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2 **TWO DIFFUSION PATHWAYS IN QUARTZ: A COMBINED UV-LASER AND RBS**
3 **STUDY**

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ABSTRACT

33
34 The diffusive behavior of argon in quartz was investigated with three analytical depth
35 profiling methods: Rutherford Backscattering Spectroscopy (RBS), 213 nm laser ablation,
36 and 193 nm (Excimer) laser ablation on the same set of experimental samples. The
37 integration of multiple depth profiling methods, each with different spatial resolution and
38 sensitivity, allows for the cross-checking of methods where data ranges coincide. The use of
39 multiple methods also allows for exploration of diffusive phenomena over multiple
40 lengthscales. Samples included both natural clear rock crystal quartz and synthetic citrine
41 quartz. Laser analysis of clear quartz was compromised by poor coupling with the laser,
42 whereas the citrine quartz was more easily analyzed (particularly with 193 nm laser).
43 Diffusivity measured by both RBS and 193 nm laser ablation in the outermost 0.3 μm region
44 of citrine quartz are self-consistent and in agreement with previously published RBS data on
45 other quartz samples (including the clear quartz measured by RBS in this study). Apparent
46 solubilities (extrapolated surface concentrations) for citrine quartz are in good agreement
47 between RBS, 213 nm, and 193 nm laser analyses. Deeper penetration of argon measured up
48 to 100 μm depth with the 213 nm laser reveal contributions of a second, faster diffusive
49 pathway, effective in transporting much lower concentrations of argon into the crystal
50 interiors of both clear and citrine quartz. By assuming such deep diffusion is dominated by
51 fast pathways and approximating them as a network of planar features, the net diffusive
52 uptake can be modeled with the Whipple-LeClaire equation, yielding δD_b values of $1.32 \times$
53 10^{-14} to 9.1×10^{-17} cm^3/sec . While lattice solubility values from the measured profiles
54 confirm suggestions that quartz has a large capacity for argon uptake (making it a potentially
55 important sink for argon in the crust), the slow rate of lattice diffusion may limit its capability
56 to take up argon in shorter lived geologic environments and in experiments. In such shorter

57 lived systems, bulk argon diffusive uptake will be dominated by the fast pathway and the
58 quartz lattice may never reach its equilibrium capacity.

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60

1. INTRODUCTION

61 1.1 Introduction

62 In this study we seek to investigate the potential role of quartz as a ‘sink’ mineral for
63 argon (and by analogy, perhaps for the other noble gases) as hypothesized recently in field
64 based (e.g., Baxter et al. 2002) and experimental (e.g., Watson and Cherniak 2003) studies.
65 Quartz would be an effective sink for argon if, (1) the solubility of argon in quartz relative to
66 the solubility of surrounding phases (i.e., partitioning) is high, and (2) if the diffusivity of
67 argon into quartz is high enough to permit argon to enter the quartz over available timescales.
68 However, apparent discrepancies have been identified when comparing the experimental
69 studies of Watson and Cherniak (2003) and that of Roselieb et al. (1997) whose studies
70 suggest argon diffusivity and solubility in quartz differ by several orders of magnitude. This
71 apparent discrepancy may be because these studies approached the question of argon
72 diffusivity and solubility from different experimental and analytical directions: Thomas et al.
73 (2008) and Watson and Cherniak (2003) used Rutherford Backscattering Spectroscopy
74 (RBS) to measure diffusive uptake profiles in quartz at the 10’s of nanometer scale, while
75 Roselieb et al. (1997) used bulk analysis and electron microprobe.

76 While the absolute solubility limit for argon in quartz (using either Watson and
77 Cherniak 2003 or Roselieb et al. 1997) would rarely be reached in nature (i.e., there will
78 rarely be enough argon in a natural system to saturate quartz), the parameter of greater
79 importance is the partitioning of argon between quartz and other available system phases
80 (e.g., minerals, fluids, grain boundaries). In this regard, the disparate conclusions of Watson

81 and Cherniak (2003) and Roselieb et al. (1997) lead to different partition coefficients when
82 compared to existing solubility data on other minerals. As this study highlights, depending
83 upon the analytical method used, very different apparent diffusivities and apparent
84 solubilities may be determined on the same mineral specimens. This shows the challenges in
85 using existing solubility data measured by different methods to calculate mineral-mineral
86 partition coefficients.

87 This is the first time a dual-study using both RBS and 193/213 nm UV-laser ablation
88 mass spectrometric analyses has been undertaken on the same mineral samples, which
89 illuminate heretofore unrecognized complexities in quantifying argon diffusivity. In
90 comparing these three analytical methods, we are able to identify the presence of two
91 distinctly different diffusive pathways in quartz: (1) slow lattice diffusion and, (2) fast-path
92 diffusion that may be controlled by defects, dislocations or internal crystal imperfections.
93 While our study focuses on quartz, the analytical lessons and noble gas behaviors learned
94 here may well inform us about similar issues affecting the measurement of argon diffusivity
95 solubility in other minerals, (e.g., Watson et al., 2007) concerning the long term storage of
96 argon in the solid earth.

97 **1.2 Fast-Path and Multi-Diffusion**

98 An understanding of the diffusion mechanisms by which geochronologically
99 significant isotopes (e.g., Ar, He) are transported over geologically relevant timescales is
100 crucial to geochronologic interpretations. It is likely because of this that studies to quantify
101 argon diffusion in minerals have been numerous (e.g., Foland, 1974; Giletti, 1974; Giletti and
102 Tullis, 1977; Harrison, 1981; Harrison et al., 1985; Wartho et al. 1999; Watson and Cherniak,
103 2003; Thomas et al., 2008). In the past (Turner, 1968; Schärer and Allègre, 1982),

104 mechanisms of volume diffusion have been studied indirectly through geochronologic
105 experiments concerning both single crystals and bulk mineral separates.

106 With the advent of high-resolution micro-sampling techniques, maps of intergrain
107 spatial distribution of geochronologically important isotopes can be obtained. Some (Scaillet
108 et al., 1990; Kelley and Turner, 1991; de Jong et al., 1992; Hames and Hodges, 1993; Hodges
109 et al., 1994; Watson and Cherniak, 2003) found that most of their samples adhered to volume
110 diffusion, resulting in concentration profiles interpretable in terms of simple diffusion
111 through the crystalline lattice. Some studies (Phillips and Onstott, 1988; Onstott et al., 1991;
112 Scaillet, 1992; Kelley et al., 1994), however, determined that samples yielded distinct
113 concentration gradients, reflecting a mechanism other than volume diffusion. Crystal defects
114 (micro-structural defects, edge/screw dislocations, micro-fractures, nanopores, etc.) have
115 been shown to allow for ‘enhanced’ or fast-path diffusion (Smoluchowski, 1952; Hart, 1957;
116 Harrison, 1961; Le Claire, 1963; Ruoff and Baluffi, 1963; Baluffi, 1970; Le Claire and
117 Rabinovitch, 1984; Lee, 1995).

118 Most early work towards quantification of diffusion rates within “fast paths” used
119 measurements from low-angle grain-boundary diffusion rates (Whipple, 1954; LeClaire and
120 Rabinovitch, 1984), relying on the assumption that the transport along dislocations can be
121 related to the transport along an equivalent grain boundary slab, whereby the cross-sectional
122 area of the grain boundary slab is equivalent to the sum of the area of the dislocations.
123 LeClaire and Rabinovitch (1981, 1982, 1983, and 1984) considered the diffusion into and
124 along isolated, individual dislocations.

