

Manuscript 5345 Revision 1

1 **Effect of fluid composition on growth rate of monazite in quartzite at 1.0 GPa**
2 **and 1000 °C**

3
4 John C. Ayers^{1*}, Derek L. Bryant^{1,2}, Kevin Giles¹

5 1. Department of Earth and Environmental Sciences, Vanderbilt University, Nashville, TN
6 37235, U.S.A., john.c.ayers@vanderbilt.edu

7 2. Visual Risk Technologies, Inc., 210 25th Ave. North, Suite 1015, Nashville, TN 37203,
8 dbryant@vrisk.com

9 *Corresponding author

10 Submitted to *American Mineralogist* March 4, 2015

11 Revised April 27, 2015

12 **ABSTRACT**

13 The dependence of monazite coarsening rate on fluid composition was evaluated by
14 performing growth experiments in a piston cylinder apparatus at 1.0 GPa and 1000 °C. Results
15 show that the rate of monazite coarsening in quartzite + fluid is strongly sensitive to fluid
16 composition. Although other studies have shown that monazite solubility is higher in acidic
17 fluid, addition of 2 molal HCl to H₂O decreased the growth rate. Textural observations and
18 modeling indicate that monazite growth in 2 molal HCl occurs through a combination of Ostwald
19 ripening and coalescence. Addition of 2 molal NaCl to H₂O should have increased monazite
20 aqueous solubility and made the fluid interconnected, but the expected increase in monazite
21 growth rate did not occur, with monazite size distributions showing no change between 0 and
22 165 h and no measurable growth. Ion adsorption on the surface of monazite may have slowed the

23 rate of monazite growth on addition of HCl and stopped growth on addition of NaCl. The strong
24 dependence of monazite coarsening rate on fluid composition suggests that the size of crystals
25 produced by metamorphic coarsening may not be a reliable indicator of duration of
26 metamorphism, and that adsorption of ions on mineral surfaces may be significant even at 1000
27 °C.

28 **Keywords:** monazite, mineral growth, growth kinetics, metamorphism, coarsening, textural
29 development, Ostwald ripening

30 INTRODUCTION

31 Textural development during metamorphism affects the measured size and age distributions
32 of, and therefore the growth history recorded by, dateable minerals (Eberl et al. 1990; Ayers et al.
33 1999). Recrystallization can reset mineral isotopic clocks, so that measured ages correspond to
34 recrystallization events. According to Evans et al. (2001), the three driving forces of
35 recrystallization, in decreasing order of driving force magnitude, are reduction in system energy
36 through heterogeneous chemical reactions (chemical recrystallization involving multiple phases),
37 reduction of energy stored in defects (mechanical recrystallization), and reduction of interfacial
38 energy by reduction of surface area through grain growth (coarsening). Only heterogeneous
39 reaction leads to new growth of a phase. Existing grains may shrink by heterogeneous reaction or
40 mechanical recrystallization, and can grow by heterogeneous reaction or coarsening. While the
41 decrease in system energy caused by coarsening is relatively small, the driving force is always
42 present and so the process is common. Coarsening causes mean grain size and sphericity (ratio of
43 the surface area of a sphere of equal volume to the surface area of the particle) to increase with
44 metamorphic grade even in the absence of heterogeneous growth, as shown for quartzites and
45 marbles (Joesten 1991).

46 For dispersed phases such as monazite or other accessory minerals coarsening occurs by the
47 process of Ostwald ripening. Although the rare earth phosphate mineral monazite often grows
48 by heterogeneous reaction during prograde metamorphism (Kohn and Malloy 2004; Finger and
49 Krenn 2007), studies have provided natural and experimental evidence of Ostwald ripening of
50 monazite during metamorphism (Kingsbury et al. 1993; Ayers et al. 1999).

51 Ostwald ripening can produce homogeneous metamorphic rims on larger grains that grow at
52 the expense of smaller grains. These rims can be used to date the coarsening event (Ayers et al.
53 1999). The thickness of rims and the final size of grains should depend on the duration of
54 metamorphism and on the rate of coarsening. Since crystal growth is a thermally activated
55 process, crystal growth rates increase exponentially with temperature so that most crystal growth
56 will occur at the maximum metamorphic temperature, and grain size will depend on the duration
57 of peak metamorphism. If the rate of coarsening at peak metamorphic conditions is known, the
58 duration of metamorphism theoretically can be estimated from the maximum thickness of
59 metamorphic rims or size of unzoned grains. However, estimates will be accurate only if all
60 factors that affect monazite coarsening rate are quantified and accounted for.

61 **Limiting Factors on Growth Rate**

62 Ostwald ripening has been shown to affect clays and metamorphic minerals, causing grain
63 size distributions to broaden and mean grain radius to increase with time or increasing
64 metamorphic grade (Eberl et al. 1990). Evidence of Ostwald ripening is also preserved in the
65 shapes of grain size distributions: they are self-similar, meaning that reduced grain size profiles
66 (frequency/max frequency versus radius/mean radius) do not change during Ostwald ripening, so
67 it is a steady-state process. Theoretically, thermodynamic equilibrium is not fully achieved until
68 only one grain remains, or when all grains are the same size (Eberl et al. 1990). Practically,

69 neither is likely to happen on geological timescales, as Ostwald ripening is only efficient for
70 grain sizes $< 10\text{-}20\ \mu\text{m}$, depending on the mineral (Cabane et al., 2001, 2005). If Ostwald
71 ripening causes growth throughout the duration of peak metamorphism (i.e., the size limit of 10-
72 $20\ \mu\text{m}$ is not reached), the largest crystal will record the entire coarsening event, the duration of
73 which may be estimated from radiometric ages measured in-situ on the innermost and outermost
74 growth layers.

75 Ostwald ripening requires dissolution of small grains, transport of dissolved material, and
76 then precipitation onto larger grains. As these processes occur in series, the slowest step is rate-
77 limiting. In a rock containing a static fluid the growth rate of the dispersed phase can be limited
78 by the rate of transport by diffusion or the rate of surface reaction (mineral dissolution and
79 precipitation). The transport rate of dispersed phase constituents from small to large grains may
80 be highest for grain boundary diffusion or for volume diffusion through the matrix phase. Grain
81 boundary diffusion will be faster in the presence of an interconnected fluid than along dry grain
82 boundaries.

