A new all-metal induction furnace for noble gas extraction

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1   # Development of a new full-metal induction furnace for

2   # noble gas extraction

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15

16 Abstract

17   Noble gases (He, Ne, Ar, Kr, Xe) are excellent geochemical tracers of volatile

18 origins and geochemical processes between the main terrestrial reservoirs (mantle,

19 crust, atmosphere). As inert elements they are affected by physical phenomena such

20 as supply of volatile elements to the Earth, degassing and subduction into the Earth's

21 mantle.

22   Producing accurate and valuable data from geological samples is often a

23 challenge for scientists, since it requires a mass spectrometer with a very good

24 resolution and sensitivity to measure noble gases, a purification line to purify them,

25 and especially a heating system to efficiently extract them from the minerals with

26 negligible blank amounts

27   We have developed at the CRPG a new full-metal induction furnace to extract,

28   in vacuum, all noble gases from minerals typically analysed in geochemical

29   laboratories such as pyroxene, olivine, quartz or barite.

30   The grain(s), 125 to 3000 μm in size, are packed into a metallic foil and loaded

31   onto a carrousel before their analysis. The Sample, with a mass of up to 1 g are then

32   sequentially dropped into a Ta-crucible, which has previously been degassed. Only 3

33   minutes are necessary to reach a temperature of > 1500°C inside the crucible.

34   Helium and neon are easily extracted from pyroxene and olivine at 1770°C, as well

35   as from quartz at 1500°C. Heavy noble gases are extracted at > 1700°C from the

36   same minerals. Noble gas blanks, measured under the same analytical conditions as

37   the samples are extremely low: 1.64×10^{-15} mole ^{4}He, 5.80×10^{-17} mole ^{20}Ne, 2.13 x

38   10^{-18} mole ^{84}Kr and 4.81×10^{-18} mole ^{132}Xe. Hence, our new furnace represents a

39   powerful tool for the noble gas extraction from small sample amounts and/or gas-

40   poor minerals, with the capacity of targeting even the most refractory phases.

41

42   1/ Introduction

43

44   Due to their chemical inertness, noble gases are mostly impacted by physical

45   processes such as phase changes and nuclear reactions, and they constitute a

46   powerful set of geochemical and cosmochemical tracers (Ozima and Podosek,

47   2002). Several isotopes of noble gases are produced by nuclear reactions such as

48   radioactive decay (e.g. ^{40}K to ^{40}Ar or ^{129}I to ^{129}Xe), and spontaneous fission (e.g. ^{238}U

49   to $^{131-136}$Xe). Various noble gas isotopes are also the final products of interactions

50   between cosmic rays and Earth's surface material (e.g., through spallation reactions

51   on Mg,Si, Fe to cosmogenic ^{3}He and ^{21}Ne). In such a case, cosmic ray-produced

52 isotopes can be used to derive surface exposure ages (e.g. Blard et al., 2014).

53 Meteoritic noble gases permit to establish the exposure duration of meteorite parent

54 bidies in space using cosmogenic isotopes to explore the origin of solar system

55 matter, and to investigate the genetic relationships between planetary reservoirs (Ott

56 1988).

57   The determination of the noble gas composition of rocks and minerals requires

58 four main steps: extraction, purification, separation and analysis of a pure noble gas

59 fraction (Wieler et al. 2014). Each step is critical for ensuring that: (i) all noble gases

60 have been extracted from the sample; (ii) the gas fraction does not contain other

61 chemicals known to create isobaric interferences with noble gas isotopes (e.g. $^{1}H^{35}Cl$

62 with ^{36}Ar, $^{44}CO_2^{++}$ with ^{22}Ne); (iii) noble gases are well separated and do not compete

63 with each other in the ion source and (iv) the mass spectrometer is well tuned to

64 ensure accurate and precise results.

65   Generally, the amount of noble gases in rocks is extremely small, typically of

66 the order of the femtomole. In addition, the blank, that is the amount of noble gases

67 degassed by the analytical system, must be much lower than the sample. A major

68 source of blank noble gases is the extraction system. In order to get a sufficient

69 signal, several tens to hundreds of mg of sample are often necessary. Such amounts

70 are generally heated sequentially in a furnace (stepwise heating). However, noble

71 gas degassing of the inner part of the furnace increases drastically with temperature,

72 and can overcome the signal of the the sample at high temperature (i.e., 1600°C and

73 over) for gas-poor rocks and minerals

74   In this paper, we present the conceptual design and the technical details of an

75 Ultra-High Vacuum (UHV) full metal induction furnace, which was conceived, built,

76 and developed at CRPG, (Nancy, France). This new apparatus permits to extract, by

77 fusion, more than 99% of noble gases (He, Ne, Ar, Kr and Xe) contained in minerals

78 such as quartz, pyroxene, olivine, barite or sulfide, with negligible blank amounts.

79 This furnace is easy to use, safe, efficient and robust.

80

81 2/ Description of the furnace

82

83 <u>2.1/Design of the vacuum vessel</u>

84

85 The furnace vacuum vessel is mainly composed of two CF160 flanges. A

86 CF40 flange, welded onto the upper part, permits to connect the vacuum vessel to a

87 carrousel containing samples and to the purification line. A pyrex viewport is also

88 connected to this flange in order to allow monitoring the temperature of the crucible

89 with an optical pyrometer. A funnel has been machined into the CF160 flange to

90 guide samples toward the Ta crucible. The top flange is cooled by water circulating

91 through the metallic disk N°1 (Figure 1). A double wall was welded on the second

92 CF160 flange in order to cool the lateral surface of the furnace. A second metallic

93 disk (metallic disk N°2) was welded onto this double wall to cool the entire inner

94 surface (Figure 1).

95 A 15 cm^3 crucible containing the sample, made of tantalum (Neyco Company®,

96 LTA15CC) is heated by induction. It is maintained in the middle of the vacuum vessel

97 by a ceramic holder (Figure 1).

98 A quartz cylinder enclosing the crucible protects the induction coil and the

99 inner surface of the furnace against condensable species such as Al and Sn from the

100 metallic foils and carbon, chlorides, sulphides released upon heating of the minerals

101 (Figure 2).

102   The induction coil is placed around the quartz tube. It is connected to a high

103   frequency (HF) electrical feedthrough cooled by a water circulation. This coil has

104   been adapted to the geometry of the tantalum crucible in order to optimize the

105   heating.

106   Because the inner volume of the furnace is important ($\approx$ 2100 cm^3), we

107   recommend using a cryogenic trap outside the furnace to concentrate noble gases

108   into a smaller volume of the purification line.

109   During extraction, two fans are used to cool the external HF connexion of the

110   furnace. One of the fans is used to cool the ceramics of the HF electrical

111   feedthrough, while the second one cools the CF63 flange. A triple water cooling

112   system ($\approx$ 60 l.h^{-1}) passing through the top CF160 flange, the vertical wall of the

113   vessel and the bottom metal disk is cooling the inner surface (Figure 3). The

114   temperature, measured at points A, B, and C (Figure 1), remains below 30°C after a

115   heating duration of 20 minutes at 1800°C of the crucible. The temperature of the

116   CF63 flange can reach up to 50°C (point D, Figure 1).

117   The samples are packed into a metallic foil (Sn, Al or Cu) of high purity

118   (99.99%). They are stored in a metal carrousel connected to the upper part of the

119   furnace.