125 Potential fast-paths, through which rapid diffusion can occur, have been observed in
126 different minerals (Veblen and Buseck, 1980; Skrotziki, 1990; Worden et al., 1990; Hacker
127 and Christie, 1991; Dohmen et al., 2002; Zhang et al., 2006), and as a result, multiple

152 0.0052 ± 0.0041 and 0.0123 ± 0.0041 ppm argon within a short depth profile in the citrine
153 quartz and similarly for the clear quartz at 0.0299 ± 0.0072, 0.0015 ± 0.0005 and 0 ppm
154 argon. The clear quartz is the same as that used in Watson and Cherniak (2003), where the
155 presence of localized patches of fluid inclusions was documented. Such inclusions are
156 typically unavoidable due to their small size (down to 10 -20 nm or less; see Watson and
157 Cherniak, 2003 for discussion). The clear quartz samples were pre-annealed at 1000 °C for 3
158 to 7 days prior to polishing. While this does not heal any damage induced by mechanical
159 polishing (see discussion in section 6.1 regarding effects of sample preparation on argon
160 uptake), it negates any influence that the presence of hydrous species in the quartz lattice may
161 have on argon diffusion and uptake into the quartz lattice (Watson and Cherniak, 2003).
162 Electron microprobe data on the citrine quartz suggest that the crystal is chemically
163 homogenous, however some heterogeneity in color within the citrine may indicate slight
164 variations in Fe content, or ferrous/ferric ratios. No fluid inclusions in the citrine were
165 observed optically or during electron microprobe analyses, however, due to the hydrothermal
166 synthesis of the citrine quartz, it must be assumed that fluid inclusions are present on a small
167 scale. Commercial, synthetically-grown quartz is changed to 'citrine' quartz through the
168 addition of ferric iron impurities. This Fe is present in the quartz lattice in trace quantities
169 (citrine quartz is 99.8 % SiO₂). The presence of even trace Fe in the citrine is potentially
170 noteworthy, as the study of Thomas et al. (2008) documented higher argon concentrations in
171 the Fe-bearing minerals enstatite and San Carlos olivine than the pure end-member
172 compositions, suggesting that oxidation of Fe could cause defects and thereby enhance
173 uptake of argon.

174 The citrine quartz was cut and polished using a low-speed Buehler Isomet precision
175 diamond-blade saw. Chips were then mounted in epoxy and polished using Milli-Q water and

176 60 to 1 μm polishing papers. Samples were removed from the epoxy using an acetone bath
177 and then cleaned ultrasonically in ethanol and de-ionized water. Pre-annealed, 3 x 3 x 1 mm
178 cuts of clear quartz were prepared from the study of Watson and Cherniak (2003) and were
179 polished in the same manner as the citrine quartz cuts. No information on the crystallographic
180 orientation of the samples was recorded following the study of Watson and Cherniak (2003)
181 which demonstrated that crystallographic orientation does not strongly affect diffusivity.

182 **2.2 Experimental Procedure**

183 Argon diffusion in quartz was investigated using “in-diffusion” experiments. The
184 polished mineral samples were loaded into a ceramic tray, which was inserted into a cold-seal
185 pressure vessel and furnace. The vessel was pressurized at 160-170 MPa with pure argon gas.
186 During the experiment, samples are bathed in this pressurized argon atmosphere allowing
187 argon to diffuse into the polished sample surface. Each cold-seal run can hold approximately
188 16-20 minerals. Each location within the sample tray (four containers per tray, each
189 containing 4-5 minerals) is independently monitored with a thermocouple which monitors the
190 temperature within a few millimeters of the sample. Temperature is known to within
191 approximately ± 2 °C. A thermal gradient present along the vessel allowed for four distinct
192 temperature environments during the course of a single experiment (Table 1).

193 Two experiments were conducted in this study: the first at 170 MPa and a temperature
194 range of 824 to 489 °C over a duration of 480 hours and the second at 160 MPa, a
195 temperature range of 724 to 419 °C over a duration of 360 hours. The first experiment
196 contained clear quartz, the second contained both clear and citrine quartz. Experiment details
197 and run conditions (pressure, temperature and duration) are listed in Table 1. Each
198 experiment was run with not only multiple samples of quartz, but also other silicate minerals
199 including plagioclase feldspar, K-feldspar and phlogopite, in order to allow for the

200 calculation of partition coefficients between these phases. However, because of unavoidable
201 isobaric interferences of Ca and K on ^{40}Ar , RBS analysis could only be performed on quartz,
202 which is the focus of this contribution. Data from feldspar experiments will be reported in a
203 separate contribution.

204 **2.3 Analytical Techniques and Data Acquisition**

205 For all quartz samples, we employed RBS and 213 and/or 193 nm UV-laser ablation
206 depth-profiling techniques to investigate diffusion of argon occurring over different length
207 scales within the crystal lattice. Details of all three analytical techniques are reviewed below.

208 *2.3.1 Argon Depth Profiling: Rutherford Backscattering (RBS)*

209 Non-destructive RBS analysis was undertaken first, providing information about
210 argon concentrations within the outer ~ 100 nm of the crystal lattice. Full details of the RBS
211 method are presented in Watson and Cherniak (2003). Quartz is well suited for RBS as there
212 are no mass interferences on argon, as is often the case with other crustal silicate minerals –
213 in particular those bearing significant potassium or calcium. The strength of the RBS method
214 is the spatial resolution, which can be a few nanometers to 10's of nanometers. This fine
215 spatial resolution illuminates features in the outermost portions of the quartz lattice that
216 would be blurred or obscured by more crude techniques. The limitation of RBS, however, is
217 the sensitivity. Argon concentrations below a few hundred ppm fall into the background
218 noise of RBS. This technique has been used in previous studies of argon diffusion in
219 minerals, including quartz (e.g., Watson and Cherniak 2003; Thomas et al., 2008).

220 *2.3.2 Argon Depth Profiling: Ultra-violet laser ablation mass spectrometry*

221 After RBS analysis, two UV-laser ablation depth-profiling techniques were
222 undertaken, including 213 nm laser measurements, followed later by 193 nm laser
223 measurements on one citrine quartz sample only (see section 2.3.5). 213 nm laser ablation of

224 the quartz surface was accomplished by rastering the beam over a fixed area, removing one
225 thin layer at a time, with increasing depth into the sample (Fig. 1). Depending on the laser
226 conditions used and the material ablated, the depth of each layer ranged from 0.2 to 10
227 microns; this dimension determines the spatial resolution of the technique. The benefit of
228 UV-laser ablation combined with noble gas mass spectrometry is the sensitivity to low argon
229 concentrations. For the rastered layer volumes used in our samples, the detection limit was
230 approximately 0.02 ppm argon (or about 1.12×10^{-5} cc-STP/g during analyses). This
231 technique has been used in previous studies and described at length in Wartho et al. (1999),
232 Arnaud and Kelley 1995 and Wartho et al. (2005). All measurements were undertaken using
233 a MAP-215-50 noble gas mass spectrometer.

234 A “surface stripping” (Fig. 1) technique was used to remove the uppermost argon-rich
235 layer of the mineral, in order to prevent interference with later measurements of argon
236 concentrations from deeper within the lattice. In this study, the surface strip was removed
237 (over an area of $300 \mu\text{m}^2$), but argon concentrations released from this strip could not be
238 measured because the high amount of argon present exceeded the limit of the mass
239 spectrometer’s detectors (but see below). Subsequent layers in the depth profile were over an
240 area of $200 \mu\text{m}^2$, precluding the possibility that these analyses might have clipped and
241 incorporated some of the surface layer.

242 In order to quantify the argon concentrations within the surface layer removed in this
243 style of analysis, a smaller surface area measurement was made on each sample where the
244 argon released could be measured within the limits of the detectors. For most samples, a
245 linear trough $5 \times 100 \mu\text{m}$ was used. These measurements were used to provide information
246 about concentrations within the uppermost surface of the mineral. Such measurements would

247 technically include both contributions from any absorbed argon on the surface (if present) as
248 well as argon within the outermost layer of quartz.