83 Ostwald ripening is a coupled dissolution-precipitation process, and for minerals with low to
84 moderate solubilities at ambient conditions the rates of dissolution and precipitation are generally
85 surface reaction controlled rather than transport controlled (Berner, 1978). Because surface
86 reactions involve breaking and forming of bonds, they typically have higher activation energies
87 than transport by diffusion, so their rates increase faster with increasing temperature (Murphy et
88 al. 1989). Thus, at high temperatures in rocks with a static, interconnected fluid (no advection)
89 Ostwald ripening should be rate-limited by the slower process of diffusive transport. This is
90 consistent with the interpretation of Ayers et al. (1999) that, in the presence of a fluid that is not
91 interconnected (H_2O), monazite growth rate in quartzite at 1.0 GPa and 1000 °C in a matrix of

92 larger quartz crystals grew by grain boundary diffusion, while monazite in a matrix of fine-
93 grained quartz crystals of similar size grew by matrix volume diffusion.

94 The growth rate equation has the form:

95 Eq. (1) $\langle D \rangle^n - \langle D_0 \rangle^n = k(t-t_0)$

96 where $\langle D \rangle$ is the mean diameter, t is time, $\langle D_0 \rangle$ is the mean diameter for the shortest
97 experiment of duration t_0 in the series, and k is a thermally activated rate constant with a
98 temperature dependence described by the Arrhenius equation (Joesten 1991). The standard
99 procedure to identify the form of the growth rate equation is to plot $\log(\langle D \rangle^n - \langle D_0 \rangle^n)$ versus
100 $\log(t - t_0)$ for integer values of $n = 2, 3$ and 4 , and identify the value of n that provides the best fit
101 (e.g., Ayers et al., 2003). According to Lifshitz and Slyozov (1961) and Wagner (1961) (LSW)
102 theory, a value of $n = 2$ indicates that growth is controlled by surface reaction (first-order
103 kinetics), $n = 3$ by volume diffusion (through a continuous fluid or solid matrix phase, second-
104 order kinetics), and $n = 4$ by grain boundary diffusion (Joesten 1991). In all three cases
105 increasing the aqueous solubility of monazite would increase the rate of monazite growth if all
106 monazite grains are in contact with an interconnected aqueous fluid (see Equations 15, 18 and 20
107 in Joesten (1991)).

108 LSW theory assumes that the volume of the dispersed phase is zero so that dispersed grains
109 don't interact. This assumption is violated when grains are close enough to come into contact and
110 agglomerate, or for their diffusion fields to overlap. The observation that grain size distributions
111 of clays and metamorphic minerals do not correspond to LSW distributions but rather tend
112 toward a log-normal distribution during Ostwald ripening (Eberl et al. 1990) may be due to this
113 assumption being invalid. In most cases two agglomerated grains coalesce when the grain
114 boundary migrates through the smaller grain and disappears. Grains of a dispersed phase can

115 come into close contact when they are dragged by migrating grain boundaries of the matrix
116 phase as it coarsens (Ayers et al., 1999; Watson et al., 1989). For example, grains of the
117 dispersed phase surrounding a small matrix grain will migrate toward each other as the small
118 matrix grain shrinks and eventually becomes consumed by surrounding larger grains. Models
119 that allow for interactions between grains of the dispersed phase such as coalescence generally
120 find that $n = 3$ (Evans et al. 2001).

121 Overall, the factors that may affect the growth rate of monazite in fluid-bearing quartzite
122 include 1) presence of a fluid phase; 2) degree of interconnectivity of the fluid phase; 3)
123 solubility of monazite in the fluid phase; 4) adsorption of ions on grain surfaces that could inhibit
124 growth or dissolution; and 5) temperature. Ayers et al. (1999) experimentally evaluated (1) by
125 measuring the growth rate of monazite in quartzite \pm H₂O at 1.0 GPa and 1000°C and
126 demonstrated that monazite growth rate is much higher when free water is present than when it is
127 absent. In this study we planned to evaluate the effects of (2) and (3), but our results provide
128 insights into (4). Specifically, in quartzite + H₂O monazite growth rate may be affected by
129 factors (2)-(4) when NaCl is added, and by factors (3)-(4) when HCl is added. Many of the
130 monazite crystals in our experiments are smaller than the few tenths of a micrometer above
131 which the effects of surface free energy on solubility are estimated to be negligible (Morse and
132 Wang 1996; Carlson 1999) and therefore should be affected by Ostwald ripening, as observed by
133 Ayers et al. (1999).

134 **Effect of Fluid Geometry on Growth Rate**

135 The rate of transport through a network of fluid-filled pores is influenced by the degree of
136 interconnectivity of the fluid. If the dihedral angle is less than 60° then the fluid is interconnected
137 (Watson and Brenan 1987). At conditions similar to those of this study (0.96 GPa, 1000°C)

138 Holness (1993) measured a dihedral angle for H₂O in quartzite of 72°, indicating that H₂O is not
139 interconnected at these conditions. Adding NaCl to the fluid decreases the dihedral angle to <
140 60°, making the fluid interconnected (Watson and Brenan 1987; Holness 1992).

141 If monazite growth rate is limited by solute transport in the fluid, then it should increase if
142 the fluid becomes interconnected because dissolving grains will be connected directly to growing
143 grains by an interconnected fluid, which should increase fluxes of monazite solutes. If monazite
144 growth rate is limited by the rate of reactions on the monazite surface (attachment of ions on
145 growing crystals and detachment from dissolving crystals), then making the fluid interconnected
146 will increase the rate of monazite growth by increasing the surface area of monazite in contact
147 with the fluid, which catalyzes surface reactions and thereby increases the rates of dissolution
148 and precipitation. We therefore predict that, regardless of whether the growth rate is transport or
149 surface reaction limited, decreasing the dihedral angle below 60° to make the fluid
150 interconnected should increase the rate of monazite Ostwald ripening.

151 In this study we performed a time series of experiments with starting materials and
152 conditions identical to those of Ayers et al. (1999), who measured monazite growth rate in
153 quartzite + H₂O at 1.0 GPa and 1000°C, but we added NaCl to make the fluid 2m NaCl. Our
154 expectation was that this would make the fluid interconnected and would increase the monazite
155 coarsening rate. We also wanted to see if kinetic control changed from matrix volume diffusion
156 to grain boundary diffusion.