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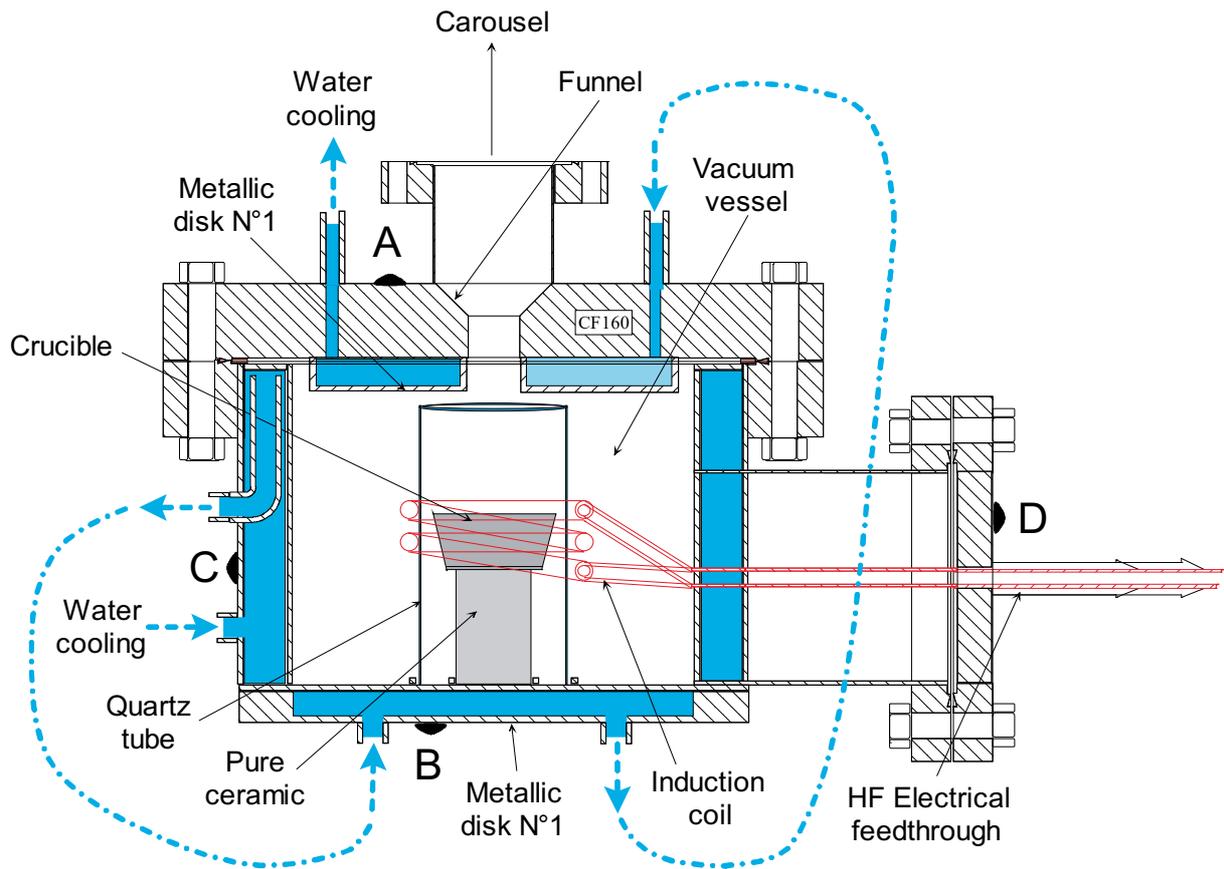
Figure 1: Schematic diagram of the full metal induction furnace showing the induction coil with the tantalum crucible and the triple water circulation used to cool the inner surface of the vacuum vessel.
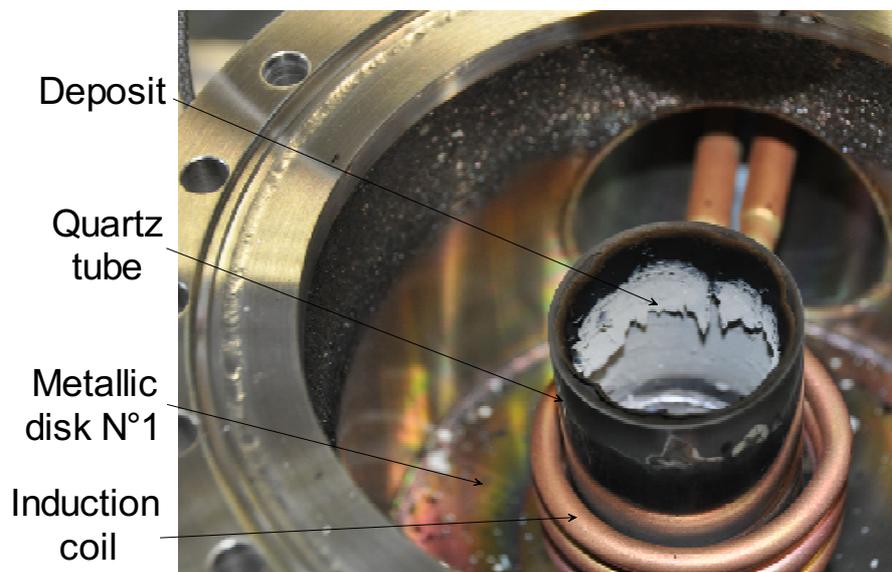
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129 Figure 2: Detailed view of the bottom part of the furnace. The distance between the

130 top of the quartz tube and the top CF160 flange has been reduced to 2 mm in order

131 to favour deposits of carbon, sulphides and chlorides on the inner surface of the

132 quartz tube. Secondary deposits can be observed on the top part of the double wall.