249 *2.3.3 UV-Laser ablation: Citrine quartz vs. clear quartz*

250 Disparate responses to the 213 nm UV-laser were observed between the citrine quartz
251 and the clear quartz. Due to its optically-clear nature, the clear quartz didn't couple strongly
252 with the laser and ablation occurred by damage and fracture as much by ablation. Evidence
253 of this fracturing is seen in the pit dimension measurements (see section 2.3.4) of the clear
254 quartz, where the excavated pits are jagged, non-uniform and exhibit evidence of fracturing
255 and remaining debris (Fig.1). Our later discussion takes into consideration the proportion of
256 material outgassed relative to the volume of material excavated and whether or not 213 nm
257 UV- laser analysis is suitable for this particular quartz variety.

258 Conversely, the citrine quartz coupled with the UV laser (213 nm and 193 nm; see
259 section 2.3.5 below) efficiently with no apparent fracturing and little or no edge fracturing in
260 the excavated pits (Fig. 1). The citrine also appears to yield a consistent, reproducible amount
261 of ablated material in each layer measured, and a desirable flat-bottomed pit.

262 *2.3.4 213 nm laser pit dimension measurements: Talysurf analysis*

263 In order to calculate argon concentrations present in the ablated quartz, the volume of
264 ablated material was calculated from measured pit dimensions using a Taylor Hobson
265 "Talysurf II", which employs a diamond stylus mounted to a piezometer to raster along the
266 bottom of the ablated pit or troughs and measure the pit dimensions. The Talysurf is capable
267 of 0.1 micron precision. The limitation here occurs when the depth of the pit is greater than
268 twice the width of the pit, as the stylus cannot achieve measurements of the true bottom. To
269 avoid this problem, sufficiently large and/or shallow pit dimensions were used.

270 *2.3.5 Additional Argon Depth Profiling: ArF 193 nm Excimer laser ablation*

271 In order to complement the spatial resolution limitations of the 213 nm laser, laser
272 ablation profiles were performed at greater spatial resolution on synthetic citrine sample SC-
273 1 (samples denoted in text and tables as five profiles, SC-E1 to SC-E5). Samples were
274 ablated using a UP-193 nm ArF Excimer laser, in order to achieve fine-resolution, flat-
275 bottomed laser pits. Samples were ablated repeatedly using as few as two 10 ns pulses around
276 0.5 mJ energy to achieve depth profiles. Final depths were measured using a Zygo white light
277 interferometer. All pits exhibited depth variations but these were less than 0.05 microns and
278 thus we have assigned this error to the individual pit depth measurements. Argon
279 concentrations were calibrated using similar pits ablated in the international standard FCT
280 sanidine. Measurements were undertaken using a Nu Instruments Noblesse noble gas mass
281 spectrometer and automated extraction line.

282 **3.0 DATA**

283 Depth profiling data sets for each mineral sample includes two concentration versus
284 depth profiles; one from RBS and one from 213 nm UV laser ablation. For sample SC-1, two
285 sets of UV-laser ablation profiles exist from 213 nm laser analyses and from further 193 nm
286 (these five profiles from sample SC-1 are denoted SC-E1 to SC-E5) laser analyses. All RBS,
287 213 nm- and 193 nm- laser data are available in a supplementary online data appendix.

288 **3.1 RBS Data**

289 A compilation of the clear and citrine quartz RBS diffusion profiles is given in Figure
290 2. The most notable features of the profiles are the high concentrations seen (1000's of ppm)
291 and shallow diffusive depth scale (~ from 60 to nearly 250 nm), with measurable profiles
292 reaching only a maximum of a few 100 nanometers into the crystalline lattice. There is a
293 significant range in maximum surface concentration from sample to sample (ranging from
294 1050 to 13450 ppm), and a fairly smooth and clear diffusional uptake profile emerges in each

295 analysis. Citrine quartz generally shows higher maximum surface concentrations (7120 ± 100
296 to 13450 ± 200) than clear quartz (1050 ± 100 to 10050 ± 200). Diffusion and concentration
297 data for RBS analyses are detailed in Table 2. Maximum surface concentrations in clear
298 quartz are consistent with the study of Watson and Cherniak (2003), but much higher than
299 Roselieb et al. (1997). This is not unexpected as we employ the same method (RBS) and used
300 the same clear quartz starting material as Watson and Cherniak (2003).

301 **3.2 213 nm UV Laser Data**

302 The argon diffusion profiles measured using a 213 nm UV laser to ablate samples in
303 clear and citrine quartz exhibit significant variability in concentration, depth and shape
304 (Table 3). A compilation of 213 nm laser data for clear and citrine quartz is given (Fig. 3).
305 These profiles exhibit the key features seen in the laser measured profiles, including: (1) ~
306 10's up to 150 microns depth of detectable argon penetration into the sample with
307 concentrations ranging from 0.04 to 55 ppm in the clear quartz and 0.21 to 27 ppm in the
308 citrine quartz, (2) a markedly higher surface concentration (e.g., up to 3012 ppm for SC-1;
309 surface concentrations not shown on Figure 3 due to drastically different concentration
310 scales), (3) a sharp kink in the diffusive uptake profile slope as defined by the higher surface
311 concentration point and subsequent one to two near-surface points (shown, for example, in
312 Fig. 3a, occurring between 10-20 μm depth) and (4) considerable and variable scatter in the
313 data.

314 A comparison of laser concentration-depth profiles for citrine and clear quartz can be
315 made (Fig. 3a/b to Fig. 3c). The profiles exhibit different characteristics, with the clear quartz
316 demonstrating lower argon concentrations, deeper penetration and more variable profiles,
317 while the citrine quartz shows higher argon concentrations, considerably more smooth and
318 well-behaved profiles, with shallower penetration into the crystal.

319 **3.3 193 nm UV Laser Data**

320 Sample SC-1 (724 °C, 160 MPa, 360 hours) was selected for further laser ablation
321 experiments using an ArF 193 nm laser. The 193 nm laser coupled well with the citrine
322 quartz, yielding smooth flat bottom pits, and permitting much finer scale depth profiling with
323 depth resolution as good as 0.06 μm per analysis. Five argon diffusion profiles were
324 measured in this sample, revealing diffusion profiles with similar depths of penetration but
325 with significant scatter in the maximum surface concentrations of argon. Concentrations
326 ranged between 260 and 8792 ppm argon (measured). Laser profiles SC-E2, SC-E4 (Fig. 4b,
327 Fig. 4d) show a kink in the diffusional uptake profile) labeled as 'kink point' on each profile.
328 Laser profiles SC-E3, SC-E5 (Fig. 4c, 4e) show uptake patterns that do not indicate an
329 obvious kink. SC-E1 (Fig. 4a) shows an unexpected drop in concentration at the surface, as
330 if some post-experimental loss of argon from the nearest surface had occurred. How this
331 could be the case for this profile but not for the other four in this same mineral is unclear; we
332 regard the nearest surface point in profile SC-E1 as anomalous and disregard it.

333

334 **4.0 DATA EXTRACTION: DIFFUSION MODELING APPROACHES FOR ARGON**

335 **DEPTH PROFILES**

336 Below, the methods used to model these profiles in order to quantify diffusivity in
337 each case, are described.

338 **4.1 Modeling Lattice Diffusion**

339 The simplest argon uptake behavior would be pure lattice diffusion. Diffusion of
340 argon is treated as 1-dimensional diffusion into semi-infinite planar medium, with a
341 concentration-independent diffusivity. Diffusivities were thus obtained by fitting the profiles
342 to the appropriate diffusion equation (Crank, 1975):

343
$$C = C_0 \left[\operatorname{erfc} \left(\frac{x}{\sqrt{4Dt}} \right) \right] \quad (1)$$

344 where C is the concentration of argon (diffusing in), C_0 is equivalent to the equilibrium
345 solubility of argon in quartz (with respect to the pure pressurize argon gas medium), D is the
346 diffusion coefficient (m^2s^{-1}), and t is the duration of the experiment run. The best fit provides
347 both the relevant diffusivity and equilibrium surface concentration or apparent solubility (i.e.,
348 the maximum concentration extrapolated all the way to the surface of the crystal in
349 equilibrium with its surroundings). All RBS profiles were modeled this way as the shape of
350 the RBS diffusion profiles reveals a smooth error function form.