157 **Effect of Solubility on Growth Rate**

158 When mineral solubility is low mineral dissolution rates are generally surface reaction
159 limited, but as solubility increases the rate of surface reaction increases until it exceeds the
160 transport rate, and the dissolution rate becomes transport limited (Berner, 1978). At 1.0 GPa and

161 1000°C the solubility of monazite in pure H₂O is low (< 0.2 wt. % or 1 millimolal) compared
162 with other minerals (Ayers and Watson 1991), but monazite growth rate in quartzite + H₂O is
163 still transport limited because the temperature is high (Ayers et al. 1999). As experiments in this
164 study are identical to those of Ayers et al. (1999) except for addition of NaCl or HCl to the fluid,
165 both of which should increase monazite aqueous solubility, we expect that monazite growth is
166 transport limited in our experiments.

167 Even for transport control, the rate of Ostwald ripening of a mineral in contact with a fluid
168 phase should increase as its solubility in the fluid phase increases because higher solubility
169 translates into higher maximum concentration gradients and therefore higher fluxes in the fluid
170 (Murphy et al., 1989), although once surface equilibrium is attained the concentration gradient
171 will be determined only by the grain size dependence of the solubility. Monazite aqueous
172 solubility depends strongly on fluid composition, being higher in acidic fluids (Cetiner et al.
173 2005). Experiments at 1.0 GPa and 1000 °C show that monazite solubility is higher in acidic
174 aqueous fluid than in pure H₂O (Ayers and Watson 1991; Ayers et al. 2004). In this study we
175 performed a time series of experiments to measure monazite coarsening rate in quartzite + 2 m
176 HCl, with the expectation that it would be higher than in pure H₂O.

177 Recent experiments show that at similar conditions of 1.0 GPa and 800°C the aqueous
178 solubility of the monazite endmember CePO₄ increases from ~0.04 to 7.9 millimolal as NaCl
179 content increases from 0 to 50 mol% (Tropper et al. 2011). Thus, addition of NaCl in our
180 experiments should increase the aqueous solubility of monazite in addition to making the fluid
181 interconnected. Both factors should increase the growth rate of monazite.

182 **Effect of Adsorption**

183 While the textural property of fluid interconnectivity and the equilibrium thermodynamic

184 property of solubility may influence monazite coarsening rate, there may also be a kinetic effect
185 caused by adsorption of ions onto mineral surfaces. Impurities in a system can greatly affect the
186 rates of crystal growth and dissolution. Studies at ambient conditions and slightly elevated
187 temperatures have shown that ions can “poison” mineral surfaces by adsorbing to them,
188 preventing attachment or detachment of other ions on the surface (Zhang and Nancollas 1990).
189 However, adsorption equilibria have not been characterized at high pressures or temperatures
190 higher than a few hundred degrees. We speculate that adsorption of Na⁺, H⁺ or Cl⁻ onto
191 monazite crystal surfaces may inhibit monazite coarsening.

192 In the experiments of Ayers et al. (1999) the measured growth rate of monazite in quartzite
193 + H₂O at 1.0 GPa and 1000 °C was low because monazite has a very low solubility in H₂O and
194 the fluid was not interconnected. In this study we attempted to test the hypotheses that monazite
195 growth rate correlates positively with monazite solubility and that it is higher in the presence of
196 an interconnected fluid than a non-interconnected fluid. The growth rate of monazite was
197 measured in 2 m HCl and compared with the previously measured growth rate in H₂O (Ayers et
198 al., 1999) to see if the enhanced solubility in an acidic fluid translates into a higher growth rate.
199 We also examined the combined effects of enhancing monazite solubility and making the fluid
200 interconnected on growth rate by adding NaCl, which has been shown at similar conditions to
201 increase monazite aqueous solubility (Tropper et al. 2011) and to decrease the dihedral angle in
202 quartzite below 60°, making the fluid interconnected (Watson and Brenan, 1987; Holness 1992).
203 We chose a temperature of 1000°C to ensure that growth rates were high enough to measure; that
204 the melting temperature of ~1080°C of quartz in equilibrium with H₂O at 1.0 GPa was not
205 exceeded (Kennedy et al., 1962); and to allow comparison with results from previous studies of
206 monazite aqueous solubility, aqueous fluid interconnectivity, and monazite growth rate.

207

METHODS

208 For the growth experiments powders of natural monazite and optically clear quartz were
209 produced by grinding under alcohol for two hours in a mortar and pestle, pouring the powder
210 into an 8 in. high column of water, and collecting in a Petri dish grains that settled in a suitable
211 time interval (between 1 h 31 min. and 6 h 5 min. for quartz, 36 min. and 2 h 25 min. for
212 monazite). Measurement of mean Feret diameter (diameter of a circle with the same area as the
213 two-dimensional object) in a grain mount of the monazite starting material (MZ SM in Table 4)
214 yielded $\langle D \rangle = 0.82 \pm 0.04 \mu\text{m}$. Nitrogen adsorption measurements using a Quantachrome BET
215 yielded specific surface areas (m^2/g) of 2.16 for quartz and 15.6 for monazite. Assuming perfect
216 spheres, these values correspond to average diameters of $1.04 \mu\text{m}$ for quartz and $0.074 \mu\text{m}$ for
217 monazite. The latter value in particular seems too low, being roughly one order of magnitude
218 lower than measurements made using the SEM and a petrographic microscope, so we rejected it.
219 The starting material was obtained by mixing the powders in the proportions 98 wt.% quartz + 2
220 wt.% monazite.

221 All experiments were conducted in a piston cylinder apparatus at 1.0 GPa and 1000 °C.
222 Cold-sealing capsules of the type described by Ayers et al. (1992) were used to encapsulate
223 samples, with the following difference: the Ni capsule (4.4 mm I.D., 6.35 mm O.D., 9 - 10 mm
224 length) was fired in air for 12 h at 1000 °C to form a surface layer of NiO that prevented Ni-Pt
225 interdiffusion, before tapping in a Pt insert (4.4 mm O.D., tri-crimped and welded shut on one
226 end).

