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Citation for published version:

Zhu, W, Fousseis, F, Lisabeth, H, Xing, T, Xiao, X, De Andrade, V & Karato, S 2016, 'Experimental evidence of reaction-induced fracturing during olivine carbonation. Fracturing during olivine carbonation', *Geophysical Research Letters*, vol. 43, no. 18, pp. 9535-9543. <https://doi.org/10.1002/2016GL070834>

Digital Object Identifier (DOI):

[10.1002/2016GL070834](https://doi.org/10.1002/2016GL070834)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Geophysical Research Letters

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Experimental evidence of reaction-induced fracturing during olivine carbonation

Wenlu Zhu^{1*}, Florian Füsseis², Harrison Lisabeth¹, Tiange Xing¹, Xianghui Xiao³, Vincent De Andrade³, Shun-ichiro Karato⁴

¹Department of Geology, University of Maryland, College Park, MD 20782, USA

²School of Geosciences, University of Edinburgh, Edinburgh, EH9 3FE, UK

³Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

⁴Department of Geology and Geophysics, Yale University, New Haven, CT 06511, USA

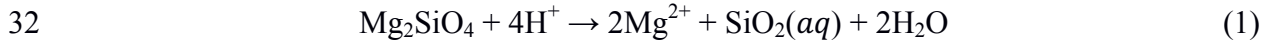
*Correspondence to: Wenlu Zhu (wzhu@umd.edu)

Abstract. Mineral carbonation, a process that binds CO₂ in the form of carbonates by silicate weathering, is widespread on the Earth's surface. Because of the abundance of silicate rocks and the permanence of the carbonated solids, sequestering CO₂ via mineral carbonation has generated lots of interests. However, it is unclear how the fluid-rock reaction proceeds to completion in spite of an increasing solid volume. We conducted a mineral carbonation experiment in which a sintered olivine aggregate reacted with a sodium bicarbonate solution at reservoir conditions. Time-resolved synchrotron X-ray microtomographic images show cracks in polygonal patterns arising in the surface layers and propagating into the interior of the olivine aggregate. The nanotomography data reveal that the incipient cracks intersect at right angles. We infer that stretching due to non-uniform volume expansion generates polygonal cracking of the surfaces. Our data shed new lights on the processes that controls hydration and carbonation of peridotite.

Introduction

Hydration and carbonation of mantle peridotite are widespread on the surface of the Earth. Such alteration exerts controls in lithosphere strength, subduction zone geodynamics, hydrothermal circulation, water and carbon cycle. Mineral carbonation, in which CO₂ is chemically incorporated in silicate rocks to form carbonate minerals, is also recognized as a potentially safe and permanent method of CO₂ sequestration [e.g., Sefriz, 1990; Lackner, 2003] and was recently successfully tested in an industrial scale [Matter et al., 2016]. The naturally abundant mineral olivine ((Fe, Mg)₂SiO₄), especially its magnesium end-member forsterite (Mg₂SiO₄), has been a focus of carbon mineralization research [Goff and Lackner, 1998; Giammar

et al., 2005; Gerdemann et al., 2007; Kelemen and Matter, 2008]. Carbonation in forsterite involves the dissolution of olivine by hydrogen ions in solution,



followed by the precipitation of magnesite (MgCO_3) via reaction between magnesium and carbonate ions in solution:



Other precipitation reactions are also possible, including formation of brucite (magnesium hydroxide) and serpentine minerals. Because the magnesium silicate is far from equilibrium with CO_2 -rich fluids, aqueous mineral carbonation of olivine is one of the kinetically fastest carbonation reactions [Kelemen and Matter, 2008; Andreani et al., 2009]. The efficiency of carbon sequestration methods is mainly determined by the supply of reactive fluids and exposure of reactive solids to the CO_2 -rich fluids [e.g., O'Connor et al., 2004]. The usefulness of ultramafic rocks as carbon storage thus hinges on the feasibility of creating and maintaining reactive surface area. Current implementation strategy includes grinding of solid reactants in *ex-situ* mineral carbonation reactors [e.g., Gerdemann et al., 2007; Lackner et al., 1995], hydrofracturing of the formations through *in-situ* deposition in ultramafic mines [Harrison et al., 2013; Power et al., 2013] or injection of CO_2 in basalts [Matter et al., 2016]. These processes are energy intensive and costly [Gerdemann et al., 2007; IPCC, 2005].