351 **4.2 Modeling Combined Effects of Lattice and Fast-Path Diffusion**

352 In many of the profiles from the 213 nm and 193 nm UV-laser analysis, a significant
353 kink, or break in slope was noted in the uptake profiles, separating higher concentrations in
354 the outermost portion of the mineral, from lower concentrations deeper in (for example, Fig.
355 4b/d, 5a). With this sharp kink, a simple error-function diffusion model can not appropriately
356 reproduce the entire profile and gives erroneous results; no error function fits to raw laser
357 data are reported. In other diffusion studies (Zhang et al., 2006), such a kink has been
358 interpreted as evidence for a second diffusion mechanism other than volume lattice diffusion,
359 which could be a significant mechanism for transport deeper into the mineral. In this
360 scenario, the nearest surface data with high concentrations and relatively steep slope
361 represent argon diffusing via the lattice, whereas deeper in the mineral, argon penetrates
362 further via a “fast path” (Lee, 1995; Zhang et al., 2006). In a few cases, the hypothesized
363 effects of lattice diffusion appeared to penetrate beyond the very first surface strip layer in
364 the 213 and 193 UV-laser profiles; that is, the “kink” in the profile occurs after the first two
365 data points in a profile. In these cases where the hypothesized effects of the two pathways

366 could be resolved and differentiated, an attempt was made to extract and separate the
367 contributions from the lattice and fast-path following the method outlined by Zhang et al.
368 (2006).

369 The Whipple-LeClaire equation (Whipple, 1954; LeClaire, 1963) has been used to
370 describe fast diffusive transport via planar grain boundaries combined with the slower effects
371 of lattice diffusion into the mineral from the grain boundaries themselves. It is used here as
372 an approximation for the “fast diffusive pathways” present in quartz (which may or may not
373 be planar features). The Whipple-LeClaire equation captures the net behavior of Ar uptake
374 and provides a first order means of quantifying the process. The equation is:

$$375 \quad \delta D_b = 1.332 \left(\frac{D}{t} \right)^{1/2} \left(-\partial \ln \bar{c} / \partial z^{6/5} \right)^{-5/3} \quad (2)$$

376 where δD_b is the product of the fast path diffusivity and the width of the planar fast path
377 feature. D is the lattice diffusion coefficient and δ is the thickness of the intracrystalline “fast
378 paths” which may (in our samples) be pipes or planar defect feature, z is the depth, t is the
379 experiment time and \bar{c} is the average concentration that occurs in a slice that is perpendicular
380 to the fast path.

381

382

5.0 RESULTS

383 5.1 RBS Profiles: Lattice Diffusion

384 Resulting diffusivities from error function fits to RBS data are listed in Table 2.

385 Citrine and clear quartz exhibit similar diffusivities, though they show highly variable

386 apparent solubilities, with the citrine quartz (7120 to 13450 ppm) exhibiting higher

387 concentrations than the clear quartz (1050 to 9750 ppm). The RBS apparent solubility data

388 for each quartz sample analyzed is summarized in Table 2. In general, the natural quartz
389 produced smoother profiles than the citrine quartz.

390 **5.2 Laser Profiles**

391 5.2.1 Modeling Laser Depth Profiles: 213 nm

392 When using the laser data to extract diffusivities, different model approaches can be
393 taken: Ignoring the high surface concentrations and disregarding it as adsorbed argon on the
394 mineral surface, whereby the rest of the profile is fit to a typical diffusion curve (given in
395 Table 3 column a), or a composite fit including both slow lattice diffusion and “fast-path”
396 diffusion using the Whipple-LeClaire equation can be made (Table 3 column b) (see section
397 5.2.1.3 below). Alternatively, another approach can be taken whereby the incorporation of
398 the high surface concentration is forced to an error function fit of all the data, however, this
399 approach is not attempted nor reported here.

400 *5.2.1.1 Shallow Diffusion Profiles*

401 In many previous studies of argon diffusion using UV laser ablation (e.g., Wartho et
402 al. 1999), nearest surface analyses appear to have unexpectedly, and inconsistently, elevated
403 concentrations deviating significantly from the rest of the profile, as do several of the
404 profiles illustrated in this study. Frequently, these elevated or “anomalous” surface points are
405 disregarded because of the possibility they include significant adsorbed argon on (rather than
406 in) the mineral surface. Following this approach, the main problem is choosing which (if
407 any) data within the profile to discard as relicts of atmospheric surface adsorption, or other
408 damage effects. There is a challenge in deciding how to model the 213 nm profile data
409 because the surface strip data indicates much higher surface concentrations than deeper with
410 the sample and cannot be fit appropriately by a forcing a single error-function fit to the
411 profile. Discarding this surface strip point produces a reasonable fit to the rest of the data,

412 giving the resulting apparent solubility given in Table 3 (column a) and diffusivity listed in
413 Table 4 (column a). While there is considerable variability in concentration, the spatial
414 resolution allows for an appropriate fit to all points of the sample.

415 The problem with this approach is illuminated when comparing the apparent
416 solubility from this modeling of 213 nm laser ablation data to the apparent solubility from
417 modeling of the RBS and 193 nm UV laser ablation data; they differ by orders of magnitude.
418 As described in greater detail in section 3.1, the RBS data show a smooth and systematic
419 diffusive uptake profile up to 250 nm into the quartz lattice and are thus internally consistent.
420 On this basis, we do not believe that ignoring the near surface laser layers is the correct way
421 to model and describe the laser data. Rather, it appears that the high near surface
422 concentrations in the laser should not be discarded as they are consistent (at least within an
423 order of magnitude) with the RBS data and shallow 193 nm laser depth profiles.

424 *5.2.1.2 Adsorption of argon?*

425 The adsorption of argon is often cited as a potential complication for studies where
426 argon solubilities were regarded as too high (Broadhurst et al., 1990, 1992; Shibata et al.,
427 1994) and contaminating argon on mineral surfaces is suggested to have affected such studies
428 (Roselieb et al., 1997; Brooker et al., 1998; Chamorro et al., 2002). Several studies (Brooker
429 et al. 1998; Wartho et al., 1999; Heber et al., 2007) also attributed high surface
430 concentrations in the outermost surface layers of polished mineral surfaces (1- 6 nm) to
431 contaminating adsorbed argon. However, recent investigation (Thomas et al., 2008) led to
432 several ‘zero-time’ experiments involving the pressurization of minerals without heating and
433 experiments following typical in-diffusion procedure, but holding at temperature for very
434 short durations (minutes) to determine if the presence of adsorbed argon could be detected.
435 Neither of the zero-time experiments revealed any measurable surface argon, demonstrating

Comment [s1]:
Thank you Jay !

436 that adsorbed argon, if present, is a transient process that will not affect diffusion profiles.
437 The findings of Thomas et al. (2008) confirm that studies involving high temperature, long-
438 duration experiments will not be compromised by any adsorbed surface contamination of
439 argon.

