This is important because Hayden et al. (2011) proposed that the HSE systematics of ureilites reflect partitioning between S-rich and S-poor metallic melts. As such, a similar process may also be relevant for the evolution of other primitive achondrites (see below). 409 The isotopic fractionation factor α for Ru between co-existing solid and liquid metal phas-410 es is unknown. It is also unclear whether α would be different for solid-liquid and liquidliquid partitioning. Nevertheless, the heavy $\delta^{102/99}$ Ru observed for primitive achondrites re-411 quires that the extracted metallic melts were isotopically light for Ru, to produce the comple-412 413 mentary heavy isotopic composition in the residual metal remaining in the primitive achon-414 drites, i.e., α must be >1. We, therefore, assumed α values of 1.001 and 1.0005 in the calcula-415 tion, but note that the chosen values mainly serve to illustrate the effect of α and D(Ru) on the 416 degree of melt depletion F required to produce the isotopic fractionations observed among primitive achondrites. 417

418 Experimental studies on the partitioning behavior of Ru between solid and liquid metal and 419 between co-existing immiscible metallic melts indicate that D(Ru) is larger for solid-liquid 420 (~100) than for liquid–liquid (~50) partitioning (Hayden et al., 2011). For solid–liquid parti-421 tioning, D(Ru) also depends on the minor element content (i.e., S, C, and P) of the melt 422 (Chabot and Jones, 2003), which in turn depends on the temperature of melting (Kullerud, 423 1962, Hsieh and Chang, 1987). As the partitioning behavior of the HSEs mainly depends on 424 the S content of the melt, whereas the influence of C and P is much smaller (Chabot, 2004), 425 we used the simplified Fe-Ni-S system to estimate the evolution of the S content in the partial 426 metallic melts and the corresponding change of D(Ru). Chabot et al. (2017) experimentally 427 determined the partitioning of Ru and other siderophile elements in the Fe-Ni-S system and 428 provide a parameterization of self-consistent values that can be used to model the evolution of 429 D(Ru) as a function of the S content in the melt as follows (Chabot and Jones, 2003):

430
$$\ln(D(E)) = \ln(D_0) + \beta_E * \ln(\frac{1 - 2 * X(S)}{1 - X(S)})$$
(7)

431 where D_0 is the solid metal-liquid metal partition coefficient in the S-free Fe-Ni system 432 with $D_0(Ru) = 1.18\pm0.05$ and β_E is an experimentally determined element specific constant 433 with $\beta_{Ru} = -3.89\pm0.37$. 434 To illustrate the effect of the composition of the system on D(Ru) we evaluated the change 435 of the molar fraction of S, X(S), as a function of temperature in the pure Fe-S system and in the Ni-rich endmember system Fe_{0.5}Ni_{0.5}-S (Hsieh and Chang, 1987). The appropriate metal 436 437 compositions in primitive achondrites likely are between these two endmember compositions. 438 The relevant temperatures for partial metal melting in primitive achondrite parent bodies 439 range from the eutectic temperature up to the estimated peak temperatures of ~ 1300 °C for 440 ureilites and brachinites (Keil, 2014; Goodrich et al., 2015). Figure 4 shows that D(Ru)441 changes drastically as a function of X(S) (i.e., temperature) and Ni content. For instance, at a 442 given temperature, D(Ru) is generally lower in the Fe-Ni-S compared to the pure Fe-S system, 443 and it may range from >100 for the first eutectic melts to <10 for partial melts at higher tem-444 peratures. Finally, D(Ru) is lowest in S-free systems, with a value of only ~1.18. As we will 445 show below, the strong dependence of D(Ru) on the S content of the melt is crucial for under-446 standing the underlying mechanism that produced the heavy Ru isotopic compositions ob-447 served in some primitive achondrites.

448 4.2.2 Ru isotope fractionation during Fe-Ni-S melt extraction

One possible explanation for the heavy $\delta^{102/99}$ Ru of primitive achondrites during partial melting is isotopic fractionation between S-rich partial metallic melt and residual, S-poor metal. As noted above, the HSE systematics of primitive achondrites indicate that Fe-Ni-S melt extraction occurred in the parent bodies of brachinites, ureilites, and acapulcoiteslodranites, and so it is important to assess how this process affected the Ru isotopic composition of these samples.