133 They represent less than 5 % wt of the total deposits.

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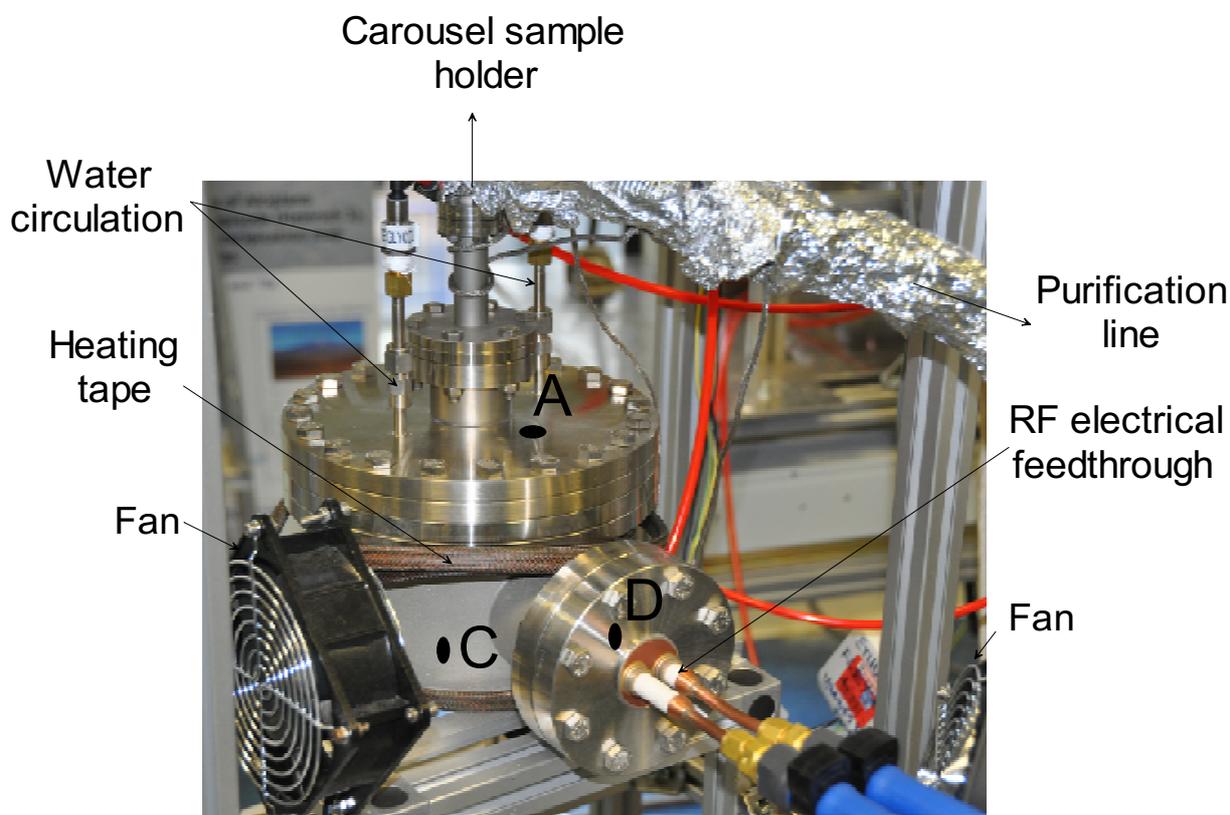
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136

137 Figure 3: External view of the all-metal induction furnace. A heating tape around the

138 vacuum vessel bakes the furnace until up to 200°C to desorb atmospheric gases

139 from the inner surfaces. After one night of baking under vacuum, the pressure (5 x

140 10^{-9} mbar) is compatible with the requirements for noble gas measurements. Three

141 water circulations, connected by red plastic tubes, cool the inner walls during an

142 extraction.

143

2.2/ Nature of the materials

145

The choice of the materials used for noble gas extraction systems is critical to ensure good thermal, electrical and mechanical properties, to prevent contaminations (e.g., chemicals, manufactering residues), and to ensure low noble gas blanks.

Although several refractory metals such as molybdenum (T_{melt} = 2623°C), tantalum (T_{melt} = 3020°C) or platinum (T_{melt} = 1768°C) can be used for the crucible, we recommend tantalum because it yields low helium blanks. For example, during an extraction at 1500°C with a double-vacuum high temperature furnace, helium blanks with a Ta crucible were 9×10^{-15} mole ^{4}He, whereas blanks analysed under the same analytical conditions but using a Mo crucible were higher by a factor 8 (4×10^{-14} mole ^{4}He). Tantalum presents also very low blanks for Kr and Xe despite the formation of alloys with elements such as Al and Sn, that are parts of the metallic foils used to pack samples. Such alloys can increase heavy noble gas blanks by a factor 3 (Niedermann et al. 1997).

Preliminary tests revealed high Ar blanks (> 10^{-10} mole of ^{40}Ar) at 1700ºC with an isotopic composition similar to that of air. This contamination is likely due to the manufacturing method of the crucible (e.g. if pure argon is used to avoid oxidation of tantalum at high temperature). To resolve this issue, we are exploring other commercial suppliers.

Nitrogen measurements remain to be developed with this induction furnace. For N analysis, Mo or Ta crucibles should be avoided because these refractory metals are known to chemically react with nitrogen (Yokochi et al. 2006). Platinum,

167 despite its low melting temperature (1768°C) and high cost, seems more appropriate

168 for this purpose.

169   The crucible sits on an ultra-pure ceramic (Al_2O_3). This material has been

170 chosen because it does not melt at the maximum temperature of the furnace (t_{melt}=

171 2030°C). Furthermore, it tolerates brutal temperature variations (> 400 °C.min^{-1})

172 without damage and its noble gas degassing rate at high temperature is low. A visual

173 control of this is usually done after opening the furnace to ensure its physical

174 integrity.

175   The vacuum chamber of the furnace is made of stainless steel (304L and

176 316LN). This material is easily to weld and has a negligible helium permeability,

177 compared to the other induction furnaces made of glass for example (Marty et al.

178 1995).

179

180 <u>2.3/ Furnace cleaning operations</u>

181

182   Before the first operation, the furnace was cleaned before the first operation in

183 three ultrasonic baths for 2-3 hours each in Decon90, a detergent used to eliminate

184 up to 99.95% of hydrocarbons present on the metallic surfaces (Chiggiato et al.

185 1999). The vacuum chamber was systematically rinsed with deionized water after

186 each bath. Finally, the furnace was dried in an oven at 100-110°C. We recommend

187 cleaning the furnace after the analyses of 20-30 samples in order to remove

188 condensates on the inner surfaces of the furnace. 90% to 95% condensates are

189 usually present on the inner surfaces of the quartz cylinder. This inexpensive

190 component is systematically replaced at each cleaning operation. Deposits observed

191 on the top part of the furnace (Figure N°2), namely less than 5 % by mass of the

192 condensed species, are eliminated by suction. The tantalum crucible can be used

193 several times, despite the crystallization traces at its surface because: (i) These

194 traces have no effects on its thermal and mechanical properties and (ii) this

195 phenomenon has not effect on the noble gas blanks. We also checked the crucible

196 under the microscope after high temperature extraction of noble gases from olivine

197 and pyroxene. The crucible was re-cristallized and corroded due to chemical

198 reactions with the melts. We therefore recommend replacind it after 40-80 analytical

199 cycles.

200

201 2.4/ Thermal properties

202

203   The temperature of the tantalum crucible is measured through a pyrex

204 viewport, connected to the top CF 200 flange (Figure 1), using an optical pyrometer

205 ((Impac®, pyrometer IS-2). Measurements of the temperatures, ranging from 900°C

206 to 1900°C, have been used to determine a precise calibration curve between the

207 temperature of the crucible and the power settings of the HF generator. Five minutes

208 between each temperature step were necessary to ensure temperature stability.

209 These tests were conducted three times (open triangle circle and diamond symbols

210 in (Figure 4) and show a good reproducibility. Temperature estimates have also been

211 verified by melting two pure metals: a Cu and a Ni foil (red and grey circle, Figure 4).