440 5.2.1.3 Whipple-LeClaire Profile Fits

441 Following Zhang et al. (2006), fitting the data to isolate the two contributions (lattice
442 and fast path) is done in several parts (see Fig. 5 for an example of the Whipple-LeClaire
443 fitting procedure on an argon diffusion profile in citrine quartz): (1) On a plot of $\ln C$ vs. $x^{6/5}$
444 (where C is concentration) the highest concentration that can be attributed to the fast path is
445 selected (i.e., the kink or separation point between what should be two roughly linear
446 relationships with different slopes, typically the first 1-2 surface points), (2) a straight line
447 segment is drawn from the origin to that highest concentration point to approximate the fast
448 path contribution in the near surface region where it overlaps with surface-perpendicular
449 lattice diffusion, (3) the fast path contribution is subtracted from the data to leave only the
450 surface perpendicular lattice diffusion contribution. The resulting profile (which may be only
451 2-3 significant points nearest the surface in this study) can then be fit using the error-function
452 curve (Eq. 1), and the resulting lattice diffusivity can be extracted. Once this lattice
453 diffusivity (D) is determined, the Whipple-LeClaire equation can be used to quantify the δD_b
454 of the fast paths.

455 If we accept that the near surface laser data represent slow diffusion of argon into the
456 quartz lattice, we must call upon a different mechanism for the argon measured in laser
457 ablation analyses deeper within the sample. There is a sharp kink between the shallow
458 profile measured using RBS and 193 nm laser ablation (including the nearest surface laser
459 layers) and the deeply penetrating 213 nm laser data. In some cases, this kink point is

460 apparent beyond the first surface layer of laser analyses. In this case, the more deeply
461 penetrating, lower concentration laser data can be described by a model of fast-path diffusion
462 as outlined in section 2.4.2. Note that the second laser-derived data point from the diffusion
463 profile of sample SC-1 (Fig. 5a) is slightly, though significantly, elevated above the trend
464 suggested by the rest of the profile, reflecting the influence of higher concentrations from a
465 slower diffusive pathway.

466 In this case, a fit ignoring the surface data point and the second data point could be
467 made. Such a fit, with results listed in Table 3 (column b), would be analogous to diffusive
468 uptake via the “fast-path” and can be modeled using the Whipple-LeClaire equation (Eq .2)
469 for an appropriate fit. However, especially in the case of the clear quartz, the kink point is not
470 always obvious, and with the highly variable profiles, a reasonable fit can be difficult to
471 make. The resulting diffusivities from the error-function fit to the Whipple-LeClaire
472 modified profile are listed in Table 4 (column b). Calculated δD_b values are listed in column
473 “c” of Table 4.

474 5.2.2 Modeling Laser Depth Profiles: 193 nm

475 Figure 4 details the profiles resulting from 193 nm analyses. The range in
476 concentrations-depth data is shown (left) and the error function fit to Whipple-LeClaire
477 corrected data (right). These profiles exemplify the variability in the argon concentrations
478 seen in citrine quartz. Profiles SC-E2 and SC-E4 (Fig. 4b and 4d) illustrate the kink point, or
479 break in slope, in the diffusion profile. The resulting LogD from fitting the profiles with
480 removal of the surface concentration is given in Table 4 (column a) and the LogD from the
481 Whipple LeClaire corrected data (right panels of Fig. 4) is given in Table 4 (column b).
482 Calculated δD_b values are listed in column “c” of Table 4.

483

484

6.0 DISCUSSION

485 6.1 Sample Preparation and the Near Surface Crystal Structure

486 Several studies have discussed the structure of the near-surface region of the crystal
487 lattice in the context of noble gas experiments (Roselieb et al., 1997; Wartho et al., 2005;
488 Heber et al., 2007) and some have suggested that the near surface region of crystals are
489 structurally anomalous compared to the interior mineral lattice. The implication of this
490 hypothesis is that high apparent solubilities are an artifact of such a structurally amorphous
491 surface layer, and are not representative of the bulk crystal lattice. In contrast, several studies
492 have carefully structurally characterized the near-surface structure (e.g., AFM, EBSD, X-ray
493 reflectivity; Fenter et al., 2000; 2001; Schlegel et al., 2002; Watson and Cherniak, 2003;
494 Thomas et al., 2008). The study of Thomas et al. (2008) demonstrated through the use of
495 electron backscatter diffraction (EBSD) that pre-annealed and polished crystal surfaces do
496 not differ from natural crystal faces, and revealed that the outer 10 nm of the crystal lattice is
497 structurally indistinguishable to the interior. From this study, Thomas et al. (2008) were able
498 to conclude that the notorious damaged ‘Bilby’ layer oft discussed in experimental studies
499 did not exist in their samples. Other studies (Fenter et al., 2000; 2001) do document the
500 presence of a structurally anomalous layer, though this layer is restricted to only the first 1-2
501 nm, after which the structure is identical to the interior lattice. Particularly for quartz, this
502 layer has been quantified to extend no more than 1.4 nm into the quartz lattice (Schlegel et
503 al., 2002). The suggestion that increased argon uptake could occur through networks of
504 fractures and dislocations induced through mechanical polishing is not corroborated by the
505 data in this study. Conversely, we see low diffusivities in the outermost ~ 100 nm of the
506 crystal, not the high diffusivities that would occur through ‘fast-path’ diffusion anticipated if
507 such a defect-rich, structurally anomalous layer were present. The agreement of the diffusion

508 data extracted from samples in this study with that of Watson and Cherniak (2003), using a
509 combination of pre-annealed, colloidal silica-polished (0.06 μm) and natural crystal faces, is
510 further testament that we are observing lattice diffusion rather than diffusion and enhanced
511 argon solution due to the presence of a mechanically polished induced Bilby layer.

512 **6.2 Diffusion Data: Lattice versus Fast Path**

513 Consistent with previous work by Watson and Cherniak (2003), we see a very
514 smooth, well-behaved diffusive profile for quartz with respect to RBS and 193 nm laser
515 ablation analysis and depth-scale (on the order of $\sim 100\text{-}250$ nm to 400 nm, respectively).
516 Data are well fit by an error-function fit to the diffusion profiles (Eq. 1). The diffusion data
517 obtained from RBS profiles for both quartz samples is plotted on an Arrhenius diagram
518 (Fig.6). The best Arrhenius fit to our new data for all quartz combined give $E_a=41$ kJ/K* mol
519 and $D_0=1.3 \times 10^{-20}$ m^2/s . As shown in Figure 6, this is in agreement with the previous work of
520 Watson and Cherniak (2003) and Thomas et al. (2008).

521 While there is a general increase of argon concentrations towards the surface of the
522 quartz surface, occasional jumps or spikes in concentration with depth in the crystal were
523 observed; this was seen most obviously in the clear quartz, but also in the citrine quartz to a
524 lesser degree. These argon concentration spikes are similar to those observed by Wartho et al.
525 (2005) and probably relate to liberation of argon from micro fluid inclusions or defects in the
526 crystal.