Figure 5a shows the calculated evolution of $\delta^{102/99}$ Ru as function of *F* using assumed α values of 1.0005 and 1.001, and using the D(Ru) values as determined for the Fe-S and Fe-Ni-S systems (Fig. 4). The calculations reveal that extraction of a eutectic Fe-Ni-S melt (i.e., X(S)~0.45) has no effect on the Ru content and isotopic composition of the residual metal, which reflects the high D(Ru) under these conditions. Even at higher temperatures of up to ~1300 °C, high fractions (>0.5) of S-rich partial metallic melt would have to be extracted to produce the $\delta^{102/99}$ Ru values observed for some primitive achondrites (Fig. 5a). The observed magnitude of isotopic fractionation would only be consistent with a lower degree of melting for hightemperature melts produced for extremely Ni-rich starting compositions (i.e., in the Fe_{0.5}Ni_{0.5}-S system), but such compositions are not appropriate for primitive achondrites.

The high degree of melting required to account for the heavy $\delta^{102/99}$ Ru of primitive achon-465 466 drites by Fe-Ni-S melt extraction appear unrealistic, given that the HSE systematics of espe-467 cially the acapulcoites-lodranites indicate a rather low degree of Fe-Ni-S melt extraction of 468 only a few percent (Dhaliwal et al., 2017). This discrepancy may be resolved by using larger 469 values for α , but in this case the isotopic fractionation between solid and liquid metal (or be-470 tween two immiscible metallic liquids) would have to be unreasonably large. Moreover, re-471 gardless of the actual value of α , producing the fairly narrow range of heavy Ru isotopic com-472 positions among primitive achondrites from different groups (Fig. 3) would require broadly 473 similar degrees of partial metal melting and extraction. This is inconsistent, however, with the 474 large variability of Fe-Ni-S melt extraction inferred from the HSE systematics of brachinites, 475 ureilites, and acapulcoites-lodranites (Hayden et al., 2011; Day et al., 2012; Dhaliwal et al., 476 2017; Rankenburg et al., 2008).

477 A final problem for producing the heavy Ru isotopic composition of primitive achondrites 478 by Fe-Ni-S melt extraction is that the direction of isotopic fractionation is inconsistent with 479 observations from magmatic iron meteorites (Hopp et al., 2018). As noted above, the heavy 480 $\delta^{102/99}$ Ru observed for late-crystallized iron meteorites most likely reflects the continued re-481 moval of isotopically light, S-poor solids during fractional crystallization, resulting in a pro-482 gressively heavier Ru isotopic composition of the remaining, S-rich melt. Thus, S-rich metal-483 lic melt appears to be isotopically heavy compared to co-existing S-poor solid metal, which is 484 the opposite direction of isotope fractionation required for producing the heavy $\delta^{102/99}$ Ru of 485 primitive achondrites by Fe-Ni-S melt extraction.

486 Taking all these observations together indicates that the heavy $\delta^{102/99}$ Ru of primitive 487 achondrites is most likely not the result of Fe-Ni-S melt extraction. Although there is little 488 doubt that this melt extraction occurred in the parent bodies of acapulcoites-lodranites, 489 ureilites, and brachinites, it does not seem to have induced a significant Ru isotopic fractiona-490 tion. It is noteworthy that Ru isotopic data for iron meteorites suggest that Fe-Ni-S melts are 491 isotopically heavy compared to their co-existing solids, and so extraction of these melts may have produced a light Ru isotopic composition in the residual solid metal. Such light $\delta^{102/99}$ Ru 492 493 values are not observed among primitive achondrites, which may suggest that the Fe-Ni-S 494 melt extraction occurred at relatively low temperatures, where D(Ru) is so high that the ex-495 tracted melts contained no significant amounts of Ru. Alternatively, any light Ru isotope 496 composition induced during Fe-Ni-S melt extraction may also have been overprinted by later 497 fractionation processes.

498 4.2.3 Ru isotopic fractionation during extraction of S-free Fe-Ni melt

The heavy $\delta^{102/99}$ Ru of primitive achondrites may also reflect isotopic fractionation between 499 500 S-free solid and liquid metal at higher temperatures and after partial Fe-Ni-S melts were ex-501 tracted and all S consumed. It has been argued that the highly fractionated relative HSE sys-502 tematics of brachinites reflect the segregation of S-poor metallic melts (Day et al., 2012), and 503 networks of S-poor metallic veins in acapulcoites-lodranites provide direct evidence for the 504 presence and migration of such melts (Dhaliwal et al., 2017). Consequently, segregation of S-505 poor metallic melts may be a potential pathway for Ru isotope fractionation in primitive 506 achondrites.