212 These metals were melted at the observed temperatures of 1060°C and 1430°C for

213 Cu and Ni, respectively which are in good agreement with the true melting

214 temperatures (1064°C and 1455°C for Cu and Ni, respectively, Handbook of

215 Chemistry and Physics).

216   In the range of 580°C-900°C, temperatures were not measured but a reddish

217   glow of the crucible was observed and the temperatures were estimated from the

218   calibration curve. Extrapolating the temperature below this range is difficult but the

219   pressure increase from 4×10^{-9} mbar to 2×10^{-7} mbar indicates heating of the

220   crucible.

221   The heating tests revealed that the tantalum crucible weighing 120 g was

222   efficiently heated up to 1800°C, in good agreement with the high temperatures

223   (>1500°C) obtained with other induction furnaces (Marty et al. 1995, Chennaoui-

224   Aoudjehane, 1992). For each step, the temperature is stable within ~ 1% (Figure 5).

225   Possible electric and thermal constraints during heating are likely to be minimal

226   because the crucible is not attached to the vessel. Thanks to this arrangement,

227   temperatures higher than 1500°C can be achieved within ~ 3 minutes without any

228   risks of damage. The heating rate ($400°C.min^{-1}$ on average), is thus improved by a

229   factor of 5 to 10 compared to those obtained with other double-vacuum high

230   temperature furnaces (Staudacher et al. 1978; Maruoka et Matsuda, 2001; Aciego et

231   al. 2007). The cooling rates are also fast (close to $300°C.min^{-1}$ for 500°C to 1500°C

232   temperature steps) because the crucible, with a weight of only 120 g, has a low

233   thermal inertia. These technical characteristics are major assets to minimize noble

234   gas blanks, reduce the duration of extraction, as well as to diminish the amounts of

235   H_2 produced upon heating.

236   The induction coil has been adapted to the geometry of the tantalum crucible

237   to increase the efficiency of the heating so that the thermal loss by conduction is

238   minimized thanks to the low thermal conductivity ($\approx$ 3-5 $W.m^{-1}.K^{-1}$ at 1000°C) of the

239   ceramic that supports the crucible.

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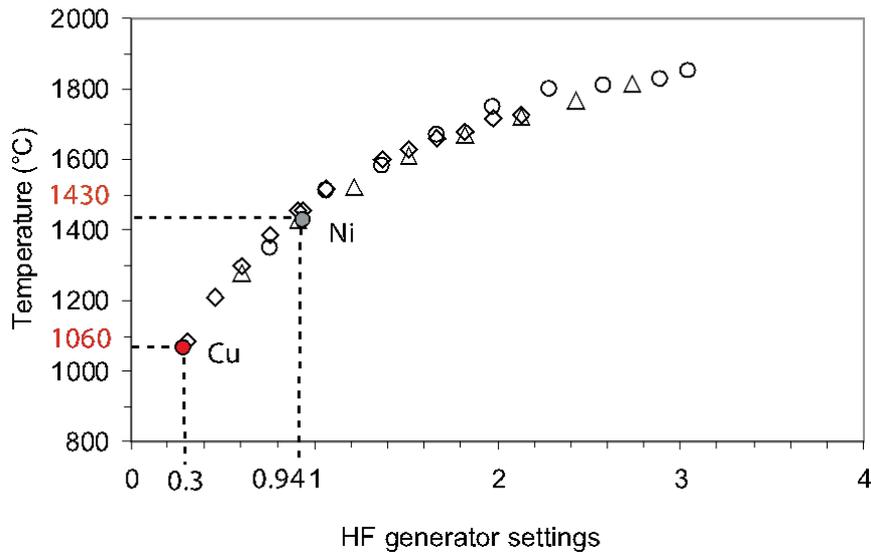
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242

243   Figure 4: Evolution of the temperature (°C) as a function of the HF generator settings

244   between 1000°C and 1500°C. The thermal loss by radiation of the crucible above

245   1500°C reduces the heating efficiency. The induction furnace has been tested up to

246   1850°C with the HF generator adjusted to 50% maximum power. We think that it will

247   be possible to further increase the temperature up to 2000°C.

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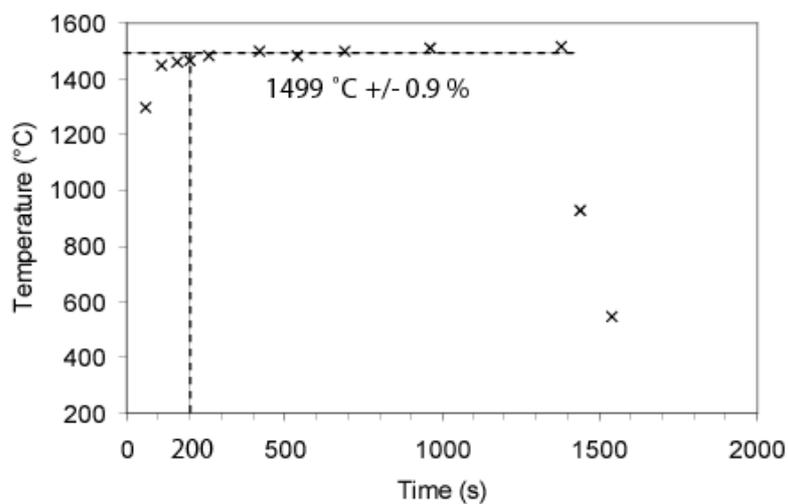
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250   Figure 5: Measurements of the temperature showing the good thermal stability of the

251   furnace, here 1499°C +/- 0.9%. The temperature was stabilized after 200 seconds.

252

253 3/ Analytical procedure

254

255   Nineteen samples were cleaned in acetone in an ultrasonic bath for 5 minutes,

256 packed into a Sn or Al foil, and loaded into a carrousel connected at the upper part of

257 the induction furnace. The carrousel and the furnace chamber were then pumped

258 and baked at 200°C for 12-14 hours. Measurements of neon have shown that the Ne

259 blanks were decreased by a factor 40 after baking. The electric power passing

260 through the induction coil was increased, and the temperature was monitored with an

261 optical pyrometer. Minerals such as pyroxenes and olivines were melted under static

262 vacuum at 1700-1800°C for 10 minutes. The temperature of the crucible was then

263 decreased to room temperature in order to reduce the H_2 pressure produced by hot

264 tantalum.

265   Helium and neon were purified using two charcoal traps held at 77K for 10

266 minutes each in order to trap argon degassed by the crucible (see description above)

267 and three titanium sponge getters (Johnson Mattey®, mesh m3N8 t2N8) for 10

268 minutes at room temperature. The two noble gases were then separated using a

269 cryogenic trap held at 10K. Krypton and Xenon were purified using several getters

270 and a glass finger to trap them at 77K. Argon trapped during this step (≈ 5 %) was

271 eliminated through several cycles of heating-cooling of the glass tube between 77K

272 and 300K. 95 % of the argon was desorbed at each cycle and pumped out. The Kr-

273 Xe fraction was completely separated from argon after three cycles. The whole

274 purification line was maintained at 320K to avoid adsorption of the heavy noble gases

275 onto the inner surfaces. Notably, this temperature does not affect the noble gas

276 blanks. The abundances of the noble gases in the samples were determined with a

277   mass spectrometer operating in static mode and calibrated through noble gas

278   standards.

