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## Two diffusion pathways in quartz: a combined UV-laser and RBS study

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How to cite:

Clay, P. L.; Baxter, E. B.; Cherniak, D. J.; Kelley, S. P.; Thomas, J. B. and Watson, E. B. (2010). Two diffusion pathways in quartz: a combined UV-laser and RBS study. *Geochimica et Cosmochimica Acta*, 74(20) pp. 5906–5925.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:  
<http://dx.doi.org/doi:10.1016/j.gca.2010.07.014>

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

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## ABSTRACT

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The diffusive behavior of argon in quartz was investigated with three analytical depth profiling methods: Rutherford Backscattering Spectroscopy (RBS), 213 nm laser ablation, and 193 nm (Excimer) laser ablation on the same set of experimental samples. The integration of multiple depth profiling methods, each with different spatial resolution and sensitivity, allows for the cross-checking of methods where data ranges coincide. The use of multiple methods also allows for exploration of diffusive phenomena over multiple lengthscales. Samples included both natural clear rock crystal quartz and synthetic citrine quartz. Laser analysis of clear quartz was compromised by poor coupling with the laser, whereas the citrine quartz was more easily analyzed (particularly with 193 nm laser). Diffusivity measured by both RBS and 193 nm laser ablation in the outermost 0.3  $\mu\text{m}$  region of citrine quartz are self-consistent and in agreement with previously published RBS data on other quartz samples (including the clear quartz measured by RBS in this study). Apparent solubilities (extrapolated surface concentrations) for citrine quartz are in good agreement between RBS, 213 nm, and 193 nm laser analyses. Deeper penetration of argon measured up to 100  $\mu\text{m}$  depth with the 213 nm laser reveal contributions of a second, faster diffusive pathway, effective in transporting much lower concentrations of argon into the crystal interiors of both clear and citrine quartz. By assuming such deep diffusion is dominated by fast pathways and approximating them as a network of planar features, the net diffusive uptake can be modeled with the Whipple-LeClaire equation, yielding  $\delta D_b$  values of  $1.32 \times 10^{-14}$  to  $9.1 \times 10^{-17} \text{ cm}^3/\text{sec}$ . While lattice solubility values from the measured profiles confirm suggestions that quartz has a large capacity for argon uptake (making it a potentially important sink for argon in the crust), the slow rate of lattice diffusion may limit its capability 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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## 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 % SiO<sub>2</sub>). 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  $\mu\text{m}$  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  $\pm 2$  °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  $^{40}\text{Ar}$ , 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  $1.12 \times 10^{-5}$  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 ( $7120 \pm 100$   
296 to  $13450 \pm 200$ ) than clear quartz ( $1050 \pm 100$  to  $10050 \pm 200$ ). 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  $\mu\text{m}$  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 ( $\text{m}^2\text{s}^{-1}$ ), 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  $\delta D_b$  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  $\delta$  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  $\delta D_b$   
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  $\delta D_b$  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  $\delta D_b$  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  $\mu\text{m}$ ) 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<sup>2</sup>/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  $\alpha$ -quartz to  $\beta$ -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/cm<sup>3</sup> 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  $^{40}\text{Ar}$  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  $\delta Db$  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  $\mu\text{m}$ , whereas 193 nm laser analyses  
646 produce 1-2 data points in the same 0.1  $\mu\text{m}$ ).

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.

## ACKNOWLEDGEMENTS

659

660

661 We are grateful to Jon Price for help in setting up experimental work. James Schwanethal is  
662 thanked for assistance with laser analyses and Richard Chater, Imperial College London, is  
663 thanked for help with laser-pit depth measurements. Constructive comments and suggestions  
664 from Steve Parman and two anonymous reviewers improved the manuscript significantly. We  
665 also thank B. Mysen for thoughtful and constructive editorial handling. This work was  
666 funded by NSF grant # EAR-0337527 awarded to Ethan Baxter.