527 **6.3 Area Normalized Argon Concentrations**

528 With both the clear quartz and in particular the citrine quartz, we see a high capacity
529 for argon manifested in the nearest surface few hundred nanometers, with concentration
530 reaching thousands of ppm. This concentration drops off dramatically with depth, with
531 subsequent data points showing concentrations less than 1 ppm. This is seen in both the RBS

532 and 193 nm laser ablation analysis, but also in the surface analyses using the 213 nm UV
533 laser (Fig. 7) With regards to the concentrations of argon in the outermost surface layer,
534 surface concentrations integrated over the outermost 200 nm of quartz were calculated to
535 investigate differences in measured surface concentrations between 213 nm, 193 nm laser
536 analyses and RBS analyses. Table 5 gives the calculated ranges for analyzed samples (in
537 argon atoms per area) , illustrating that the values determined by 193 nm laser analyses lie
538 within a similar range to the RBS determined concentrations (see also Fig. 7 for variations
539 with temperature). There appears to be some discrepancy between the argon atoms per area
540 determined by 213 nm-, 193 nm-laser analyses and RBS determined concentrations although
541 range of determined concentrations overlap and the 213 nm analyses are punctuated by
542 higher concentrations, seen especially in the two citrine analyses (Fig. 7a). The RBS analyses
543 average much larger areas so it is possible that the laser profiles (both 193 and 213 nm)
544 reveal some heterogeneity in concentration across the mineral surface, particularly the citrine
545 quartz which proved to be highly variable with regards to argon concentrations. This may in
546 turn be due to the presence of trace Fe, which has been suggested to cause enhanced uptake
547 of argon in Fe-bearing minerals (Thomas et al., 2008)

548 It should also be noted that for the temperatures and pressures that our experiments
549 were conducted, the transition between α -quartz to β -quartz is anticipated. This occurs at 573
550 °C, but increases 1 °C for each 40 bar, giving an approximate temperature of 615 °C for
551 experiment # 1 (1700 bar; samples N1-N4) and 613 °C for experiment # 2 (1600 bar; samples
552 N5-8; SC-1- SC-4). This is an instantaneous, displacive transition whereby only changes in
553 the angles and lengths of Si-O bonds occur in the change from trigonal to hexagonal
554 symmetry. While not a major structural change, there is a change in density from
555 approximately 2.65 to 2.53 g/cm³ which could result in a slightly more 'open' structure,

556 suitable for accommodating more argon. The changes in calculated argon concentrations/area
557 for each sample seen after this temperature (Fig. 7) are relatively minor, though there is a
558 general increase towards higher concentrations of argon which may be the result of further
559 accommodation of argon after this transition.

560 **6.4 Significance of Multiple Diffusion Regimes**

561 On the basis of these experiments we propose a hypothesis of two separate diffusion
562 pathways (illustrated in Fig. 8): (1) Lattice diffusion and (2) fast-path diffusion. The
563 measurements made in this study provide evidence for these two distinct diffusion pathways,
564 each operating throughout the crystal with its own rate of diffusion, geometry and
565 contributions to the net diffusive uptake of argon. It seems likely that the different
566 lengthscales achieved by RBS (and 193 nm laser ablation) compared to the 213 nm UV laser
567 ablation, reveal these two different diffusion mechanisms.

568 In the laboratory experiments, lattice diffusion is slower and thus occurs over shorter
569 lengthscales (~ 10's to 100's of nm for our experimental timescales; Fig. 8a and 8b). These
570 are extremely significant concentrations on the order of thousands of ppm but the depth to
571 which these high concentrations of gases penetrate is extremely shallow over the short
572 duration of the experiments. If these high concentrations reflect the true intrinsic lattice
573 solubility, then that value can be compared to solubilities in other phases in order to calculate
574 equilibrium partitioning coefficients (cf. Watson et al. 2007). However, given the very slow
575 lattice diffusivity, it is pertinent to consider how long it will take for quartz to reach these
576 high equilibrium concentrations, especially as virtually all of the radiogenic ^{40}Ar that might
577 accumulate in quartz must diffuse in from external K-bearing sources of fluids in the
578 intergranular transporting medium/grain boundary network.

579 6.4.1 Quartz as a sink for argon?

580 The existence of multiple paths for diffusion has significance for geochronology
581 (closure temperature models), models for evolution of terrestrial degassing, rates of argon
582 uptake/loss, and models for the presence and transport of excess argon in various geologic
583 systems. Multi-path diffusion affects how we model diffusive uptake or release of argon
584 from quartz. For example, as fast paths are generated and become more concentrated or
585 abundant (i.e., due to progressive deformation) a net effect is to decrease the effective
586 diffusion length-scales for lattice diffusion, thus also decreasing the timescale to fill the
587 quartz lattice up to the potential lattice solubility. This can be important for shorter-lived
588 systems (e.g., magmatic timescales).

589 The fast-paths are significant in determining the relative ability of quartz to act as a
590 sink for noble gases in various geologic systems (see Fig. 9). For example, despite high
591 lattice solubilities, quartz will not be an important sink for argon in magmatic systems, due to
592 the short timescales involved (~ 1 Ma). While the capacity for argon is high, there is not
593 enough time in such systems for the solubility limit to be effectively reached. Fast-paths may
594 act to move argon into the lattice over shorter durations, though never approaching
595 equilibrium concentrations. Even though significant uptake of argon into quartz would not
596 occur in magmatic timescales, any shallow uptake profiles in quartz could then be used as a
597 measure of magmatic timescales.

598 6.4.2 Physical nature of the fast paths

599 The use of the Whipple-LeClaire model to describe the deeper diffusion and fast-
600 paths provides a useful end-member conceptual and quantitative description of the
601 phenomena. However, the approximation of the fast paths as planar features is made based
602 on similarity with earlier experiments (Zhang et al. 2006) and not on the basis of evidence
603 from the present work, since the deeper concentration profiles are scattered and do not

604 provide diagnostic fits. Similar experiments in other minerals with higher Ar concentrations
605 may provide solution to this problem. Fast-path diffusion, as measured in the present
606 experiments, is not lattice-controlled (though argon having deeply penetrated a mineral via
607 fast paths may then begin to diffuse slowly into the lattice at depth) but instead is presumably
608 dominated by defects, dislocations, or planar features in the mineral. It carries much lower
609 concentrations of argon (only on the order of 1 ppm, compared to 1000's of ppm for lattice-
610 diffusion) but it appears to transport these gases faster and deeper into the crystal lattice,
611 penetrating to 100's of microns over the duration of our experiments. The transport capacity
612 of each path is determined by its width, and partitioning of argon between the fast path, the
613 intergranular transporting medium and the mineral lattice. All of this is encapsulated in the
614 δDb term (of Eq. 2) and controls how well argon can be brought deeper in to the quartz
615 before it can start diffusing out of the fast path and into the lattice.

616 It is difficult to speculate on the physical nature and properties of the fast-paths that
617 result in drastically different diffusivities. Fractures, dislocations and crystal defects (e.g.,
618 micro-structural defects, edge/screw dislocations, micro-fractures) would all have potential to
619 create such enhanced diffusion pathways. Moreover, Watson and Cherniak (2003) describe
620 the existence of "nanopores" in quartz samples from 70 nm down to the 10-15 nm pore size
621 range which can be seen in SEM images. Differences in densities of these nanopores may
622 also provide support for the general scatter present in the surface concentrations observed,
623 particularly if present in the hydrothermally, synthetically synthesized citrine quartz. Greater
624 physical quantification of potential fast-paths in mineral phases would allow for increased
625 understanding of their overall impact on the apparent solubility of argon in minerals, and how
626 such a contribution can be identified. One of the main concerns is the size, density,
627 anisotropy and interconnectivity of such paths. These parameters will ultimately affect the

628 contribution the fast paths will have on the overall diffusivity, and whether or not the two
629 distinct diffusion pathways can be appropriately decoupled.

630

631

7.0 SUMMARY

632 Analysis of a single sample using both UV laser ablation and RBS techniques has
633 allowed us to identify two different diffusive regimes in clear, natural rock crystal quartz and
634 synthetic citrine quartz. This study's laser ablation data set confirms very slow lattice
635 diffusion for argon in quartz previously observed from RBS measurements alone (Watson
636 and Cherniak, 2003; Thomas et al., 2008). This slow lattice diffusion in quartz would be
637 overlooked with the sole use of 213 nm UV laser ablation or even spatially coarser analytical
638 tools. In some previous work, high concentrations in the surface layers of UV-laser depth
639 profiles has been discarded as "anomalous" argon (e.g., Wartho et al. 1999). In the case of
640 quartz, this shallow nearest surface profile appears to represent the true intrinsic lattice
641 diffusion and solubility and should not be ignored.