507 One advantage of invoking the extraction of S-poor metallic melts to account for the heavy 508 $\delta^{102/99}$ Ru of primitive achondrites is that much lower degrees of melting are required. This is 509 because in the S-free Fe-Ni system D(Ru) is only ~1.18 (Chabot et al., 2017) and, hence, 510 much lower than in the Fe-Ni-S system (Fig. 4). Thus, for a given isotope fractionation factor 511 α , the extraction of S-poor Fe-Ni melt has a much stronger effect on the Ru isotopic composi-512 tion of the residual solid metal than removal of a Fe-Ni-S melt. This is illustrated in Fig. 5b, 513 which shows that for our assumed values of α the observed range of heavy Ru isotope compo-514 sitions of primitive achondrites can be reproduced by only ~10-30% melting. This estimate of 515 course directly depends on the assumed values of α , but these calculations nevertheless show 516 that the extraction of S-poor metallic liquids is a viable process for Ru isotope fractionation. 517 This combined with petrological and geochemical evidence for the migration and extraction 518 of S-poor metallic melts (Day et al., 2012; Dhaliwal et al., 2017) suggests that the heavy Ru 519 isotopic composition of primitive achondrites may indeed result from this process. We note, 520 however, that this mechanism still requires an inversed direction of Ru isotope fractionation 521 between solid and liquid metal compared to the fractionation inferred from the crystallization 522 of magmatic iron meteorites in S-bearing Fe-Ni melts. Clearly, a more quantitative assess-523 ment of this process will require the experimental determination of the Ru isotope fractiona-524 tion factor between liquid and solid metal in the S-free Fe-Ni system and a better theoretical 525 understanding of the Ru bonding environment in Fe-Ni-S systems.

526 The discussion up to this point has not considered the two samples of this study with superchondritic Ru concentrations and chondritic $\delta^{102/99}$ Ru (Fig. 3). These samples are the transi-527 528 tional acapulcoite-lodranite GRA 95209, and the ungrouped achondrite NWA 6112, which 529 displays affinities to brachinite-like meteorites. Dhaliwal et al. (2017) suggested that the high 530 HSE contents of transitional acapulcoite-lodranites result from local enrichments of S-poor 531 metallic melts that migrated through the parent bodies. In our model, these S-poor partial metallic melts would be characterized by light $\delta^{102/99}$ Ru values, such that mixing between these 532 melts with residual metal having heavy $\delta^{102/99}$ Ru may again result in the apparently unfrac-533

tionated Ru isotopic compositions of these samples. Although it may seem somewhat arbitrary that the mixing of two isotopically distinct components results in the bulk chondritic starting compositions, we note that the overall isotopic difference between S-free liquid and solid metal was likely not large, so that mixing between these two components naturally results in a composition that is close to the bulk composition.

539 *4.3 Isotopic and chemical fractionation during melting and melt migration*

540 The extraction of partial metallic melts should not only result in Ru isotope fractionation, but 541 also in decreasing Ru concentrations with increasing degree of melt depletion. However, as is 542 evident from Fig. 3, the data of this study do not define a statistically significant correlation between $\delta^{102/99}$ Ru and Ru concentration. Instead, several primitive achondrites have fairly 543 uniform $\delta^{102/99}$ Ru values but different Ru concentrations. However, the absolute abundance of 544 545 Ru (and other HSEs) in primitive achondrites likely do not solely reflect the degree of metal-546 lic melt extraction but are also affected by the migration and heterogeneous distribution of 547 distinct metal and sulfide phases. For instance, the HSE systematics of ureilites have been 548 interpreted to indicate mixing of residual solid metal with different metallic melts, possibly 549 including an impactor-derived metallic component (Rankenburg et al., 2008; Horstmann et 550 al., 2014). Such processes may have obscured a possible pre-existing correlation of Ru isotop-551 ic fractionation with Ru concentrations. Furthermore, whereas the Ru isotopic fractionation is 552 solely governed by metal phases, the absolute abundances of Ru (and other HSEs) also de-553 pends on the metal-silicate ratio and, therefore, on the amount of partial silicate melts extract-554 ed.