The hydration and carbonation of olivine results in an up to ~44% increase in solid molar volume [e.g., Kelemen and Matter, 2008]. The conventional wisdom is that unless the reaction products are deposited elsewhere, excess solids can clog fluid pathways and reduce the accessible reactive surface, causing negative feedback to halt further reaction. However, field observations show 100% serpentinization and carbonation of peridotite [e.g., Macdonald and Fyfe, 1985; Iyer et al., 2008; Beinlinch et al., 2012] even when the alteration is nearly isochemical [Kelemen and Matter, 2008]. The field data lead to a working hypothesis that excess solid reaction products could exert enough pressure (termed crystallization pressure) to break the host rocks [O'Hanley, 1992; Kelemen and Hirth, 2012]. This so-called reaction-driven cracking can create additional fluid pathways and expose new reactive surface. When reaction-driven cracking is assumed, numerical models show that olivine carbonation can proceed to completion at reasonable rates [e.g., Rudge et al., 2010]. Because natural rocks are often subjected to complex mechanical, chemical, and

60 thermal loads, it is unclear at what conditions these solid volume increasing reactions can proceed
61 to completion.

62 Fracturing rocks via crystallization pressure is observed in salt weathering, where the salt
63 derives from external sources [Scherer, 2004; Noiriel et al., 2010]. At reservoir conditions,
64 however, the slow precipitation of magnesium carbonate (eqn. 2) is coupled with the rapid
65 dissolution of olivine (eqn. 1) [Chen et al., 2006; Xu et al., 2013; Johnson et al., 2014]. The
66 asymmetry in dissolution-precipitation kinetics renders it difficult to generate large crystallization
67 pressure. Indeed, experimental studies of CO₂-rich brine reacting with peridotites have not
68 produced evidence for cracking via crystallization pressure in olivine [e.g., Hovelmann et al.,
69 2012]. Instead, laboratory studies consistently show that rates of carbonation and hydration
70 decrease with time [O’connor et al., 2004; Andreani et al., 2009; Hovelmann et al., 2012].

71 Whether fracturing the solid reactants is achievable without additional energy input
72 remains a critical question. We report on insights gained during an *in-situ* synchrotron-based X-
73 ray microtomography (SXμT) experiment that characterized the real-time evolution of 3-
74 dimensional (3D) pore geometry during olivine carbonation and highlight an alternative
75 mechanism that might facilitate natural carbonation reactions.

76 **Data Collection and Reduction**

77 A sintered porous olivine aggregate was chosen to react with a sodium bicarbonate solution
78 (NaHCO₃, 1.5 mol) at a confining pressure of 13 MPa, a pore fluid pressure of 10 MPa and a
79 temperature of 200°C (Supporting Information fig. S1). We utilized an x-ray transparent version
80 of a Hassler core holder [Fusseis et al., 2014] to investigate the 3D microstructure evolution during
81 olivine carbonation. The core holder was installed in a SXμT beamline at the Advanced Photon
82 Source, where the change of rock’s microstructure was recorded.

83 From the moment when the temperature at the sample reached 200°C, every 30 minutes
84 1500 projections were collected with an exposure time of 50 ms while the sample was rotated over
85 180° with 1.2 °s⁻¹. Between 128 and 135 hours, data were acquired in 5-minute intervals. Each
86 dataset was acquired in 150 s. A total of 360 3D datasets amounting to 35 TB of raw data cover
87 the entire experiment. From the radiographic projection data, 3D SXμT data with a spatial
88 resolution of ~2 μm were reconstructed using a single-distance phase retrieval algorithm
89 implemented in TomoPy [Paganin et al., 2002; Gürsoy et al., 2014].