227 Methods used are very similar to those described in detail by Ayers et al. (1999). After
228 weighing the capsule, we added ~ 100 mg of powdered starting material to the capsule, weighed
229 the filled capsule to find the weight of starting material, and then added 1 - 2 wt% H₂O with a

230 microsyringe. Each sample placed in a capsule contained more than 1 billion monazite crystals.
231 Sampling statistics suggest that samples taken from our starting material should be unbiased and
232 therefore representative. A Pt lid topped by a Ni lid was placed on top and cold-sealed to the
233 capsule by pressurizing in a 1.91 cm piston-cylinder apparatus. All experiments used the
234 assembly and corresponding pressure calibration described by Ayers et al. (1992). A W Re₃/W
235 Re₂₅ thermocouple and temperature controller maintained temperature within ± 5 °C of the
236 setpoint, while pressure was manually maintained within ± 500 bars. The thermocouple was
237 calibrated by its manufacturer (Engelhardt) and is accurate to ± 1.5 °C.

238 Upon completion of each experiment, we sectioned the capsule lengthwise to maximize
239 observable surface area, mounted the sections in and impregnated their surfaces with epoxy, and
240 polished to 0.06 μm . Energy dispersive analysis, x-ray diffraction of run products, and
241 identification in optical grain mounts of selected samples showed that monazite and quartz were
242 the only minerals present in our run products.

243 To measure the dimensions of monazite crystals sample mounts were coated with a carbon
244 film and then imaged in backscattered electron mode using a Hitachi S-4200 scanning electron
245 microscope at 1000x and an accelerating voltage of 15 keV. Traverses made along the length of
246 each capsule revealed no systematic change in monazite size or modal abundance.

247 Crystal size was measured from 300 dpi, 256 grey-scale level 3.5 in. x 4 in. digital
248 backscattered electron images using computer-automated image analysis (details of methods
249 described in Ayers et al., 1999). We applied a median filter to reduce electronic noise without
250 affecting the size of features, and then calibrated the spatial scale using a scalebar in the image.
251 To measure monazite crystal size we thresholded (segmented) the image by classifying as
252 monazite each pixel with grayscale level greater than a specified threshold value. Monazite

253 crystals that were touching were "separated" by drawing a line between them before making
254 measurements. For every crystal we measured area, perimeter, Feret diameter, and maximum
255 and minimum diameters.

256 Histograms of monazite crystal size (Feret diameter) in starting materials (Fig. 1) and run
257 products (Figs. 2 and 3) have distributions closest to being lognormal, although only the shortest
258 experiment FQMZ-HCl#2 has a distribution of $\log D$ values that passes the Kolmogorov-
259 Smirnov normality test at the 95% significance level. Because parametric statistics require
260 normally distributed data, the antilog of the mean value of $\log D$ (the geometric mean) provides
261 the best estimate of the population mean of D . However, the $\log D$ distribution deviates most
262 from a normal distribution in the upper and lower tails of the distribution, where we made the
263 smallest number of measurements and errors are greatest. Thus, we obtained the most robust
264 estimate of population mean by calculating the 95% trimmed mean of $\log D$ by deleting the
265 extreme values in the uppermost and lowermost 5% of the distribution, calculating the mean of
266 $\log D$, and taking the antilog to obtain the mean diameter $\langle D \rangle$. Uncertainties are presented as 95%
267 confidence limits.

268 RESULTS

269 Textural Development

270 The crushed FQMZ starting material consisted of loosely packed angular fragments of
271 quartz and monazite (Fig. 1). A grain mount of the starting material (FQMZ SM, Fig. 1a) yielded
272 monazite $\langle D \rangle = 0.76(13) \mu\text{m}$ (Table 1). To establish the precision of our experimental and
273 image analysis methods we ran two zero time ($t = 0$ h) experiments with 2m NaCl in which the
274 samples were pressurized to 1.0 GPa, heated to 1000°C and then immediately quenched. The
275 first yielded $\langle D \rangle = 0.70(8) \mu\text{m}$ (FQMZ-NaCl#5, Fig. 1b), and the second $\langle D \rangle = 0.76(8) \mu\text{m}$

276 (FQMZ-NaCl#5b, Fig. 1c), identical within error. The Crystal Size Frequency Histogram
277 (CSFH) of monazite in the starting material is nearly lognormal (Fig. 1).

278 Run products of the FQMZ-NaCl experiments containing 2m NaCl are shown in Fig. 2 and
279 the FQMZ-HCl experiments containing 2m HCl in Fig. 3. No fluid inclusions are visible in
280 quartz or monazite, and monazite grains were not occluded by growing quartz grains. Monazite
281 grains appear to be uniformly dispersed, i.e., the spatial distribution seems to be isotropic and
282 homogeneous. Finally, volume fraction of monazite in all experiments should be roughly the
283 same. All of these features simplify grain size measurements and interpretations.

284 In both time series of experiments quartz crystals appeared to grow with time, as observed in
285 our previous studies (Ayers et al., 1999, 2003), but we could not accurately measure quartz grain
286 sizes because grain boundaries frequently were not visible in the backscattered electron images.
287 Pores also grew, but their sizes were also impossible to measure accurately because they were
288 not uniformly black and therefore could not be automatically classified based on greyscale levels
289 (Figs. 2 and 3). Sample textures show strong evidence of coarsening, with development of near-
290 equilibrium textures in the longest experiments characterized by location of both monazite
291 crystals and pores at quartz grain boundaries (rather than as segregations or occlusions),
292 especially at quartz triple junctions. Where quartz grain boundaries are visible, quartz triple
293 junctions show angles of $\sim 120^\circ$. The median circularity shape factor, which ranges from 0 for a
294 line to 1 for a perfect sphere, shows a systematic increase for monazite from 0.74 in the starting
295 material to 0.89 in the longest 2 m NaCl experiment (Fig. 4) and to 0.83 in the longest HCl
296 experiment (Fig. 5). These results are consistent with Ostwald ripening decreasing curvature of
297 grain surfaces in order to minimize interfacial energy (Evans et al. 2001).