555 To avoid these complications, it is more useful to evaluate relative abundances of HSEs, 556 which record the partitioning of the HSEs between different Fe-Ni-S phases independent of 557 variations in absolute concentrations (Rankenburg et al., 2008; Day et al., 2012; Dhaliwal et 558 al., 2017). Moreover, some HSEs display distinct solid–liquid and liquid–liquid partitioning 559 behavior (Hayden et al., 2011). For example, the D(Pt)/D(Ru) ratio for solid-liquid and liq-560 uid-liquid partitioning is 1.57 and 0.81, respectively, so that Pt/Ru ratios can be used to dis-561 tinguish between these two fractionation mechanisms. To this end, Hayden et al. (2011) used 562 a plot Pt/Os versus Pt/Ru (Fig. 6a) to show that ureilites plot along a liquid-liquid fractiona-563 tion trend and on this basis argued that the HSE systematics of ureilites do not record the ex-564 traction of S-rich partial melts from solid metal, but rather the partitioning between a S-rich 565 and a S-poor but C-rich partial metallic melt. Surprisingly though, acapulcoites-lodranites and 566 brachinites plot along the same trend as ureilites, suggesting that all three groups of primitive 567 achondrites were subject to the same or similar fractionation processes. However, unlike the 568 ureilites, acapulcoites-lodranites and brachinites are not thought to be C-rich, so that no C-rich 569 metallic melt should have formed on their parent bodies. Interestingly, in a S-free Fe-Ni sys-570 tem the D(Pt)/D(Ru) ratio between solid and liquid metal is also 0.81 (Chabot et al., 2017), 571 which is identical to the ratio for partitioning between co-existing S-rich and C-rich metallic 572 melts. Thus, the fractionated HSE systematics of acapulcoites-lodranites, ureilites, and bra-573 chinites are consistent with the same fractionation process, namely the extraction of S-free 574 partial Fe-Ni melts, where the degree of fractionation is smallest for acapulcoites-lodranites 575 and largest for brachinites (Fig. 6a).

576 One problem of this and other models for the fractionation of HSEs in primitive achondrites is 577 that simple batch melting requires unrealistically high (>0.90) degrees of melt extraction (Rankenburg et al., 2008; Hayden et al., 2011; Day et al., 2012). Therefore, such simplified 578 579 models cannot realistically account for the complex evolution of HSEs in primitive achon-580 drites, which likely included multiple steps of melting and melt segregation (Day et al., 2012). 581 One possible scenario is incremental melting and melt extraction, but for the case described 582 here (extraction of S-free metallic melt) the partition coefficients of Os, Pt, and Ru a very 583 similar and do not change with progressive melting (Chabot et al., 2017). Thus, the required 584 degrees of melt extraction are similar to the batch melting model and still unrealistically large. 585 Nevertheless, these models allow distinguishing between different fractionation mechanisms for the HSEs and they also allow assessing whether the fractionation of elemental HSE ratios 586 587 and Ru isotopes may have had a common origin. As argued above, extraction of S-free Fe-Ni 588 melts may be the main driver for producing the heavy Ru isotopic composition of primitive achondrites, and so in this case a correlation of $\delta^{102/99}$ Ru with Pt/Ru is expected, where sam-589 ples with the most fractionated Pt/Ru should also display the heaviest Ru isotopic composi-590 591 tion. Figure 6b shows that the data of this study indeed plot along a trend of increasingly heavy $\delta^{102/99}$ Ru with decreasing Pt/Ru. This correlation is not clearly resolved, which mostly 592 reflects the overall small degree of Ru isotopic fractionation, so that the $\delta^{102/99}$ Ru values of 593 594 primitive achondrites are rarely resolved from each other. Nevertheless, samples with the lowest Pt/Ru tend to have the heaviest $\delta^{102/99}$ Ru values, as would be expected for a common 595 origin of the fractionated Pt/Ru ratios and heavy $\delta^{102/99}$ Ru by the extraction of S-free Fe-Ni 596 597 partial melts.

598 4.4 Implications for distinct differentiation histories of meteorite parent bodies

As noted above, the uniform $\delta^{102/99}$ Ru of chondrites suggests that there was little Ru isotopic 599 fractionation among bulk planetary bodies (Hopp and Kleine, 2018). The bulk $\delta^{102/99}$ Ru of 600 601 primitive achondrite parent bodies should, therefore, also be chondritic. This is also evident from the chondritic $\delta^{102/99}$ Ru of winonaites determined in this study, which are the primitive 602 603 achondrites with the lowest degree of partial melting and melt migration and, therefore, pro-604 vide a good proxy for the initial Ru isotopic composition of primitive achondrite parent bodies prior to partial differentiation. The chondritic bulk $\delta^{102/99}$ Ru of primitive achondrite parent 605 bodies combined with the heavy $\delta^{102/99}$ Ru of residual metal in their mantles then implies that 606 607 the incompletely formed metallic cores of primitive achondrite parent bodies are isotopically light for Ru. So far, this putative core material of primitive achondrite parent bodies has not 608