After the reacted olivine sample was retrieved, Synchrotron-based X-ray nanotomography data were collected from a $65 \times 65 \times 63 \mu\text{m}^3$ fragment of the post-reaction olivine aggregate, using a transmission X-ray microscope at beam line 32-ID of APS [Paganin et al., 2002]. The instrument uses an 8 keV monochromatic beam and an X-ray objective lens to magnify radiographs onto a detection system assembly comprising a scintillator (LuAG single crystal scintillator), a Zeiss 5X optical microscope objective lens and an Andor Neo sCMOS camera. The Fresnel zone plate limits the spatial resolution to 60 nm, while the voxel size is 57 nm after binning. A total of 720 projection images were acquired over a 180° rotation angle range (i.e., in 0.25° angular steps) with 2s exposure time for each image.

Because of the weak x-ray absorption contrast between magnesite and olivine at 8 keV, an iterative reconstruction method, penalized maximum-likelihood (PML) [De Carlo et al., 2014] is integrated in Tomopy [Chang et al., 2004; Gürsoy et al., 2014] to enhance the signal to noise ratio. This algorithm is proven to produce high quality reconstructions, especially for tomograms with noisy radiographs and sampling below the Nyquist criterion [De Andrade et al., 2016]. The reconstruction of a full volume with such high computational requirements method necessitates the use of a supercomputer at the Argonne Leadership Computing Facility (ALCF), where a new large-scale parallelization approach has been implemented [Biçer et al., 2015].

For geochemical analyses of the post-reaction sample, the retrieved fragments were embedded in epoxy and exposed in a polished surface. Mineral phases were identified with energy-dispersive x-ray spectroscopy in a JEOL JXA-8900 Electron probe microanalyzer operating at a 15 keV accelerating voltage and a beam current of 15 nA. Collection time for EDS data was 120 s per spot.

The reconstructed data were visualized and analyzed using the commercial software Avizo Fire. No image processing other than cropping was applied. To determine the threshold value, grey value histograms (Supporting Information, figs. S2) were computed from all analyzed time steps, smoothed, and the individual distributions superposed, following an approach described in [Fusseis et al., 2012]. The gray value distribution in each dataset is a direct function of the sample composition and changes during the reaction. Since porosity is produced, the proportion of dark voxels increases systematically at the expense of the intermediate grey voxels, causing the individual lines to intersect in a narrow region. The gray value at which the lines intersect was used for thresholding. An increase in the brightest voxels, which can also be seen in the histograms,

121 is a consequence of phase contrast around newly produced pores (Supporting Information, figs.
122 S3).

123 **Results**

124 The SX μ T time-series data provide clear evidence that the carbonation reaction progressed
125 steadily while volume expansion and fracturing of the olivine aggregate took place as a result of
126 olivine carbonation (Figs. 1, 2). Fine-grained reaction products precipitated in the interior of the
127 cup wall and appear as growing clusters with smoother textures and less contrast (magenta outlines
128 in Fig. 1). The sizes of the clusters increase with time. Nanotomography and energy-dispersive
129 spectroscopy confirm that the precipitate clusters are formed by new carbon-rich minerals, likely
130 magnesite (Fig. 3). Changes in the position of individual olivine grains (yellow arrows in Figs. 1,
131 2), which act as strain markers, are evidence for the volume expansion caused by the reaction.