298 **2 molal NaCl.**

299 Comparison of the CSFHs of the starting material FQMZ SM (Fig. 1a) and the two zero
300 time experiments (Figs. 1b and 1c) show no significant change in monazite grain size during
301 pressurization to 1.0 GPa and heating to 1000°C. As expected from previously reported
302 measurements (Watson and Brenan 1987; Holness 1992), addition of NaCl decreased the quartz-
303 fluid dihedral angle to below 60° (pore walls change from concave-in to convex-in), causing the
304 fluid to become interconnected. Although quartz crystals appear to grow with time, from 8 h
305 (FQMZ-NaCl#2, Table 4) to 165 h (FQMZ-NaCl#4) neither $\langle D \rangle$ nor the shape of the CSFH of
306 monazite changed significantly, even though Ostwald ripening should increase $\langle D \rangle$ and change
307 the CFSSH from lognormal to normal. $\langle D \rangle$ values for all run products are indistinguishable from
308 values for starting materials (Fig. 6), unlike results from Ayers et al. (1999) where mean size
309 decreased between 0 and 8 h and then increased with time t . A least squares linear regression
310 line on a $\log \langle D \rangle$ vs. $\log t$ plot passes through all of the data points within error and has a slope
311 not significantly different from zero (Fig. 6). We conclude that no significant growth of
312 monazite occurred in quartzite containing 2m NaCl.

313 **2 molal HCl.**

314 Pore shapes in run products from experiments containing 2 m HCl show dihedral angles
315 close to 60° and nearly straight pore walls, making it unclear whether the fluid was
316 interconnected (Fig. 3). In run products from the longest experiment ($t = 167$ h, FQMZ-HCl#4,
317 Fig. 3d) pores are less abundant but larger; in other images there appears to be a high proportion
318 of dry grain boundaries, suggesting the fluid was not interconnected.

319 Only the shortest experiment FQMZ-HCl#2 ($t = 3$ h) has a monazite CSFH distribution that
320 is lognormal at the 95% level (Fig. 3a), similar to what it would be at the completion of

321 nucleation and the onset of coarsening during progressive metamorphism. The mean grain size
322 for this experiment is not significantly different from that in the starting material (Fig. 7). With
323 increasing time monazite CSFH distributions moved closer to normal (although all distributions
324 remain closer to lognormal than normal), and monazite $\langle D \rangle$ values increased from 0.79(7) μm
325 at $t = 3$ h (FQMZ-HCl#2, Fig. 3a) to 1.03(7) μm at $t = 72$ h (FQMZ-HCl#3, Fig. 3c). However,
326 no further growth occurred between 72 h and 167 h (Figs. 3d, 7). Although the monazite CSFH
327 did not change greatly from its initial distribution, the number of crystals in the largest size bin
328 ($> 4.5 \mu\text{m}$) increased steadily with time (Figs. 3a-d).

329 To identify the form of the growth rate equation we plotted $(\langle D \rangle^n - \langle D_0 \rangle^n)$ versus $\log(t - t_0)$
330 for integer values of n . However, because $\langle D \rangle$ did not change significantly between 0 and 3 h,
331 the starting material and run products from the time-zero experiments do not fall on the trend
332 defined by experiments of longer duration (all fall above the 95% C.L. of the linear regression
333 line defined by the longer experiments), requiring the use of $\langle D \rangle$ from the 3 h experiment
334 (FQMZ-HCl#2) as $\langle D_0 \rangle$ and reducing the number of data points to three; furthermore,
335 measured values of $\langle D \rangle$ at $t = 72$ h and $t = 167$ h are identical, resulting in a very poor fit.
336 Thus, we simply present an empirical fit to the four data points without theoretical justification:
337 $\log \langle D \rangle = 0.071 \log t - 0.39$, with $r^2 = 0.96$ (Fig. 7).

338

DISCUSSION

339 Effect of Fluid Composition on Monazite Growth Rate

340 Although addition of NaCl should increase the aqueous solubility of monazite (Tropper et al.
341 2011) and make the fluid interconnected, which should increase the transport rate of solutes and
342 the total area of fluid in contact with monazite, no measurable growth occurred between 8 and
343 165 h (Fig. 6). This result is even more surprising when considering the obvious growth in the

344 size of quartz crystals and pores (Fig. 2). In contrast, monazite crystals grew at a measurable rate
345 in 2 m HCl (Fig. 7).

346 In the HCl series size does not increase between 0 and 3 h, but then increases between 3 and
347 72 h (Table 1). Size may have initially decreased before increasing, as observed by Ayers et al.
348 (1999) for experiments between 0 and 8 h duration. In Fig. 7 the intercept corresponds to an
349 initial mean monazite diameter $\langle D_0 \rangle = 0.4 \mu\text{m}$, slightly smaller than that in the starting material
350 $= 0.76 \mu\text{m}$, suggesting that monazite may have initially recrystallized. However, it's impossible
351 to know if mean monazite grain size initially decreased and then increased without doing
352 additional experiments between 0 and 3 h duration.

353 To compare monazite growth rate in different fluid compositions the 95% trimmed means of
354 the logarithm of measured mean intercept lengths L_3 of monazite are plotted as a function of time
355 (Fig. 8). The growth rate expressed as the slope of the line dL_3/dt is ~ 0 for 2 m NaCl. Adding
356 NaCl to the fluid phase causes monazite growth to stop, or at least decrease to a rate too low to
357 detect, suggesting that ion adsorption must cancel the effects of increased aqueous solubility and
358 fluid interconnectivity.

359 The slope for the H₂O data from Ayers et al. (1999) is defined by only three points, but it
360 appears to be greater than the slope defined by the four data points for 2 m HCl. Adding HCl to
361 the fluid decreases the coarsening rate relative to pure H₂O, but the rate is high enough to
362 measure (the slope is significantly greater than zero). As in the FQMZ-NaCl series, it appears
363 that the effect of ion adsorption on monazite grain surfaces in the FQMZ-HCl series cancels the
364 increase in growth rate expected for an increase in monazite solubility. The only difference
365 between the two sets of experiments is that the cation is H⁺ in the FQMZ-HCl series and Na⁺ in
366 the FQMZ-HCl series. Addition of H⁺ to H₂O decreases the coarsening rate, but adding Na⁺

367 decreases it even more. If ion adsorption is inhibiting coarsening, then Na-adsorption is more
368 effective at inhibiting surface reactions than H-adsorption.