609 been sampled among meteorites, because there are no known iron meteorite groups that re-610 quire a fractionated and light bulk initial Ru isotopic compositions. Instead, the estimated $\delta^{102/99}$ Ru for bulk iron meteorite cores is chondritic, and only the IVB iron meteorite core has 611 an estimated fractionated and heavy $\delta^{102/99}$ Ru, which most likely reflects Ru isotopic fraction-612 613 ation during high-temperature evaporation-condensation processes in the solar nebula or de-614 gassing of the still molten core (Walker et al., 2008; Hopp et al., 2018). The lack of light bulk 615 Ru isotopic compositions in iron meteorite parent bodies implies quantitative metal segrega-616 tion during core formation, so that during differentiation the early-segregated, isotopically 617 light, and late-segregated, isotopically heavy metal, were combined again to the chondritic 618 bulk composition. These observations raise the question of why the extent of core formation 619 were different in the parent bodies of primitive achondrites and iron meteorites. Some prior studies argued that melting and melt migration halted due to exhaustion of ²⁶Al, the heat 620 621 source for melting, by silicate melt extraction (e.g., Wilson et al., 2008). However, this pro-622 cess would have likewise occurred during melting and differentiation of iron meteorite parent 623 bodies (Neumann et al., 2018) and so cannot be the cause for the distinct differentiation histo-624 ries of primitive achondrite parent bodies. The partial differentiation of these bodies, there-625 fore, either is related to their slightly later accretion, in which case they contained less heatproducing ²⁶Al than the iron meteorite parent bodies (e.g., Budde et al., 2015) or, alternative-626 627 ly, to impact disruption during differentiation, which led to a sudden stop of melting and melt 628 migration.

629 **5.** Conclusions

Primitive achondrites with subchondritic Ru concentrations and fractionated relative HSE
systematics, including acapulcoites-lodranites, ureilites, and brachinites are enriched in heavy
Ru isotopes compared to chondrites. This Ru isotopic fractionation most likely results from

633 the segregation of partial metallic melts during the early stages of parent body differentiation, 634 which removed isotopically light Ru from the source regions of primitive achondrites. Partial 635 Fe-Ni-S melts that segregated during the early stages of differentiation contained too little Ru 636 to significantly affect the Ru isotopic composition of the remaining residual metal. By con-637 trast, later-formed S-poor or S-free partial metallic melts contained more Ru, reflecting the 638 strong dependence of the solid metal-liquid metal partition coefficient of Ru on the S content 639 of the melt. The heavy Ru isotopic composition of primitive achondrites, therefore, most like-640 ly reflects the removal of isotopically light, S-poor partial metallic melts. The same process 641 also led to fractionated HSE systematics among ureilites and brachinites, which are character-642 ized by the strongest melt depletions among primitive achondrites. Together, the elemental 643 and isotopic systematics of HSEs, therefore, reveal the segregation of distinct partial metallic 644 melts of varying S content and, thus, at different temperatures during the early stages of core 645 formation.

646 The heavy Ru isotopic composition of residual metal remaining in the mantle of primitive 647 achondrite parent bodies implies that the partially formed metallic cores of these bodies are 648 isotopically light for Ru. Such putative core material has yet not been sampled, because no 649 light Ru isotopic composition of bulk planetesimal cores is required in models of the isotopic 650 fractionation during fractional crystallization of iron meteorites. As such, the lack of light Ru 651 isotopic signatures in bulk iron meteorite cores indicates quantitative metal segregation during 652 core formation in their parent bodies. The less efficient metal segregation in primitive achondrite parent bodies is most likely due to either lower initial amounts of heat-producing ²⁶Al 653 654 because of their later accretion, or impact disruption of the parent bodies during differentia-655 tion.

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- 848

849 **Figure captions**

- 850 **Figure 1:** Plot of $\delta^{102/99}$ Ru corrected for nucleosynthetic ('mass-independent') isotope anoma-
- 851 lies using two different correction methods. The correction methods are described in detail in
- 852 section 3.2. Correction I (x-axis) corrects for all mass-independent variations determined in an
- unspiked measurement (Table 2) by subtracting these variations during the data reduction of
- 854 the double spike measurements. Correction II (y-axis) uses the correlation of ϵ^{100} Ru (Table 2)
- and measured $\delta^{102/99}$ Ru assuming the nucleosynthetic isotope anomalies are predominantly
- 856 variations in *s*-process nuclides (Hopp et al., 2018, Hopp and Kleine, 2018). Final uncertain-
- ties are propagated uncertainties of unspiked and spiked measurements as well as an assumed

858 20% uncertainty on the modelled slope. Both correction methods give the same values within
859 <0.02 %.