279

280   4/ Furnace blank

281

282   After baking of the furnace for 12 hours at 200°C, the main source of the noble

283   gas blanks in the furnace is the crucible, especially in the high temperature range

284   above 1500°C. The crucible was thus degassed during several cycles at 1800°C-

285   1850°C while pumping. The number and the duration of each cycle depends of the

286   targeted noble gases, namely only 1 cycle of 30 minutes for He and 3-4 cycles of 60

287   minutes for Ne, Kr and Xe. Between each cycle, blanks were analysed to check their

288   evolution (Figure 6).

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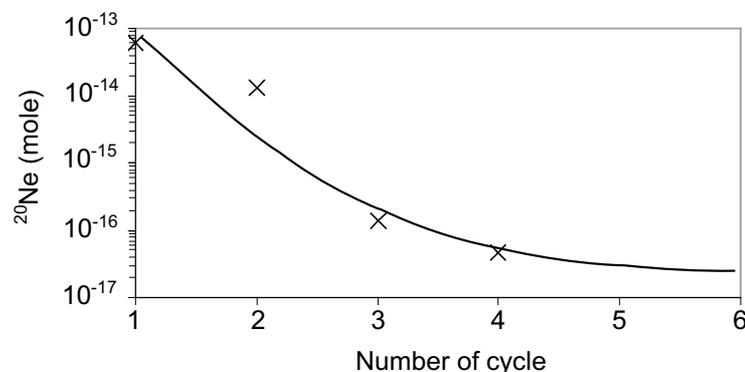
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291   Figure 6: Evolution of the neon blanks as a function of the number of degassing

292   cycles. A large amount of neon (> 10^{-14} mole ^{20}Ne) was degassed from the crucible

293   and the hot ceramics during the first two cycles at around 1800°C. After two

294   additional cycles at the same temperature, the blanks were stabilized at a low and

295   acceptable level of $\approx 5 \times 10^{-17}$ mole.

296

297   The helium blanks were measured at different temperatures with the furnace

298   closed in static vacuum for 10 minutes. They are equal to 1.84+/-1.58 x 10^{-16} mole

299   ^{4}He (n=5) at low temperature (1500°C) and 1.64+/-1.03 x 10^{-15} mole ^{4}He (n=18) at

300   1750°C.

301   We have tested the helium blank stability over a period of one month. Despite

302   periodical exposures of the furnace to the atmosphere and sequential sample

303   loading, we found that the blanks did not vary by more than 50-70% (Figure 7).
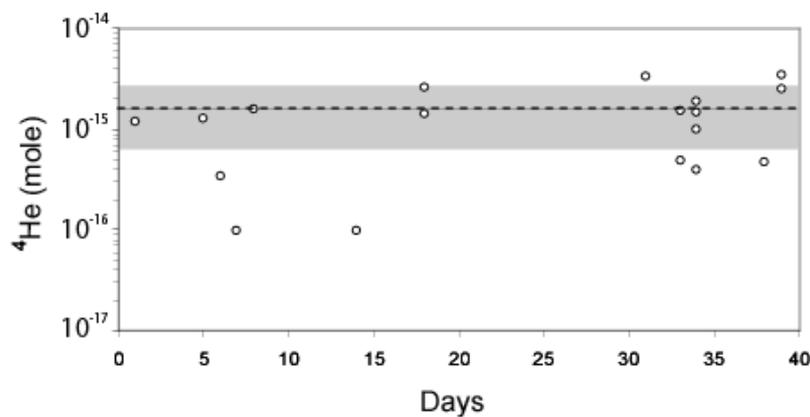
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305   Figure 7: Evolution of procedural ^{4}He blanks over a period of 40 days. The dashed

306   line represents the mean value (1.64 x 10^{-15} mole ^{4}He) and the grey band indicates

307   deviations of 50% relative to the mean value. This variability is comparable for the

308   other noble gases. Following Stuart et al. (1999), we suspect that the He blanks may

309   increase as a result of deformations of the bellow during opening and closing of the

310   furnace valve. Part of the He blank may also be derived from helium diffusion through

311   the pyrex viewport connected to the top CF200 flange.

312

313   The neon blanks (with the furnace left for 20 minutes under static vacuum)

314   were 5.82+/-2.26 x 10^{-17} mole ^{20}Ne (n=7) at 1500°C and 1.65+/-0.54 x 10^{-16} mole

315   ^{20}Ne (n=6) at 1600-1700°C, respectively. At temperatures below 1200°C, the neon

316   blanks were similar to those of the whole purification line, that is ~ 2.5 x 10^{-17} mole

317   ^{20}Ne.

318

319   An analytical protocol of 10 minutes at high temperature in static vacuum has

320   been applied to determine the heavy noble gas blanks. The amounts of ^{84}Kr

321   degassed by the crucible were 2.61+/-0.33 x 10^{-19} mole at 800°C and 2.13+/-0.29 x

322   10^{-18} mole at 1700°C. The xenon blanks, in the same range of temperature, were

323   4.45+/-0.42 x 10^{-18} mole ^{132}Xe.

324

325   Most samples are packed into a metallic foil before melting in the crucible.

326   Although ideal to manipulate powders, this type of packaging is difficult to degas and

327   chemical reactions between metallic foils and the Ta crucible might increase noble

328   gas blanks upon heating (Niedermann et al. 1997). In order to determine the gas

329   fraction derived from the metallic foils (Sn, Al), they were rolled to form a package

330   similar to those containing the samples and analysed after baking at 200°C for 12

331   hours. These analyses demonstrated that atmospheric noble gases were completely

332   removed since He and Ne blanks were similar to those measured without a Sn or Al

333   foil. The blanks of the heavy noble gases were systematically larger with metallic foils

334   than without them. The krypton blanks were increased by a factor 4 in the range

335   800°C-1220°C, and then by a factor 7 at 1700°C. The Xe blanks were stable until

336   1200°C but then increased up to 1.4 x 10^{-17} mole ^{132}Xe at 1700°C. We propose that

337   the higher blanks result from the formation of alloys between the tantalum of the

338   crucible and other metals from the foils, as already noted by **Niedermann et al.**

339   **1997**, and observed under a binocular microscope.