132 Outlined by the surrounding pores, the precipitation clusters become more discernible in
133 the tangential sections underneath the outer cup surface (Figs. 2A-E). A polygonal crack system
134 emerges after 84 hours (Fig. 2C). In Fig. 1, it becomes apparent that the integrity of the cup wall
135 is deteriorated by these cracks, which propagate into the cup wall from about 64 hours into the
136 experiment. Fractures are seen to form at both the inner and outer surfaces of the cup wall (Fig. 1),
137 and then propagate towards the interior as carbonation continues (Supporting Information, movie
138 M1). These cracks widen to several tens of μm as reaction continues (Fig. 1) and eventually
139 disintegrate the cup, as a post-mortem examination of the sample revealed.

140 Simultaneously, the total porosity evolves in the sintered cup wall (Fig. 4). The total
141 porosity, which is normalized to the starting porosity, increases by a factor of 1.2 in both
142 subvolumes v1 and v2 during the first 90 hours of reaction. After that, the porosity of v1 continues
143 to increase to a factor of 1.3 until ~ 100 hours, when it starts a steady decline. In contrast, the
144 porosity of v2 remains at just above 1.2, with only minor declines followed by recovery. (Fig. 4B).

145 We evaluated the porosity distribution within the two subvolumes by means of quantifying
146 porosity on 2-dimensional (2D) tangential sections extracted from the segmented subvolumes
147 along the radius of the sample (Figs. 4C&D, Supplementray Information fig. S4). At the early
148 stages of the reaction (i.e., < 90 hours), porosity of all the tangential sections increases, likely due
149 to dissolution of olivine grains (Figs. 4C&D). After that, porosity of the interior tangential sections
150 decreases monotonically, consistent with the appearance of precipitants (Figs. 1, 2). In contrast,

the porosity of the 2D sections near the (inner) surface of v1 continues to increase after 90 hours (Fig. 4C). The sections near the (outer) surface of v2 exhibits similar porosity increases (Fig. 4D). The contrast between the porosity decreasing interior and the porosity increasing surfaces indicates that more reaction products are precipitated in the interior of the cup wall (cf. Fig. 1). This non-uniform precipitation corroborates with the observed total porosity changes in v1 and v2: the total porosity in v1 with more pores from the interior regions decreases, whereas the total porosity of v2 with less interior regions remains constant (Fig. 4B).

The carbonation reaction also constantly modifies the surface roughness of the olivine grains inside the cup. The rhombohedral shape of the new crystals on the surface of the olivine sand grains suggests that they are magnesite MgCO_3 (Fig. 5A). Both the population and size of these magnesite grains increase steadily during the entire experiment (Fig. 5B), with no indication of self-limiting behavior.

Discussion

Our experiment elucidates the real-time evolution of 3D microstructure during olivine carbonation, provides insight into the processes controlling the metamorphic reaction. Our data reveal a positive feedback between reaction progress and porosity evolution. Of particular importance is the polygonal crack pattern initiated on the surfaces of the cup wall (Figs. 1, 2). Growth of these cracks helps maintain reactive surfaces, and eventually leads to the disintegration of the sample (Supporting Information, movie M1).

Polygonal crack patterns are frequently observed in drying mud ponds [Goehring et al., 2010], cooling lava flows [Aydin and DeGraff, 1988], and ice wedge fields [Plug and Werner, 2002; Kessler and Werner, 2003]. Formation of polygonal cracks requires volume mismatch between the surface and the interior of the material, which leads to a stress buildup in the surface layer [Shorling et al., 2000]. When the stress exceeds the tensile strength, cracks develop in the surface layer. Cracking at the surface results in accelerated water loss (in desiccating mud), heat loss (in cooling lava), or thermal contraction (in ice wedge) from the interior of the material. Consequently, the cracks propagate into the interior of the material. We infer these processes to have also controlled reaction advance in our experiment and may affect natural carbonation.