Figure 2: Mass-dependent Ru isotopic compositions of primitive achondrites. The $\delta^{102/99}$ Ru 860 861 values are corrected for nucleosynthetic isotope anomalies according to Fig. 1 and equation 3. 862 Error bars correspond to the associated 95% confidence intervals of the sample measurements 863 (for N \geq 4) or the standard deviation (2 s.d.) of repeated analysis of Ru doped reference sam-864 ples and seven Allende digestions (for $N \leq 3$) including a propagated uncertainty induced 865 through the correction for nucleosynthetic isotope anomalies (see Table 1). Grey shaded area corresponds to the mean $\delta^{102/99}$ Ru value of chondrites (including all major groups) and the 866 867 associated 95% confidence interval (Hopp and Kleine, 2018).

Figure 3: Mass-dependent Ru isotopic compositions *vs.* the obtained Ru concentration for all investigated primitive achondrites. Samples with chondritic (ordinary - OC; enstatite - EC; carbonaceous - CC) or superchondritic Ru concentration have chondritic $\delta^{102/99}$ Ru values (except one brachinite). Primitive achondrites with subchondritic Ru content in general display heavier Ru isotopic compositions. Data of chondrite groups from Fischer-Gödde et al. (2010) and Hopp and Kleine (2018).

Figure 4: Plot of D(Ru) as a function of X(S) following the approach described by Chabot et al. (2017). The points on the calculated model line represent examples for two different compositions at different temperatures representing the temperature range observed in primitive achondrites. The fraction of S in a Fe-Ni-S partial melt depends strongly on the temperature and the composition of the system. Partial melts formed at higher temperatures will have less S ,and hence, a smaller D(Ru).

Figure 5: a) Batch-melting calculations of the expected Ru isotopic composition ($\delta^{102/99}$ Ru) in the residue as a function of melt depletion *F* and *D*(*Ru*) determined for the example compositions defined in Fig. 4 and calculated with equation 6 and 7. Solid and dashed lines are cal883 culated with an isotopic fractionation factor $\alpha = 1.0005$ (solid lines) and 1.001 (dashed lines), 884 respectively. The colors correspond to the compositions and defined in Fig. 4. The grey area displays the average chondritic $\delta^{102/99}$ Ru with corresponding 95% confidence intervals (Table 885 1). b) Batch-melting calculations in a S-free Fe-Ni system. S-poor partial metallic melts can 886 887 form at higher temperatures and after the removal of most S in early partial melts. The parti-888 tion coefficient of Ru between S-free solid and liquid metal is close to unity (Chabot et al., 889 2017). Solid and dashed lines are calculated using equation 6 using isotopic fractionation fac-890 tors $\alpha = 1.0005$ (solid lines) and 1.001 (dashed lines), respectively. Hence, isotopic fractiona-891 tion of S-poor solid and liquid metal can reproduce the observed isotopic fractionations in 892 primitive achondrites with a fraction of <0.4 of melt removal and a realistic isotopic fractiona-893 tion factor. The S-poor metallic liquid is required to be isotopically light to produce an isotop-894 ically heavy residual metal.

895 Figure 6: a) Batch-melting extraction model calculations and achondrite data for Pt/Ru vs. 896 Pt/Os (after Hayden et al., 2011). Literature data from Rankenburg et al. (2008), Dhaliwal et 897 al. (2017), Day et al. (2012) were normalized to CI chondrite composition (Fischer-Gödde et 898 al., 2010). Colored points represent samples investigated in this study for which HSE data are 899 available. The lines show the calculated concentration ratio in the residual metal for partition-900 ing between different phases. The black dashed line represents partitioning between solid 901 metal and S-rich melt. The solid black line represents partitioning between two immiscible 902 metallic melts (Fe-C and Fe-S). Tick marks indicate the fraction of S-rich liquid removed. 903 The short dashed red line represents partitioning between S-free solid metal and S-free melt (Chabot et al., 2017). **b**) Plot of $\delta^{102/99}$ Ru versus the Pt/Ru ratio of the samples investigated in 904 905 this study. No clear correlation of $\delta^{102/99}$ Ru and the Pt/Ru can be observed. However, most 906 samples with fractionated Pt/Ru ratio are isotopically heavy and the samples with the most