369 The growth rate of a dispersed phase can be affected by many different factors influenced by
370 fluid composition, and our results suggest that it is difficult to predict which factor will
371 predominate. The effect of ion adsorption in particular is hard to predict, since ion adsorption has
372 not been quantified at metamorphic conditions. Thus, the strong and currently unpredictable
373 dependence of monazite growth rate on fluid composition renders the approach of estimating
374 duration of metamorphism from crystal size or rim thickness unfeasible.

375 **Growth Mechanism: Ostwald ripening or coalescence?**

376 Ayers et al. (1999) originally developed the methods used in this study to characterize the
377 process of Ostwald ripening, but they recognized from textural criteria that coalescence resulting
378 from coarsening of the matrix phase quartz was also an important growth mechanism. In this
379 study also there is clear evidence of monazite grain agglomeration and coalescence in the
380 experimental run products, including the presence of irregular composite crystals and grain
381 necking (Figs. 2 and 3).

382 The shape of the grain size distribution does not rule out either Ostwald ripening or
383 coalescence because they both change crystal size distributions from lognormal to normal.
384 Likewise, both Ostwald ripening and coalescence can show a linear dependence of $\log D^n$ on \log
385 t , but the distribution of sizes for coalescence is much broader than for Ostwald ripening (Evans,
386 2001). This is what we observe in our run products, even for the longest duration experiment
387 (FQMZ-HCl#4, 167 h), but this may be because the CSFH has only changed slightly from that in
388 the starting material (Fig. 9).

389 We used the Galoper program (Eberl 1998) to model both Ostwald ripening and coalescence

390 to see which best reproduced the distribution of crystal sizes observed in the longest experiment
391 in the FQMZ-HCl series (FQMZ-HCl#4, $t = 167$ h). The Galoper program uses equations from
392 the LSW theory of Ostwald ripening in numerical simulations of grain growth. It simulates the
393 process of coalescence simply by assigning a probability that two or more grains will meet; when
394 they do, the crystal sizes are added and only one of the grains remains for subsequent simulation
395 steps (Eberl 1998). We found that normalized frequencies of occurrence of crystal sizes were
396 best reproduced using only coalescence (Eberl, pers. comm.), suggesting that it is the dominant
397 growth mechanism (Fig. 10). Modeling the results of the zircon growth experiments of Ayers et
398 al. (2003) produced similar results: coalescence alone could reproduce the observed distribution
399 of crystal sizes. However, perhaps the best test of the relative importance of ripening and
400 coalescence is provided by the FQMZ-NaCl series of experiments in which the host quartz
401 crystals coarsened significantly. This should have promoted monazite coalescence and growth,
402 but no measurable growth occurred, suggesting that coalescence is less important than Ostwald
403 ripening. Thus, while we see evidence of both Ostwald ripening and coalescence in our
404 experiments, it remains unclear whether one process dominates over the other.

405

IMPLICATIONS

406 Fluid composition strongly affects monazite growth rate by Ostwald ripening and
407 coalescence because dissolved solutes in aqueous fluids affect monazite solubility, the degree of
408 fluid interconnectivity, and the reactivity of monazite surfaces. The strong effect of fluid
409 composition on monazite growth rate limits the practical use of kinetic growth rate equations for
410 estimating duration of monazite growth and metamorphism from measured crystal or rim
411 dimensions.

412

ACKNOWLEDGEMENTS

413 This research was made possible by NSF grants EAR-9506551 and EAR-0126020 to Ayers.
414 Any opinions, findings, conclusions or recommendations expressed in this material are those of
415 the authors and do not necessarily reflect the views of the National Science Foundation. The
416 NaCl series of experiments were performed by Giles for his Senior Honors thesis. Thanks to
417 Chuck Lukehart for use of his Quantachrome BET, to Deborah Boxall for running our samples,
418 and to Dennis Eberl for performing some of the simulations in Galoper.

419

REFERENCES

- 420 Ayers, J.C., and Watson, E.B. (1991) Solubility of Apatite, Monazite, Zircon, and Rutile in
421 Supercritical Aqueous Fluids with Implications for Subduction Zone Geochemistry.
422 Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering
423 Sciences, 335, 365–375.
- 424 Ayers, J.C., Miller, C., Gorisch, B., and Milleman, J. (1999) Textural development of monazite
425 during high-grade metamorphism; hydrothermal growth kinetics, with implications for U,
426 Th-Pb geochronology. American Mineralogist, 84, 1766.
- 427 Ayers, J.C., Loflin, M., Miller, C.F., Barton, M.D., and Coath, C. (2004) Dating fluid infiltration
428 using monazite. In R.B. Wanty and R.R. Seal II, Eds., Proceedings of the Eleventh
429 International Symposium on Water-Rock Interaction Vol. Vol. 1, pp. 247–251. A.A.
430 Balkema Publishers, Saratoga Springs, NY.
- 431 Berner, R.A. (1978) Rate control of mineral dissolution under earth surface conditions. American
432 Journal of Science, 278, 1235–1252.
- 433 Cabane, H., Laporte, D., and Provost, A. (2001) Experimental investigation of the kinetics of
434 Ostwald ripening of quartz in silicic melts. Contributions to Mineralogy and Petrology, 142,