In our experiment, reaction advance is strongly affected by the sample geometry (Fig. 6). Dissolution of olivine in the cup wall is expected to be vigorous because smaller crystals dissolve

181 more rapidly [Adamson, 1990; Emmanuel and Ague, 2009]. The surge in magnesium ions in
182 solution promotes precipitation of new crystals (Figs. 1-3). At the wall's interior, precipitation
183 causes the infill of the pore space and solid volume expansion (Fig. 6). At the surfaces, however,
184 the fine olivine grains in the cup wall are adjacent to the olivine sand grains, both the ones filled
185 inside the cup as well as the ones spilled to its outside. These sand grains are ~ 2 orders of
186 magnitude larger than the grains in the cup wall. Since crystallization rate negatively correlates
187 with the curvature of the substrate [Garcia et al., 2013; Ziese et al., 2013], precipitation of new
188 crystals preferentially takes place on the large olivine sand grains at the expense of the neighboring
189 fine grains (Fig. 6). The lack of precipitation at the surfaces of in the cup wall is confirmed by
190 porosity measurements (Fig. 4). The non-uniform precipitation causes the interior of the cup wall
191 to expand faster than its surfaces, thus generating the tensile stresses necessary for cracking to
192 occur at the surfaces (Fig. 6). The polygonal patterns (Fig. 2) suggest that the cracks are generated
193 by the same mechanism as for the shrinkage cracks [e.g., Shorlin et al., 2000]. In our experiment,
194 the volume mismatch between the surface and interior of the sintered olivine aggregate is
195 instigated by rapid dissolution and non-uniform precipitation. In contrast to the crystallization
196 pressure hypothesis, the mechanism proposed here is based on the mismatch between the volume
197 changes in different parts of the sample and can tear the surface for tension values less than the
198 confining pressure. Coalescence of the polygonal cracks leads to fractures disintegrating the
199 cylindrical samples. Because of the cylindrical geometry of the samples, radial expansion is
200 counteracted by the hoop stress it would generate. Due to this effect and the different loading
201 systems in the axial and radial directions, the axial stress on the sample is the least compressive
202 and the largest fractures are horizontal (Fig. 2).

203 In homogeneous materials, the primary shrinkage cracks intersect at right angles because
204 the first set of cracks releases the stress normal to their surface, and consequently the second set
205 of cracks forms perpendicular to the preexisting first set to alleviate stress in that direction [e.g.,
206 Goehring et al., 2010]. The geometric attribute can be used to verify the cracking mechanism during
207 olivine carbonation in our experiment. Indeed, the nanotomography data of the post-reaction cup
208 wall reveal nanometer scale cracks intersecting each other orthogonally (Supporting Information,
209 movie M2), in good agreements with the predicted right angle of the primary cracks formed in a
210 layer under tension [e.g., Goehring et al., 2010].

211 **Conclusion**

212 The time-resolved microtomography study reveals an experimentally tested mechanism for
213 self-sustained olivine carbonation. The mechanism is the similar to that in the shrinkage cracking
214 observed in other geological settings, though during olivine carbonation, it is the volume expansion
215 of the interior, instead of the contraction of the surface, that causes the volume-mismatch between
216 the surface and the interior. Compared to the crystallization pressure hypothesis, the polygonal
217 pattern associated with tensile cracking at the surface is more consistent with fracture patterns
218 observed in rocks that undergo natural weathering [e.g., Iyer et al., 2008]. Understanding the
219 mechanism of reaction-induced cracking can lead to new implementation strategy of more efficient
220 carbonation reactors. Although our experiment was conducted on porous aggregates at reservoir
221 conditions, it is possible that cracking by the same mechanism takes place in other geological
222 settings. In nature, carbonation of mantle peridotite can start with a pre-existing fracture network,
223 and proceed to completion with reaction-induced cracking, as long as the non-uniform volume
224 expansion is maintained.