- 907 fractionated Pt/Ru ratio, i.e. brachinites, belong also to the samples that have the most frac-
- 908 tionated Ru isotopic composition.
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Tables

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	Wt. [g]	Nª	Ru conc.[ng/g] ^b	$\delta^{102/99}Ru_{meas.}^{c}$	δ ^{102/99} Ru _{correction} I ^d	$\delta^{102/99}Ru_{\text{corrrection II}}^{\text{e}}$
Winonaites						
Hammadah al Hambra 193	0.519	4	903	0.02 ± 0.02	0.01 ± 0.03	0.02 ± 0.03
Acapulcoite-Lodranites						
Dhofar 125 (ACA)	0.301	5	741	0.10 ± 0.02	0.09 ± 0.03	0.08 ± 0.03
MET 01195,42 (ACA)	0.251	4	783	0.14 ± 0.03	0.13 ± 0.04	0.11 ± 0.04
GRA 95209,274 (ACA-LOD)	0.296	7	2479	0.06 ± 0.02	0.03 ± 0.03	0.03 ± 0.03
NWA 7474 (LOD)	0.497	6	1120	0.06 ± 0.01	0.04 ± 0.03	0.03 ± 0.02
Ureilites						
DaG 319	0.326	2	249	0.13 ± 0.05	0.08 ± 0.06	0.09 ± 0.06
Dhofar 1519	0.265	2	461	0.10 ± 0.05	0.07 ± 0.06	0.08 ± 0.06
NWA 6356	0.358	3	339	0.10 ± 0.05	0.08 ± 0.06	0.09 ± 0.06
NWA 6378	0.377	2	180	0.05 ± 0.05	0.02 ± 0.06	0.02 ± 0.06
NWA 7630	0.365	3	460	0.15 ± 0.05	0.13 ± 0.06	0.12 ± 0.06
NWA 6399	0.358	1	105	0.07 ± 0.05	0.04 ± 0.07	0.05 ± 0.07
NWA 5938	0.351	1	72	0.14 ± 0.05	0.10 ± 0.07	0.12 ± 0.07
Brachinites						
NWA 3151	0.500	5	433	0.08 ± 0.01	0.11 ± 0.02	0.10 ± 0.02
NWA 4882	1.006	2	189	0.16 ± 0.05	0.18 ± 0.05	0.17 ± 0.05
NWA 10637	0.252	2	868	0.17 ± 0.05	0.17 ± 0.05	0.16 ± 0.05
Ungrouped Achondrites						
NWA 6112	0.269	4	1683	0.05 ± 0.01	0.01 ± 0.03	0.00 ± 0.03
NWA 8548	0.503	4	536	0.10 ± 0.02	0.00 ± 0.05	0.00 ± 0.05
Chondrites ^{\$}						
avg. Enstatite		14				0.03 ± 0.01
avg. Ordinary		26				-0.03 ± 0.02
avg. Carbonaceous		47				-0.01 ± 0.04

^a Number of analyses (N).

^b Uncertainty (2 s.d.) of individual measurements is <1%.

^e Measured Ru isotopic mass fractionation relative to an Alfa Aesar standard solution. Uncertainties correspond to the associated 95% conf. interval of the sample measurements (for N \geq 4) or the standard deviation (2 s.d.) of repeated analysis of Ru doped reference samples and seven Allende digestions (for N \leq 3); including a propagated uncertainty induced through the correction for nucleosynthetic isotope anomalies.

^d Ru isotopic mass fractionation corrected for nucleosynthetic effects by subtraction of the isotope anomalies measured in an unspiked measurement (Table 2) from the spiked measurement prior inversion. Final uncertainties are propagated uncertainties of unspiked and spiked measurements. Of note, the double spike inversion uses ⁹⁸Ru, ⁹⁹Ru, ¹⁰¹Ru, and ¹⁰²Ru, hence, any uncertainties and deviations on ⁹⁶Ru do not affected the correction of mass-dependent isotopic fractionations.

 e Ru isotopic mass fractionation corrected for nucleosynthetic effects using the correlation of ϵ^{100} Ru (Table 2) and the measured $\delta^{102/9}$ Ru assuming the nucleosynthetic isotope anomalies are predominantly variations in s-process nuclides (Hopp et al., 2018, Hopp and Kleine, 2018). Final uncertainties are propagated uncertainties of unspiked and spiked measurements as well as an assumed 20% uncertainty on the modelled slope. ^f Literature data by Hopp and Kleine (2018).