- 435 361–373.
- 436 Cabane, H., Laporte, D., and Provost, A. (2005) An experimental study of Ostwald ripening of
437 olivine and plagioclase in silicate melts: implications for the growth and size of crystals in
438 magmas. *Contributions to Mineralogy and Petrology*, 150, 37–53. Carlson, W.D. (1999) The
439 case against Ostwald ripening of porphyroblasts. *Canadian Mineralogist*, 37, 403–413.
- 440 Cetiner, Z.S., Wood, S.A., and Gammons, C.H. (2005) The aqueous geochemistry of the rare
441 earth elements. Part XIV. The solubility of rare earth element phosphates from 23 to 150 °C.
442 *Chemical Geology*, 217, 147–169.
- 443 Eberl, D.D. (1998) Deducing growth mechanisms for minerals from the shapes of crystal size
444 distributions. *American Journal of Science*, 298, 499–533.
- 445 Eberl, D.D., Srodon, J., Kralik, M., Taylor, B.E., and Peterman, Z.E. (1990) Ostwald ripening of
446 clays and metamorphic minerals. *Science*, 248, 474–477.
- 447 Evans, B., Renner, J., and Hirth, G. (2001) A few remarks on the kinetics of static grain growth
448 in rocks. *International Journal of Earth Sciences*, 90, 88–103.
- 449 Finger, F., and Krenn, E. (2007) Three metamorphic monazite generations in a high-pressure
450 rock from the Bohemian Massif and the potentially important role of apatite in stimulating
451 polyphase monazite growth along a PT loop. *Lithos*, 95, 103–115.
- 452 Holness, M.B. (1992) Equilibrium dihedral angles in the system quartz-CO₂-H₂O-NaCl at 800C
453 and 1-15 kbar: the effects of pressure and fluid composition on the permeability of
454 quartzites. *Earth and Planetary Science Letters*, 114, 171–184.
- 455 ——— (1993) Temperature and pressure dependence of quartz-aqueous fluid dihedral angles:
456 the control of adsorbed H₂O on the permeability of quartzites. *Earth and Planetary Science*
457 *Letters*, 117, 363–377.

- 458 Joesten, R.L. (1991) Kinetics of coarsening and diffusion-controlled mineral growth. In P.H.
459 Ribbe, Ed., *Reviews in Mineralogy* Vol. 26: Contact Metamorphism pp. 507–582.
460 Mineralogical Society of America, Washington, D.C.
- 461 Kennedy Wasserburg, G.J., Heard, H.C., Newton, R.C., G.C. (1962) The upper three-phase
462 region in the system SiO₂-H₂O. *American Journal of Science*, 260, 501–521.
- 463 Kingsbury, J.A., Miller, C.F., Wooden, J.L., and Harrison, T.M. (1993) Monazite paragenesis
464 and U-Pb systematics in rocks of the eastern Mojave Desert, California: Implications for
465 thermochronometry. *Chemical Geology*, 110, 147–168.
- 466 Kohn, M.J., and Malloy, M.A. (2004) Formation of monazite via prograde metamorphic
467 reactions among common silicates: implications for age determinations. *Geochimica et*
468 *Cosmochimica Acta*, 68, 101–113.
- 469 Lifshitz, I.M. and Slyozov, V.V. (1961) The kinetics of precipitation from supersaturated solid
470 solutions. *Journal of Physics and Chemicals of Solids*, 19, 35–30.
- 471 Morse, J.W., and Wang, Q. (1996) Factors influencing the grain size distribution of authigenic
472 minerals. *American Journal of Science*, 296, 989–1003.
- 473 Russ, J.C. (1995) *The Image Processing Handbook*, 2nd ed. p. 674. CRC Press.
- 474 Tropper, P., Manning, C.E., and Harlov, D.E. (2011) Solubility of CePO₄ monazite and YPO₄
475 xenotime in H₂O and H₂O-NaCl at 800 °C and 1 GPa: Implications for REE and Y
476 transport during high-grade metamorphism. *Chemical Geology*, 282, 58–66.
- 477 Wagner, C. (1961) Theorie den Alterung von Nieder schlaegen durch Umloesen (Ostward
478 Reifung). *Zeitschr. Elektrochemie*, 65, 581–591.
- 479 Watson, E.B., and Brenan, J.M. (1987) Fluids in the lithosphere, Part I: experimentally-
480 determined wetting characteristics of CO₂-H₂O fluids and their implications for fluid

481 transport, host-rock physical properties and fluid inclusion formation. *Earth and Planetary*
482 *Science Letters*, 85, 497–515.

483 Watson, E.B., Vicenzi, E.P., and Rapp, R.P. (1989) Inclusion/host relations involving accessory
484 minerals in high-grade metamorphic and anatectic rocks. *Contributions to Mineralogy and*
485 *Petrology*, 101, 220–231.

486 Zhang, J.W., and Nancollas, G.H. (1990) Mechanisms of growth and dissolution of sparingly
487 soluble salts. In M.F. Hochella Jr. and A.F. White, Eds., *Mineral-water interface*
488 *geochemistry* Vol. 23, pp. 365–396. Mineralogical Society of America.

489

TABLE 1. Experimental conditions and measured monazite crystal size parameters

Expt.	Composition*	t (h)	# images	n	Area (μm^2)	N_A^\dagger (μm^{-2})	$A_A = V_V$	Shape Factor	$\langle D \rangle$ (μm) ‡	95% CL	$\langle L \rangle$ (μm)	L_3 (μm) §
MZ SM	Mnz		5	2946	45780	6.4E-02	14(5)	0.72	0.82	0.04	0.81	0.83
FQMZ SM	Qz-Mnz		12	273	109872	2.5E-03	0.5(3)	0.74	0.76	0.13	0.77	0.70
FQMZ-NaCl#5	Qz-Mnz-2m NaCl	0	20	730	183120	4.0E-03	0.7(3)	0.70	0.70	0.08	0.69	0.68
FQMZ-NaCl#5b	Qz-Mnz-2m NaCl	0	15	634	137340	4.6E-03	0.9(6)	0.72	0.76	0.09	0.76	0.68
FQMZ-NaCl#2	Qz-Mnz-2m NaCl	8	29	1418	265524	5.3E-03	1.0(4)	0.88	0.79	0.05	0.88	0.76
FQMZ-NaCl#1	Qz-Mnz-2m NaCl	24	22	1403	201432	7.0E-03	1.2(5)	0.89	0.72	0.05	0.81	0.74
FQMZ-NaCl#3	Qz-Mnz-2m NaCl	70	20	1233	183120	6.7E-03	1.3(4)	0.89	0.78	0.06	0.92	0.85
FQMZ-NaCl#4	Qz-Mnz-2m NaCl	165	20	811	183120	4.4E-03	0.7(2)	0.91	0.70	0.06	0.81	0.75
FQMZ-HCl#2	Qz-Mnz-2m HCl	3	20	816	183120	4.5E-03	0.8(3)	0.76	0.79	0.07	0.8	0.70
FQMZ-HCl#1	Qz-Mnz-2m HCl	17.3	24	1033	219744	4.7E-03	1.3(5)	0.77	0.91	0.07	0.94	0.88
FQMZ-HCl#3	Qz-Mnz-2m HCl	72	40	939	366240	2.6E-03	0.7(3)	0.79	1.03	0.07	1.08	0.82
FQMZ-HCl#4	Qz-Mnz-2m HCl	167	46	1158	421176	2.7E-03	1.0(6)	0.79	1.03	0.09	1.07	1.02

490 * Mnz = Monazite, Qz = Quartz, m = molal. All experiments at 1000°C and 1.0 GPa. All starting materials contain 98% quartz
 491 powder.