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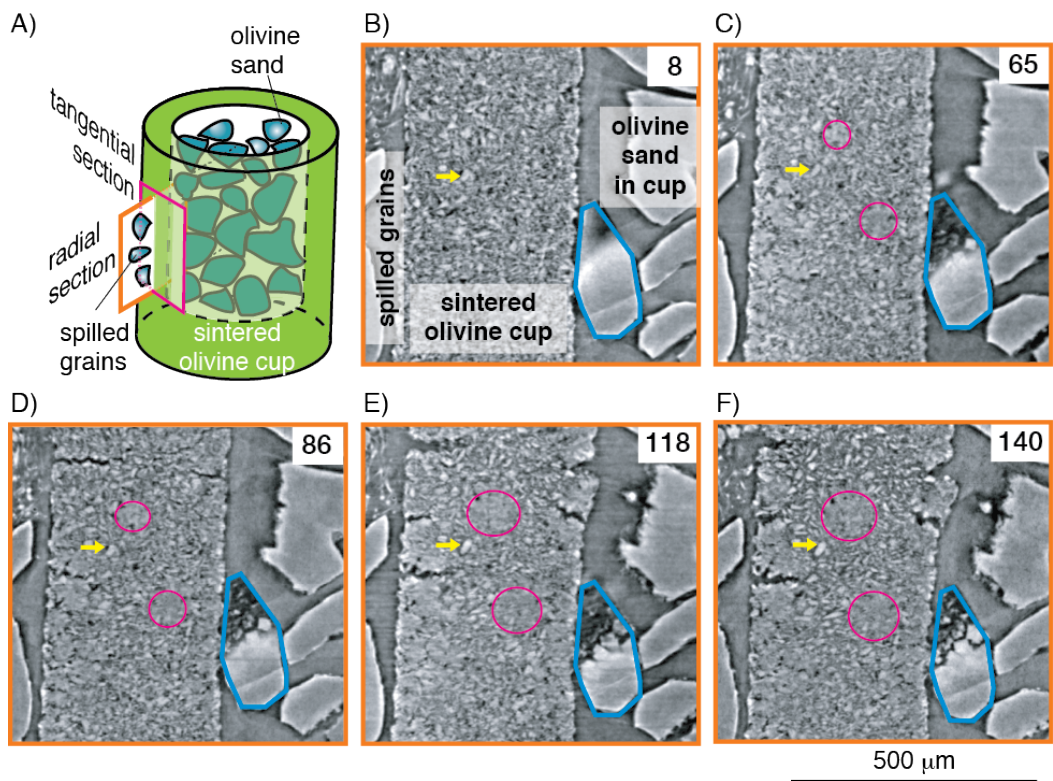
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323 **Acknowledgments:** This material is based upon work primarily supported by the U.S. Department
 324 of Energy (DOE), Office of Science, the Office of Basic Energy Sciences (BES), Chemical
 325 Sciences, Geosciences, & Biosciences Division under Award Number DE-FG-0207ER15916;
 326 DOE, Office of Science, National Energy Technology Laboratory under Award Number DE-FE-
 327 0004375; and Royal Society Grant RG140191. This research used resources of the Argonne

328 Leadership Computing Facility, which is a DOE Office of Science User Facility supported under
329 Contract DE-AC02-06CH11357. All data needed to evaluate the conclusions in the paper are
330 present in the paper and/or the Supplementary Materials. Additional data related to this paper may
331 be requested from the authors. We thank T. Tamarkin, G. Amulele and P. Shevchenko for sample
332 preparation, P. Candela, and L. Montesi for discussions and I. Butler for technical assistance. We
333 thank Dr. H. Stunitz and an anonymous reviewer for their insightful comments.