642 The 193 nm laser yields fine enough spatial resolution to capture and reproduce the
643 RBS lattice diffusion for argon in quartz. Both methods of analysis produce meaningful and
644 consistent results; the only difference is in the scale and resolution of observation (RBS
645 analysis produces many tens of data points within 0.1 μm , whereas 193 nm laser analyses
646 produce 1-2 data points in the same 0.1 μm).

647 The existence of fast diffusion pathways has been observed in the deeper diffusive
648 profiles measured by 213 nm laser ablation. If the high concentration seen in the lattice
649 represents the true lattice solubility and diffusivity, than the deeper portions of laser analysis
650 represent the effect of the fast-path diffusivity. This observation raises the issue for other UV
651 laser ablation measured profiles such as that measured in K-feldspar (e.g., Wartho et al.

652 1999). While the Wartho et al. (1999) measurements are real and valid, they have been
653 interpreted in the past as lattice diffusivity and the implication from the present experiments
654 may be that they, and other geochronologically important argon diffusion measurements,
655 may represent fast-path diffusivity. As discussed above, the fast paths are no less important
656 in controlling the manner in which argon enters (or exits) a crystal, but the mathematical
657 treatment of multi-path diffusion is fundamentally different and may need to be considered in
658 many minerals.

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659

660

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TABLES

866 **Table 1 Experiment conditions.** Cold-seal run conditions for two experiments in this study. “N”

867 refers to natural clear quartz. “SC” refers to synthetic citrine quartz.

868

Sample	T, °C	P, MPa	Duration, h
Experiment #1			869
N1	824	170	480
N2	764	170	480 ⁸⁷¹
N3	642	170	480
N4	489	170	480 ⁸⁷²
Experiment #2			870
N5	724	160	360 ⁸⁷³
SC-1	724	160	360
N6	669	160	360 ⁸⁷⁴
SC-2	669	160	360 ⁸⁷⁵
N7	561	160	360
SC-3	561	160	360 ⁸⁷⁶
N8	419	160	360
SC-4	419	160	360 ⁸⁷⁷

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891 **Table 2 Quartz RBS data.** Extrapolated diffusivities and equilibrium concentrations for all quartz
 892 minerals from RBS analysis. Errors on Log D were taken to be 0.6 log units (Watson and Cherniak,
 893 2003). R² values represent the goodness of the error-function fit to the data.

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Sample	T, °C	P, MPa	Log D	R ²	Ar PPM	Solubility ⁸⁹⁶ Ar (cc-STP/g-bar)
N1	824	170	-20.9	0.92	8000 ± 150	0.00263 ⁸⁹⁷
N2	764	170	-20.8	0.93	9750 ± 250	0.00321 ⁸⁹⁸
N3	642	170	-20.9	0.76	1050 ± 100	0.00034
N4	489	170	-21.0	0.91	3200 ± 300	0.00105 ⁸⁹⁹
N5	724	160	-20.1	0.65	2950 ± 200	0.00103
SC1	724	160	-20.4	0.98	12500 ± 150	0.00437 ⁹⁰⁰
N6	669	160	-20.7	0.93	10050 ± 200	0.00351
SC-2	669	160	-20.7	0.91	13450 ± 200	0.00470 ⁹⁰¹
N7	561	160	-20.9	0.94	1800 ± 100	0.00063
SC-3	561	160	-20.9	0.84	9600 ± 150	0.00336 ⁹⁰²
N-8	419	160			<i>Not analyzed</i>	
SC-4	419	160	-20.9	0.78	7120 ± 100	0.00249 ⁹⁰³

904

905 **Table 3 Laser concentration extrapolations.** (a) Resulting extrapolated concentrations for
906 the error-function fit to all laser data, disregarding the surface concentration measurement.
907 This fit done to 213 nm data only. (b) Resulting extrapolation from the Whipple-LeClaire fit
908 to the laser data. (c) Measured surface concentrations from surface strip analyses (see text for
909 discussion) for all samples with the 213 nm laser.
910

Sample	T, °C	P, MPa	Duration, h	a (ppm)	b (ppm)	c (ppm)
N1	824	170	480	<i>nm</i>	<i>nm</i>	<i>nm</i>
N2A	764	170	480	50	190	91
N2B	764	170	480	0.6	<i>x</i>	
N2C	764	170	480	2.3	230	
N3	642	170	480	12	240	123
N4	489	170	480	9	150	74
N5	724	160	360	4	<i>x</i>	<i>nm</i>
SC-1	724	160	360	120	7350	3012
SC-E1	724	160	360	10000	14500	<i>na</i>
SC-E2	724	160	360	3300	9500	<i>na</i>
SC-E3	724	160	360	<i>x</i>	65	<i>na</i>
SC-E4	724	160	360	530	1900	<i>na</i>
SC-E5	724	160	360	250	135	<i>na</i>
N6	669	160	360	<i>nm</i>	<i>nm</i>	<i>na</i>
SC-2	669	160	360	7	850	810
N7	561	160	360	--	--	--
SC-3	561	160	360	<i>nm</i>	<i>nm</i>	<i>nm</i>
N8	419	160	360	--	--	--
SC-4	419	160	360	<i>nm</i>	<i>nm</i>	<i>nm</i>

nm, not measured

na, by 193 nm laser analysis only

--, profiles measured but concentration information not extracted due to incomplete ablation of sample

x, no appropriate fit could be made

911 **Table 4 Calculated laser diffusivities.** (a) Calculated diffusion data for all minerals from laser
912 concentration-depth profiles excluding the surface concentration. (b) Calculated 213 and 193 nm
913 laser diffusion data for all minerals using the Whipple-LeClaire fit to exclude the fast-path component
914 and fitting the resultant data to the error-function. (c) Calculated δDb for 213 and 193 nm laser
915 diffusion profiles.

Sample	T, °C	P, MPa	Duration, h	a, Log D (m ² /s)	R ²	b Log D (m ² /s)	R ²	c, δD (cm ³ /s)
N1	824	170	480	<i>nm</i>		<i>nm</i>		<i>nm</i>
N2A	764	170	480	-16.3	0.58	-16.5	0.99	7.46 x 10 ⁻¹⁵
N2B	764	170	480	-14.3	0.98	<i>x</i>	-	3.53 x 10 ⁻¹⁴
N2C	764	170	480	-15.5	0.51	-16.7	0.99	2.18 x 10 ⁻¹⁴
N3	642	170	480	-16.7	0.99	-17.3	0.98	9.94 x 10 ⁻¹⁵
N4	489	170	480	-17.0	0.92	-17.3	0.98	1.32 x 10 ⁻¹⁴
N-5	724	160	360	-16.2	0.10	<i>x</i>		<i>x</i>
SC-1	724	160	360	-18.1	0.97	<i>x</i>	0.98	2.15 x 10 ⁻¹⁵
SC-E1	724	160	360	-20.2	0.95	-20.5	0.95	8.78x 10 ⁻¹⁷
SC-E2	724	160	360	-20.0	0.95	-21.0	0.95	9.10x 10 ⁻¹⁷
SC-E3	724	160	360	<i>x</i>		-20.0	0.29	8.14x 10 ⁻¹⁷
SC-E4	724	160	360	-19.3	0.78	-20.7	0.95	3.13x 10 ⁻¹⁶
SC-E5	724	160	360	-20.0	0.93	-21.0	0.84	1.16 x 10 ⁻¹⁶
N-6	669	160	360	<i>na</i>		<i>na</i>		<i>na</i>
SC-2	669	160	360	-17.0	0.87	-21.0	0.99	9.33 x 10 ⁻¹⁵
N-7	561	160	360	<i>na</i>		<i>na</i>		<i>na</i>
SC-3	561	160	360	<i>na</i>		<i>na</i>		<i>na</i>
N-8	419	160	360	<i>na</i>		<i>na</i>		<i>na</i>
SC-4	419	160	360	<i>na</i>		<i>na</i>		<i>na</i>

nm, not measured

na, by 193 nm laser analysis only

--, profiles measured but concentration information not extracted due to incomplete ablation of sample

x, no appropriate fit could be made

917 **Table 5 Surface-area normalized argon concentrations.** Area-normalized argon surface
 918 concentrations in quartz for (a) RBS, (b) laser-determined concentrations and (c) 193 nm
 919 laser determined concentrations for sample SC-1.