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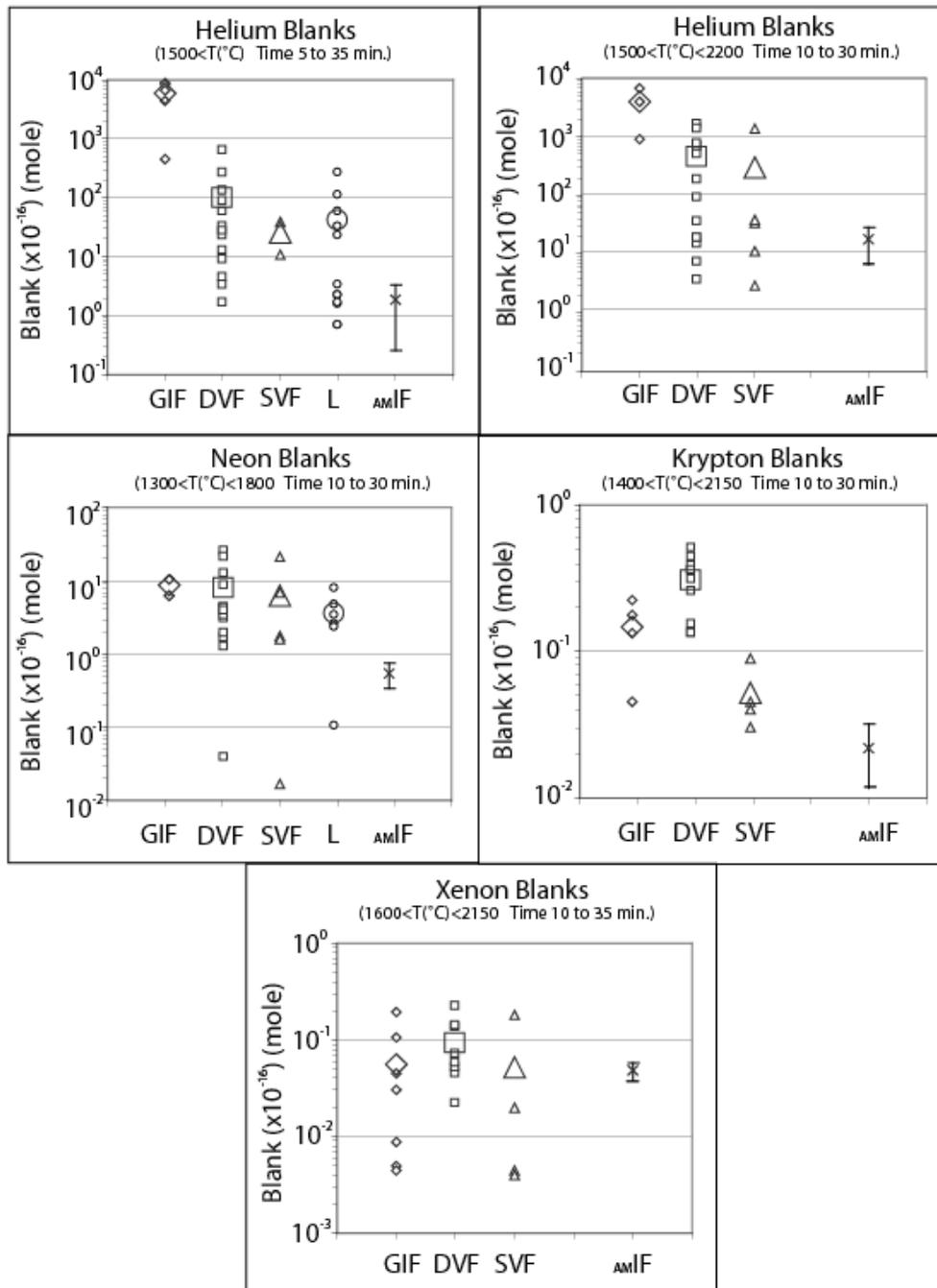
341

342 Figure 8: Summary of the noble gas blanks measured with different heating methods:

343 glass induction furnaces (GIF; diamonds); double vacuum resistance furnaces (DVF,

344 open squares), simple vacuum resistance furnaces (SVF; triangle), lasers heating (L;

345 open circles) and the full-metal induction furnace presented here ($_{am}$IF; cross). Large

346 symbols represent the average blank for each method. The all metal induction blanks

347   have been measured without melting metallic foils. Values and references are

348   provided as supplementary material.

349

350   4.1/ Comparison with other heating extraction methods

351

352   With our newly developed all-metal induction furnace, the blank amounts

353   have been reduced by 60% to 99% for helium, neon and krypton when compared to

354   those of others extraction methods such as glass induction furnaces (e.g. Ott 1988;

355   Marty et al. 1995; Moreira & Allègre, 2002), double vacuum resistance furnaces (e.g.

356   Niedermann et al 1997; Maruoka & Matsuda 2001; Blard et al. 2015), simple vacuum

357   resistance furnaces (e.g. Honda et al. 1987; Burgess et al. 2009; Zimmermann et al.

358   2012) and lasers (e.g. Stuart et al. 1999; Farley et al. 2006; Füri et al 2015). No clear

359   improvement has been noted for xenon blanks with this new apparatus (Figure 8).

360

361   In double vacuum resistance furnaces, crucibles are heated by an electrical

362   resistance which heats a tantalum liner (see for example Takaoka, 1976 and

363   Staudacher et al. 1978). Extraction temperatures up to 1800°C can be achieved,

364   resulting in blanks in the ranges of 1.66×10^{-16} - 7.54×10^{-14} mole ^{4}He, 1.34×10^{-16} -

365   2.68×10^{-15} mole ^{20}Ne, 3.0×10^{-18} - 5.13×10^{-17} mole ^{84}K and 0.04×10^{-17} - 0.22×10^{-16}

366   mole ^{132}Xe (Figure 8). Lavielle et al. (1999) describe a similar double-walled

367   vacuum furnace where the heat is produced by electron bombardment onto a Ta

368   crucible, which has very low helium and neon blanks of 1.78×10^{-15} mole ^{4}He and

369   0.04×10^{-16} mole ^{20}Ne respectively. This type of furnace has low blanks, but also has

370   several drawbacks; first, the heating cycle of the sample is long because of a gradual

371   and long increase of the temperature ($<100°C.min^{-1}$) to protect the heating

components against electrical and thermal constraints. Furthermore, the Ta-tube is heavy (0.7 to 1 Kg), resulting in an important thermal inertia. Typical durations of temperature increase and decrease steps are about 20 min, potentially increasing the noble gas blanks. Second, this technology is costly since it requires expensive electrical resistances and thermal shields, a turbomolecular pumping system connected to the double vacuum vessel with yearly service and a regular replacement of the tantalum crucible after the melting of the samples (≈ 1500 €/crucible). Third, noble gases extracted from samples may be pumped by the external pumping system through cracks produced by the recrystallisation of the crucible walls after several heating cycles

Others furnaces have been developed in order to avoid a loss of gas through the crucible wall. In a simple vacuum resistance furnace, a W, or Ta, coil is heated by an electric current up to >2100°C (Honda et al. 1987; Burgess et al. 2009; Sumino et al. 2011). As for the double vacuum furnaces, their use to extract noble gases is limited for several reasons: (i) they are not designed to be used with large samples because the inner volume of the coil is limited to a few cm^3; (ii) all the samples must be packed into a metallic foil whose the degassing could increase the blanks (Niedermann et al. 1997); (iii) this metallic foil must remain in a solid state (without melting) during the extraction to avoid the loss of the sample through the coil wires.