492 $^\dagger N_A$ is number of crystals per unit area. The modal abundance is the area of crystals per unit area A_A , and is equal to the volume
 493 fraction V_V , the volume of monazite crystals per unit volume. The shape factor is grain circularity, which equals $4\pi A/P^2$ where A is
 494 area and P is perimeter of a grain, ranges from 0 for a line to 1 for a circle.

495 ‡ Because measured values of Feret diameter D and mean intercept length L are log-normally distributed except in the upper and
 496 lower tails, we calculated a 95% trimmed mean of the log10 transformed values and took the antilog to obtain our best estimate of the
 497 population means $\langle D \rangle$ and $\langle L \rangle$. 95% CL is the 95% confidence limit on estimate of mean value of D , e.g., for FQMZ-NaCl#1 there
 498 is a 95% probability that the population (true) mean falls within the range $0.72 \pm 0.05 \mu\text{m}$.

499 $^\S L_3$ is the global mean intercept length (Russ 1995).

500

FIGURES

501 **FIGURE 1:** Backscattered electron images and Crystal Size Frequency Histograms (CSFH) of
 502 starting materials. In these and all subsequent images monazite grains are bright white, quartz is
 503 grey, and pores and cracks are black. D = Feret diameter, n = number of grain size
 504 measurements, μ_{95} is the population mean with 95% confidence limits, and no./cm² is the number
 505 of grains per square centimeter. The solid curve is the measured cumulative frequency in percent.

506 a) FQMZ SM powder. b) zero-time experiment FQMZ-NaCl#5. c) duplicate zero-time
 507 experiment FQMZ-NaCl#5b used to evaluate precision.

508

509 **FIGURE 2.** Backscattered electron images of run products and CSFH of monazite from FQMZ-
 510 NaCl experiments containing 2 molal NaCl. a) FQMZ-NaCl#2, $t = 8$ h. b) FQMZ-NaCl#1, $t = 24$
 511 h. c) FQMZ-NaCl#3, $t = 70$ h. d) FQMZ-NaCl #4, $t = 165$ h.

512

513 **FIGURE 3.** Backscattered electron images of run products and CSFH of monazite from FQMZ-
 514 HCl experiments containing 2 molal HCl. a) FQMZ-HCl#2, $t = 3$ h. b) FQMZ-HCl #1, $t = 17.3$ h.
 515 c) FQMZ-HCl#3, $t = 72$ h. d) FQMZ-HCl #4, $t = 167$ h.

516

517 **FIGURE 4.** The circularity shape factor, which equals $4\pi A/P^2$ where A is area and P is perimeter
 518 of a grain, ranges from 0 for a line to 1 for a circle. Here median values of monazite grain
 519 circularity shape factor are plotted as a function of $\log_{10} t$ (s) for the FQMZ-NaCl time series of
 520 experiments with error bars equal to \pm half of the interquartile range = 75th percentile – 25th
 521 percentile. Initial values plotted at $\log_{10} t = 0$ calculated from pooled values from FQMZ SM,
 522 FQMZ-NaCl#5 and FQMZ-NaCl#5b.

523 **FIGURE 5.** Median values of monazite circularity shape factor plotted as a function of $\log_{10} t$ (s)
 524 for the FQMZ-HCl time series of experiments with error bars equal to \pm half of the interquartile
 525 range = 75th percentile – 25th percentile. Initial values plotted at $\log_{10} t = 0$ calculated from
 526 pooled values from FQMZ SM, FQMZ-NaCl#5 and FQMZ-NaCl#5b.

527

528 **FIGURE 6.** Time dependence of mean monazite grain diameter in FQMZ-NaCl experiments. Y
 529 values are 95% trimmed means of the base 10 logarithm of measured Feret diameters of
 530 monazite grains for each experiment. Error bars are 95% confidence limits. Average of the
 531 starting material FQMZ SM and the zero-time experiments FQMZ-NaCl#5b and FQMZ-NaCl#5
 532 used for the data point at $\log t = 0$. Least squares regression line fit: $\log \langle D \rangle = -0.12 -$
 533 $0.0016 * \log_{10} t, r^2 = 0.027$ where r is the Pearson correlation coefficient.

534

535 **FIGURE 7.** Time dependence of mean monazite grain diameter in FQMZ-HCl experiments
 536 plotted as open circles. Y values are 95% trimmed means of the base 10 logarithm of measured
 537 Feret diameters of monazite grains for each experiment. Error bars are 95% confidence limits.
 538 Least squares regression line does not include the starting material FQMZ SM plotted as a filled
 539 circle: $\log \langle D \rangle = 0.071 * \log t - 0.39, r^2 = 0.96$.

540

541 **FIGURE 8.** Comparison of 95% trimmed means of the logarithm of measured mean intercept
 542 length L_3 of monazite grains in run products of experiments containing H₂O (Ayers et al., 1999),
 543 2 m NaCl and 2 m HCl (this study).

544

545

546 **FIGURE 9.** Comparison of normalized CSFHs for monazite in run products corresponding to
547 initial (FQMZ-NaCl#5b, $t = 0$ h) and final (FQMZ-HCl#4, $t = 167$ h) experiments. Shown for
548 comparison are theoretical LSW distributions for control by surface reaction ($n = 2$), matrix
549 volume diffusion ($n = 3$), and grain boundary diffusion ($n = 4$). r^* is the mean grain radius.

550

551 **FIGURE 10.** Results from Galoper model (Eberl, 1998) assuming monazite growth only by
552 coalescence fit the data from the longest duration experiment FQMZ-HCl#4 ($t = 167$ h) very well
553 (t-test comparing Galoper and measured values gave $P = 0.884$).



