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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 <sup>871</sup>
N3	642	170	480
N4	489	170	480 <sup>872</sup>
Experiment #2			870
N5	724	160	360 <sup>873</sup>
SC-1	724	160	360
N6	669	160	360 <sup>874</sup>
SC-2	669	160	360 <sup>875</sup>
N7	561	160	360
SC-3	561	160	360 <sup>876</sup>
N8	419	160	360
SC-4	419	160	360 <sup>877</sup>

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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). R<sup>2</sup> values represent the goodness of the error-function fit to the data.

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 895

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

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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  $\delta D_b$  for 213 and 193 nm laser  
 915 diffusion profiles.

Sample	T, °C	P, MPa	Duration, h	a, Log D (m <sup>2</sup> /s)	R <sup>2</sup>	b Log D (m <sup>2</sup> /s)	R <sup>2</sup>	c, $\delta D$ (cm <sup>3</sup> /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 <sup>-15</sup>
N2B	764	170	480	-14.3	0.98	<i>x</i>	-	3.53 x 10 <sup>-14</sup>
N2C	764	170	480	-15.5	0.51	-16.7	0.99	2.18 x 10 <sup>-14</sup>
N3	642	170	480	-16.7	0.99	-17.3	0.98	9.94 x 10 <sup>-15</sup>
N4	489	170	480	-17.0	0.92	-17.3	0.98	1.32 x 10 <sup>-14</sup>
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 <sup>-15</sup>
SC-E1	724	160	360	-20.2	0.95	-20.5	0.95	8.78x 10 <sup>-17</sup>
SC-E2	724	160	360	-20.0	0.95	-21.0	0.95	9.10x 10 <sup>-17</sup>
SC-E3	724	160	360	<i>x</i>		-20.0	0.29	8.14x 10 <sup>-17</sup>
SC-E4	724	160	360	-19.3	0.78	-20.7	0.95	3.13x 10 <sup>-16</sup>
SC-E5	724	160	360	-20.0	0.93	-21.0	0.84	1.16 x 10 <sup>-16</sup>
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 <sup>-15</sup>
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	$1.1 \times 10^{14}$	<i>nm</i>	<i>nm</i>
N2	764	170	480	$1.9 \times 10^{14}$	$5.8 \times 10^{15}$	<i>nm</i>
N3	642	170	480	$1.9 \times 10^{13}$	$3.1 \times 10^{15}$	<i>nm</i>
N4	489	170	480	$4.6 \times 10^{13}$	$1.8 \times 10^{15}$	<i>nm</i>
N5	724	170	480	$3.7 \times 10^{16}$	$1.2 \times 10^{15}$	<i>nm</i>
SC-1	724	160	360	$3.9 \times 10^{15}$	$1.7 \times 10^{16}$	<i>nm</i>
SC-E1	724	160	360	<i>193 only</i>	<i>193 only</i>	$1.8 \times 10^{15}$
SC-E2	724	160	360	<i>193 only</i>	<i>193 only</i>	$2.7 \times 10^{15}$
SC-E3	724	160	360	<i>193 only</i>	<i>193 only</i>	$1.8 \times 10^{15}$
SC-E4	724	160	360	<i>193 only</i>	<i>193 only</i>	$7.3 \times 10^{15}$
SC-E5	724	160	360	<i>193 only</i>	<i>193 only</i>	$1.2 \times 10^{14}$
N6	669	160	360	$2.5 \times 10^{15}$	<i>nm</i>	<i>nm</i>
SC-2	669	160	360	$3.1 \times 10^{15}$	$1.0 \times 10^{16}$	<i>nm</i>
N7	561	160	360	$3.3 \times 10^{14}$	<i>nm</i>	<i>nm</i>
SC-3	561	160	360	$1.7 \times 10^{15}$	<i>nm</i>	<i>nm</i>
N8	419	160	360	<i>nm</i>	<i>nm</i>	<i>nm</i>
SC-4	419	160	360	$1.5 \times 10^{15}$	<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 ( $\mu\text{m}$ ) 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 ( $\mu\text{m}$ ) 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  $\alpha$ -quartz  $\rightarrow$   $\beta$ -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