Zimmermann et al. (2012) developed another design for a simple vacuum resistance furnace. The metal coil used by Honda et al. (1987) has been replaced by a Ta-resistance positioned around a boron nitride (BN) crucible. This furnace has satisfactory helium and neon blanks, but it is unable to melt refractory samples such as high-Mg olivines because its temperature is limited to ≤ 1450°C. Furthermore, it produces large amounts of nitrogen (>10^{-2} mbar) at high temperatures from BN,

397 which require extensive purification. In order to increase the lifetime of the resistance,

398 it is recommended to respect a low heating rate around 70°C.min^{-1}.

399   Farley et al. (1999) described a helium diffusion system developed specifically

400 for He analyses. The samples are heated by radiation using a halogen lamp (250W).

401 The He blanks are exceptionally low (1 - 4 x 10^{-15} mole ^{4}He at 750°C), but its

402 maximum temperature of 800°C to 1000°C limits the system to He diffusion

403 experiments.

404   The induction furnaces using a glass vacuum vessel are sometimes used to

405 extract noble gases from refractory samples such as olivine or barite (e.g. Becker &

406 Pepin 1984; Ott 1988; Marty et al. 1995; Moreira & allègre 2002; Avice et al. 2015).

407 Crucibles are heated by an external induction coil and the glass walls are cooled by

408 water circulation. These furnaces can reach high temperatures (>1800°C) and their

409 Ne, Kr and Xe blanks are similar to, or lower than, those of all-metal furnaces.

410 Despite these interesting features, their use to extract gases is often challenging

411 because (i) the heating rate to reach high temperatures is low, < 50°C.min^{-1}, in order

412 to minimize thermal constraints on the crucible holder made of quartz; (ii) the volume

413 of the crucible, < 3 cm^3, is low; (iii) helium blanks are very high, generally > 9 x 10^{-14}

414 mole ^{4}He due to He diffusion through the pyrex or kovar vacuum envelope and (iv)

415 neon blanks are also high, possibly due to degassing of the quartz screen.

416   Laser systems (CO$_2$, Nd-Yag, Diode) are also used to heat/melt mineral

417 grains. They have the advantage of rapidly reaching high temperatures in excess of

418 2000°C. They also yield low blanks: the furnace walls and the sample holders are

419 moderately heated since the samples absorb most of the energy. However, the small

420 sizes of the beams and their low power for most commercial instruments limit these

421 devices to small sample sizes, typically below 10 mg. Further complication may arise

422   from vapor deposition onto the windows, or degradation of the latter by the laser

423   beam.

424

425   5/ Noble gas extraction yields

426

427   Quartz, pyroxenes, olivine and barites samples have been analysed to

428   determine the key parameters (temperature, grain size, duration) controlling the

429   extraction efficiency. The results are given in the table 9A and 9B for He and Ne and

430   Kr and Xe, respectively.

431   Helium was completely released by heating pyroxene and pyroxene-olivine at

432   1750°C during 10 minutes. For pure refractory olivine, we nevertheless recommend

433   to increase the temperature to 1770°C and the duration to 20 minutes in order to

434   achieve complete extraction. 98% - 100% Ne was released from quartz of different

435   grain size during the first step at 1500°C for 20 minutes. More than one hundred He

436   and Ne analyses have been performed without any extraction problems and we did

437   not observe a memory effect in the furnace for these gases.

438   Helium and neon were also analysed in pyroxenes (n=4) (CRONUS-P

439   standard (Blard et al. 2015) and quartz (n=4) (CREU-1 standard (Vermeesch et al.

440   2015) using the analytical protocol described above. The mean concentrations

441   determined are $5.01+/-0.12 \times 10^9$ atom ^{3}He.g^{-1} and $3.48+/-0.06 \ 10^8$ atom ^{21}Ne,

442   consistent with the recommended values of $5.02+/-0.12 \times 10^9$ atom ^{3}He.g^{-1} and

443     $3.48+/-0.10 \ 10^8$ atom ^{21}Ne, respectively (Blard et al. 2015); (Vermeesch et al. 2015).

444   This comparison further demonstrates the reliable noble gas extraction efficiency of

445   our furnace.

446   Xe and Kr measurements of barite ($BaSO_4$, dissociation at 1600°C) and quartz

447   (SiO_2, decrepitation of fluid inclusions around 1600°C) samples have also been

448   conducted with this new furnace (Figure 9B). They consisted of two extractions steps

449   at 800°C and 1700°C, and an additional re-extraction ("R" in Figure 9B) at a similar

450   or slightly higher temperature (1750 °C). Overall, 90 % of the gases were released

451   during the first two steps, and 10% of the gases were extracted during the re-

452   extraction steps. Noble gases extracted during this last step had an isotopic

453   compositions close to those of the terrestrial atmosphere, probably due to an

454   increase of the blank contribution.

455

Sample	Grain size (μm)	Mass (g)	Time (min.)	Temp. (°C)	^{4}He (mol)	^{20}Ne (mol)	*Extraction yield (%)*
Pyrox. (100%)	125-250	0.160	10	1750	6.40×10^{-13}		
R			10	1750	9.77×10^{-17}		*100.2*
Pyrox. (50%)/ Ol. (50%)	125-250	0.109	10	1750	2.78×10^{-14}		
R			10	1750	n.d.		*100.00*
Ol. (100%)	125-250	0.057	10	1750	8.83×10^{-14}		
			10	1770	2.08×10^{-14}		
R			10	1770	1.59×10^{-15}		*100.05*
Quartz (100%)	100-400	0.314	20	1500		7.84×10^{-15}	
R			20	1500		9.76×10^{-17}	*99.53*
Quartz (100%)	400-1000	0.179	20	1500		8.82×10^{-15}	
R			20	1500		2.06×10^{-16}	*98.35*

457

458 Table 9A: Helium and neon extraction yield from pyroxene, olivine and quartz. Each values has been corrected for the blank

459 contributions, namely ~ 1.6 x 10^{-15} mole ^{4}He and 5.8 x 10^{-17} mole ^{20}Ne. "R" denotes re-extraction.

460

Sample	Grain size (μm)	Mass (g)	Time (min.)	Temp. (°C)	^{84}Kr (mol)	Extraction yield (^{84}Kr) (%)	^{132}Xe (mol)	Extraction yield (^{132}Xe) (%)
Barite	1000-3000	1.02	20	800	1.5×10^{-16}	39.27	1.60×10^{-16}	39.41
			20	1700	1.8×10^{-16}	47.12	2.0×10^{-16}	49.26
R			20	1700	5.2×10^{-17}	13.61	4.6×10^{-17}	11.33
Barite	1000-3000	0.87	20	800	1.0×10^{-16}	64.52	7.0×10^{-17}	45.75
			20	1700	4.2×10^{-17}	27.10	6.0×10^{-17}	39.22
R			20	1700	1.3×10^{-17}	8.39	2.3×10^{-17}	15.03
Quartz	1000-3000	0.92	20	800	1.1×10^{-15}	67.07	1.7×10^{-15}	59.65
			20	1700	4.3×10^{-16}	26.22	9.9×10^{-16}	34.74
R			20	1750	1.1×10^{-16}	6.71	16×10^{-16}	5.61

461

462   Figure 9B: Krypton and xenon extraction yield from barite and quartz. "R" denotes re-extraction.

463

6/ Conclusion

466   We have developed a new furnace design for noble gas extraction under ultra-high vacuum. A coil inside a full-metal single vacuum chamber is heating by induction a crucible located in the same chamber. This furnace can rapidly reach a temperature of at least 1850°C within only few minutes (heating/cooling rates of about 400°C.min^{-1}), thanks to its low thermal inertia and its assemblage that prevents degradation by thermal shocks. The whole furnace and the sample holder (carrousel) can be baked at 200°C for several days. The chamber envelope and upper/lower flanges are cooled down by a water circulation during heating, warranting very low noble gas blanks compared to existing furnaces.