Sample	Weight (g)	N ^a	ε ⁹⁶ Ru ^b	ε ⁹⁸ Ru [⊳]	ε ¹⁰⁰ Ru ^b	ε ¹⁰² Ru ^b	ε ¹⁰⁴ Ru ^b
Winonaites							
Hammadah al Hambra 193°	0.803	4	0.52 ± 0.35	0.39 ± 0.71	-0.06 ± 0.10	0.07 ± 0.13	0.40 ± 0.23
Acapulcoite-Lodranites							
Dhofar 125 (ACA) ^c	0.504	3	0.94 ± 0.55	0.49 ± 0.41	-0.31 ± 0.08	-0.04 ± 0.03	0.54 ± 0.18
MET 01195,42 (ACA) ^c	0.509	7	0.35 ± 0.52	0.73 ± 0.43	-0.38 ± 0.11	-0.04 ± 0.09	0.68 ± 0.19
GRA 95209,274 (ACA-LOD) ^c	0.308	7	0.90 ± 0.29	0.77 ± 0.26	-0.33 ± 0.10	-0.10 ± 0.12	0.51 ± 0.26
NWA 7474 (LOD) ^c	0.920	6	0.29 ± 0.31	0.29 ± 0.56	-0.37 ± 0.11	-0.14 ± 0.09	0.22 ± 0.08
Ureilites							
NWA7630°	0.729	3	0.78 ± 0.45	0.13 ± 0.52	-0.31 ± 0.13	-0.17 ± 0.15	0.04 ± 0.31
Dhofar 1519°	0.530	1	-0.87 ± 0.45	-0.26 ± 0.52	-0.23 ± 0.13	-0.31 ± 0.15	-0.12 ± 0.31
DaG 319	0.930	2	0.87 ± 0.45	0.25 ± 0.52	-0.42 ± 0.13	-0.32 ± 0.15	-0.19 ± 0.31
NWA 6356	1.022	1	-0.14 ± 0.45	0.61 ± 0.52	-0.22 ± 0.13	-0.28 ± 0.15	-0.16 ± 0.31
NWA 6378	1.082	2	0.49 ± 0.45	0.15 ± 0.52	-0.32 ± 0.13	-0.04 ± 0.15	0.15 ± 0.31
NWA 6399 ^d	-	-	0.22 ± 0.91	0.18 ± 0.62	-0.30 ± 0.16	-0.22 ± 0.23	-0.06 ± 0.29
NWA 5938 ^d	-	-	0.22 ± 0.91	0.18 ± 0.62	-0.30 ± 0.16	-0.22 ± 0.23	-0.06 ± 0.29
Brachinites							
NWA 3151°	1.004	4	0.92 ± 0.27	0.48 ± 0.33	0.25 ± 0.07	0.14 ± 0.10	0.33 ± 0.20
NWA 4882°	1.084	3	1.05 ± 0.45	0.40 ± 0.52	0.11 ± 0.13	0.03 ± 0.15	0.17 ± 0.31
NWA 10637°	0.974	8	0.51 ± 0.11	0.27 ± 0.16	-0.11 ± 0.05	0.02 ± 0.04	0.40 ± 0.30
ungrouped Achondrite							
NWA 6112°	1.008	8	0.53 ± 0.22	0.45 ± 0.30	-0.46 ± 0.07	-0.14 ± 0.07	0.23 ± 0.09
NWA 8548°	0.986	6	0.33 ± 0.42	-0.30 ± 0.35	-1.14 ± 0.10	-0.34 ± 0.17	0.17 ± 0.34

Table 2: Nucleosynthetic Ru isotope anomalies of primitive achondrites used for correction of the measured mass-dependent Ru isotopic fractionation

^a Number of analyses of the sample solution.

^b Ruthenium isotope ratios are internally normalized to 99 Ru/ 101 Ru = 0.7450754 using the exponential law and are reported relative to the Alfa Aesar bracketing data, given uncertainties represent the external reproducibility (2 s.d.) reported in Hopp et al. (2020) or 95% confidence interval (95% CI) for samples with N>3.

^c Ruthenium isotope anomaly data from Hopp et al. (2020). ^d Available sample mass and the low Ru content of these sample did not allow determination of mass-independent and mass-dependent isotopic signatures for NWA 6399 and NWA 5938. Therefore, the average of the isotope anomalies of the other five ureilites is given and used in the correction of the mass-dependent isotopic fractionation. Except for e⁹⁶Ru values all ureilites display uniform Ru isotope anomalies within the achievable precision.