920

Sample	Temp, °C	Pressure, MPa	Duration, hours	(a) RBS	(b) 213 Laser	(c) 193 Laser
N1	824	170	480	1.1×10^{14}	<i>nm</i>	<i>nm</i>
N2	764	170	480	1.9×10^{14}	5.8×10^{15}	<i>nm</i>
N3	642	170	480	1.9×10^{13}	3.1×10^{15}	<i>nm</i>
N4	489	170	480	4.6×10^{13}	1.8×10^{15}	<i>nm</i>
N5	724	170	480	3.7×10^{16}	1.2×10^{15}	<i>nm</i>
SC-1	724	160	360	3.9×10^{15}	1.7×10^{16}	<i>nm</i>
SC-E1	724	160	360	<i>193 only</i>	<i>193 only</i>	1.8×10^{15}
SC-E2	724	160	360	<i>193 only</i>	<i>193 only</i>	2.7×10^{15}
SC-E3	724	160	360	<i>193 only</i>	<i>193 only</i>	1.8×10^{15}
SC-E4	724	160	360	<i>193 only</i>	<i>193 only</i>	7.3×10^{15}
SC-E5	724	160	360	<i>193 only</i>	<i>193 only</i>	1.2×10^{14}
N6	669	160	360	2.5×10^{15}	<i>nm</i>	<i>nm</i>
SC-2	669	160	360	3.1×10^{15}	1.0×10^{16}	<i>nm</i>
N7	561	160	360	3.3×10^{14}	<i>nm</i>	<i>nm</i>
SC-3	561	160	360	1.7×10^{15}	<i>nm</i>	<i>nm</i>
N8	419	160	360	<i>nm</i>	<i>nm</i>	<i>nm</i>
SC-4	419	160	360	1.5×10^{15}	<i>nm</i>	<i>nm</i>

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922 *nm, not measured*

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FIGURE CAPTIONS

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930 **Fig 1. (a)** Illustration of laser ablation pits as measured by the Talysurf, the technique used
931 for 213-nm laser pit measurements, resulting in profiles seen in **(b)**. The 300 micron surface
932 strip removal is seen at the mineral surface, with subsequent 200 micron ablation squares
933 continuing at depth into the sample. Profiles for clear quartz (upper) and citrine quartz
934 (lower) are shown in **(b)**, illustrating the differences in the way the laser couples with
935 different quartz samples (see section 2.3.4).

936

937 **Fig. 2** RBS measured argon concentration (ppm) vs. depth (nm) profiles for clear quartz
938 (Expt. # 1) samples N1-N4 **(a)**; clear quartz (Expt. # 2) samples N5-N7 **(b)**; and citrine
939 quartz, samples SC1-SC-4 **(c)**. Symbols given in the legend.

940

941 **Fig. 3.** UV-Laser (213nm) depth profiles in clear quartz. **(a)** All measured 213 nm laser
942 argon concentrations (ppm) vs. depth (μm) profiles for natural quartz samples N3-N5 (Expt.
943 #1 and 2) fit to the error function **(a)**. Repeat profiles for sample N2 (N2A-N2C) are shown
944 separately in **(b)** due to differences in depth-scale. Citrine quartz profiles for samples SC-1
945 and SC-2 are shown in **(c)**. Surface strip data, which were acquired for all profiles, are not
946 shown on plots but all give concentrations between 74 to 123 ppm argon in the clear quartz
947 and 810 to 3012 ppm argon in the citrine quartz (Table 3, column d). Symbols and
948 experiment temperatures given on the plots.

949

950 **Fig. 4.** The five 193 nm-laser argon concentration (ppm) vs. depth (μm) determined profiles
951 on citrine sample SC-1 (profiles labeled SC-E1 to SC-E5). Profiles illustrate the raw data

952 with the 'kink' point in the profile (**left**) and the Whipple-LeClaire corrected fit by
953 subsequent modeling the an error-function (**right**) (R^2 given in Table 4).

954

955 **Fig. 5. (a)** 213 nm laser measured diffusion profile from citrine sample SC-1 at 724°C. Note
956 the high surface concentration point (surface strip measurement at 3012 ppm argon, not
957 illustrated on the plot due to scale differences), which makes a fit to the error-function
958 problematic. For comparison, the range represented by a typical RBS profile (as seen in Fig.
959 2) is shown by a shaded grey bar next to the axis. **(b)** Plot of $\text{Ln}C$ vs. $\text{depth}^{6/5}$, showing the fit
960 of the line (note the kink point in the curve). The second-to-last data point was discarded as
961 an outlier as it was anomalously high compared to its neighbors. The equation of the line
962 shown is used to calculate the contribution by the fast-path from the Whipple-LeClaire
963 formulation. The effect of the lattice contribution is subsequently subtracted from the profile,
964 resulting in **(c)** the modified profile showing the contribution of the fast path or pipes. This
965 resulting profile is then fit to the error function (R^2 given) **(d)** Modeled contribution of the
966 lattice diffusion (solid black line) and fast path (dotted black line), with a close up of the
967 overlapping components in panel **(e)**. The cross hatched portions represent the separate
968 contributions of each pathway, showing the area of overlap.

969

970

971 **Fig. 6.** Summary of diffusion data for combined RBS (clear quartz represented as black
972 circles and citrine quartz by white squares with black crosses) and 193 nm laser-derived data
973 (grey circles) on an Arrhenius diagram ($1/T(K) \times 10^4$ vs. $-\log D \text{ m}^2/\text{s}$). RBS clear quartz data
974 from Watson and Cherniak (2003) and Thomas et al. (2008) are represented by the pale grey
975 outlined open circles and pale grey outlined open squares, respectively.

976

977 **Fig.7.** Calculated normalized surface concentration (Ar atoms/area) variations (log scale)
978 with temperature for RBS, 213 nm laser and 193 nm laser data on citrine **(a)** and clear **(b)**
979 quartz. See text for discussion of the calculations. The temperature of each experiment is
980 given by a dashed line, and the α -quartz \rightarrow β -quartz transition for this experiment is given at
981 613-615 °C, represented by the narrow grey bar. Calculation of the transition based on
982 occurrence at 573 °C, with an increase in 1 °C per 40 bar (Expt. # 1 and # 2 are at 1700 and
983 1600 bar, respectively).

984

985 **Fig. 8.** Compilation plot of RBS, 213 nm- and 193 nm-laser data for synthetic citrine. The
986 concentration (ppm argon) vs. depth (cm) is given linearly **(a)** and also in Log-depth scale **(b)**
987 due to the vast differences in depth scales of each technique. RBS points represented by an
988 open square, 213 nm-laser points by an open circle and 193 nm-laser points by a grey circle.
989 The contribution (concentration and depth) of each path is outlined in **(b)**: RBS profile
990 encapsulated by a solid black line, 193 nm laser data by the short-dash line and the 213 nm
991 data by the long-dash line.

992

993 **Fig. 9.** Relative loss or gain of argon from quartz over magmatic timescales for K-feldspar
994 (dashed line; using diffusion data from Wartho et al., 1999), quartz using RBS and 193 nm
995 laser determined diffusion parameters (calculated at 700 °C from this study; black line) and a
996 “fast-path” equivalent, using diffusion parameters derived from a 213 nm laser (grey line;
997 data from this study). Loss/gain modeled for a spherical geometry.

998