        Future tests will focus on: (i) testing new crucibles with low Ar blanks in order to be able to analyse this noble gas in geological samples; (ii) adding a thermocouple or a new optical pyrometer to have a more rigorous control of the temperature especially in the 100 - 900 °C temperature range; (iii) testing Pt crucibles for quantitatively extracting nitrogen together with noble gases.

        A patent of this new furnace has been issued to the Institut National de la Propriété Industrielle. Its marketing mode will be ensured by the society Cryoscan.

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665

666 Supplementary

Autor(s)	Laboratories	Crucible	Temperature	^{4}He (mole) ($\times 10^{-16}$)	^{20}Ne (mole) ($\times 10^{-16}$)	^{84}Kr (mole) ($\times 10^{-16}$)	^{132}Xe (mole) ($\times 10^{-16}$)
Glass Induction Furnace							
Becker & Pepin (1984)	Univ. of Minesota		1500	4461[-]	6.69[-]	0.134[-]	0.004[-]
				6692[+]	11.15[+]	0.223[+]	0.009[+]
CRPG (unpublished data)	CRPG	Ta	1800				0.031
			2200				0.045
Marty et al. (1995)	Magie	Mo	600	460			
			1800	900			
Moreira & Allègre (2002)	IPGP	Mo	600	8923	4.46	0.054	0.005
			1500	8477	6.69	0.045	0.005
Pujol (2009)	CRPG	Ta	1850				0.194
Ott (1988)	Max Planck Institut	Mo	1600	6692	11.15	0.178	0.107
Double Vacuum Furnace							
Aciego et al. (2007)	Berkeley	-	300-1500	22.31[-]			
				58.00[+]			
Blard & Pik (2008)	CRPG	Ta	1600	88.04			
Blard et al. (2015)	GFZ Potsdam	Ta	900	1.66[-]			
				3.32[+]			
	GFZ Potsdam	Ta	1750	6.64[-]			
				33.22[+]			
	Latmont, Palissades	Mo	1350	33.22			
	Caltech, Passadena	-	1500	26.58			
Foeken et al. (2009)	Scottish Universities	-	1300	12.46			
Honda et al. (1993)	Australian National University	Ta	600-1500	133.84	1.75	0.134	0.022
		Al$_2$O$_3$	600-1500	267.69	26.29		
Jambon et al. (1986)	Max Planck Institut	Mo	1650	178.46	26.77	0.357	0.223
Kurz (1986)	Woods Hole oceanographic Institution	-		13.38[-]			
		-		17.85[+]			
Lavielle et al. (1999)	Univ. of Bordeaux I	-	1750-1800	17.85	0.04		
Maruoka & Matsuda (2001)	University of Vienna	MgO	800	642.46			
		MgO	1600	660.30	3.30[x]	0.261[x]	0.072[x]
		BN	600-800	-	3.39[x]	0.254[x]	0.020[x]
		BN	1600	481.84	3.53[x]	0.513[x]	0.045[x]
		BN	1800	1548*	4.04[x]	0.388[x]	0.052[x]
		Mo	1600	753.99*	4.50[x]	0.362[x]	0.140[x]
		Mo	1800	1307	9.20[x]	0.154[x]	0.058[x]
Niedermann et al. (1997)	GFZ Potsdam	Ta	400-800	89.23			
			1400	89.23	4.46[-][2x]		
					13.38[+][2x]		
			1400	89.22	1.34[-][3x]		
					4.02[+][3x]		
Persano et al. (2002)	-		950	4.46[4x]			
Vermeesch et al. (2015)	ETH Zurich		1750		2.01		
Williams et al. (2006)	SCUERC		1700	3.32[4x]			
Single Vacuum Furnace							
Blard et al. (2006)	CRPG		1700	9.97[-]			
				31.56[+]			
Blard et al. (2015)	CRPG	BN	1400	39.87[5x]			
Burgess et al. (2009)	University of Manchester	Ta coil	2150			0.089	0.178
Honda el al. (1987)	University of California	W coil	2000	1338	21.86	0.045	0.004
Johnson et al. (2000)	University of Manchester		1600			0.030	0.004

			2050			0.040	0.020
Sumino et al. (2011)	University of Tokyo	Ta coil	2200	$2.68^{(-)}$ $35.69^{(+)}$	$0.02^{(-)}$ $7.14^{(+)}$		
Zimmermann et al. (2012)	CRPG	BN	1450	11			
Laser System							
Ammon et al. (2009)	University of Edinburgh	808 nm		$0.67^{(-)}$ $1.52^{(+)}$			
Blard et al. (2015)	SUERC	808 nm	1400	$1.66^{(-)}$ $3.32^{(+)}$			
Farley et al. (2006)	California Institute of technology	Nd-Yag	1300	33.22			
Foeken et al. (2006)	SUERC	808 nm		0.67			
Foeken et al. (2009)	SUERC	808 nm	> 1200	2.16			
Füri et al. (2013)	CRPG	CO_2		260 23.00	5.00 3.50		
Füri et al. (2015)	CRPG	CO_2			2.45		
Nichols et al. (1994)	Washington University	Nd-Yag		111.54	0.11		
Pi et al. (2005)	University of Mexico	CO_2		60			
Stuart et al. (1999)	SUERC	Nd-Yag		2.23	2.62		
Vermeesch et al. (2015)	ETH Zurich	810 nm			8.30		
This study							
	CRPG	Ta	1500	$1.84^{(x)}$			
	CRPG	Ta	1750	$16.4^{(x)}$			
	CRPG	Ta	1500		$0.58^{(x)}$		
	CRPG	Ta	1700			$0.021^{(x)}$	$0.048^{(x)}$

$^{(x)}$: Average of the blanks, For CRPG, x=3, 13, and 7 for He blank (1500°C), He blank (1750°C) and Ne, Kr & Xe blank respectively;

$^{(-)(+)}$: minimal and maximal value given in manuscript;

$^{(2x)(3x)(4x)(5x)}$ denote blanks measured after the Ni, Al, Cu and Sn foil melting respectively.

Analytical protocol for CRPG blanks: 10 min in static vacuum at high temperature for He and 20 min for Ne, Kr and Xe.