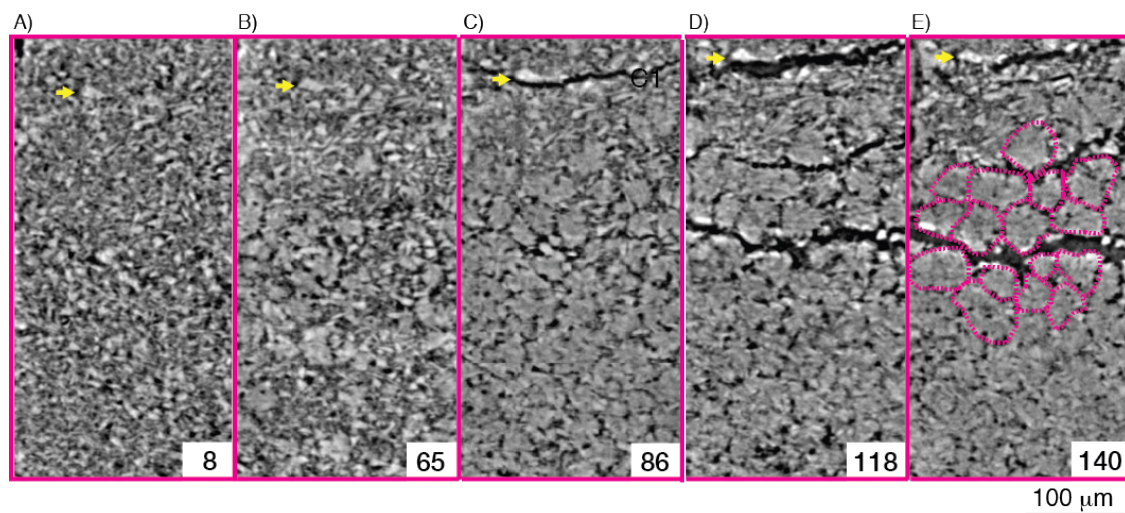
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335 **Figures**
336



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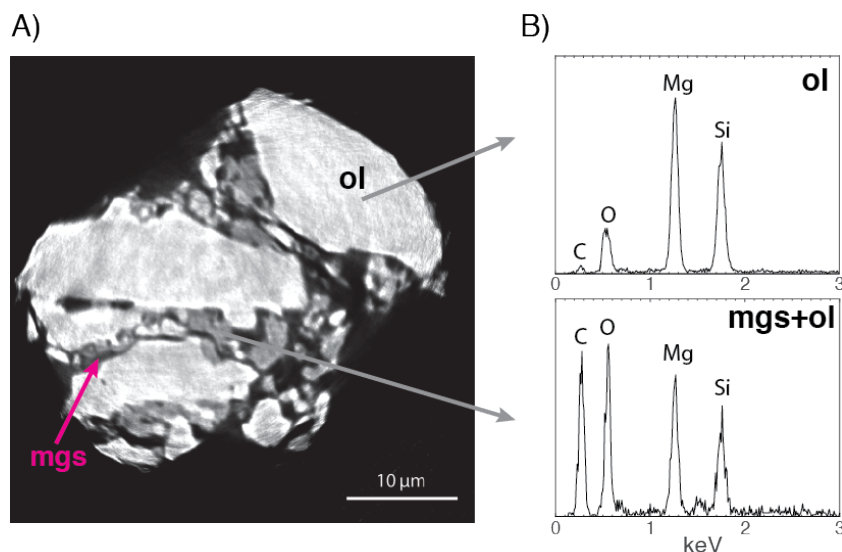
338 Figure 1. Temporal evolution of pore geometry in a radial section. A) A thick-walled cup (made
339 of a sintered olivine aggregate) filled with olivine sand. Microtomographic image of a radial
340 section (orange outline) after B) 8; C) 65; D) 86; E) 118; F) 140 hours of carbonation. Yellow
341 arrows mark an olivine grain in the interior of the cup wall. Olivine sand grains in the cup (right
342 side of the images) show considerable increase in surface roughness. Time series images of the
343 surface of a representative olivine sand grain (blue outline) are presented in Figure 5. Some olivine
344 sand grains fell between the olivine cup and the jacket during sample preparation (spilled grains
345 on the left side of the images). Fine-grained reaction products precipitated in the interior of the cup
346 wall appear as growing clusters with smoother textures (magenta outline). Cracks initiate at both
347 the inner and outer surfaces of the cup wall after 64 hours of reaction. Cracks widen as reaction
348 continues.



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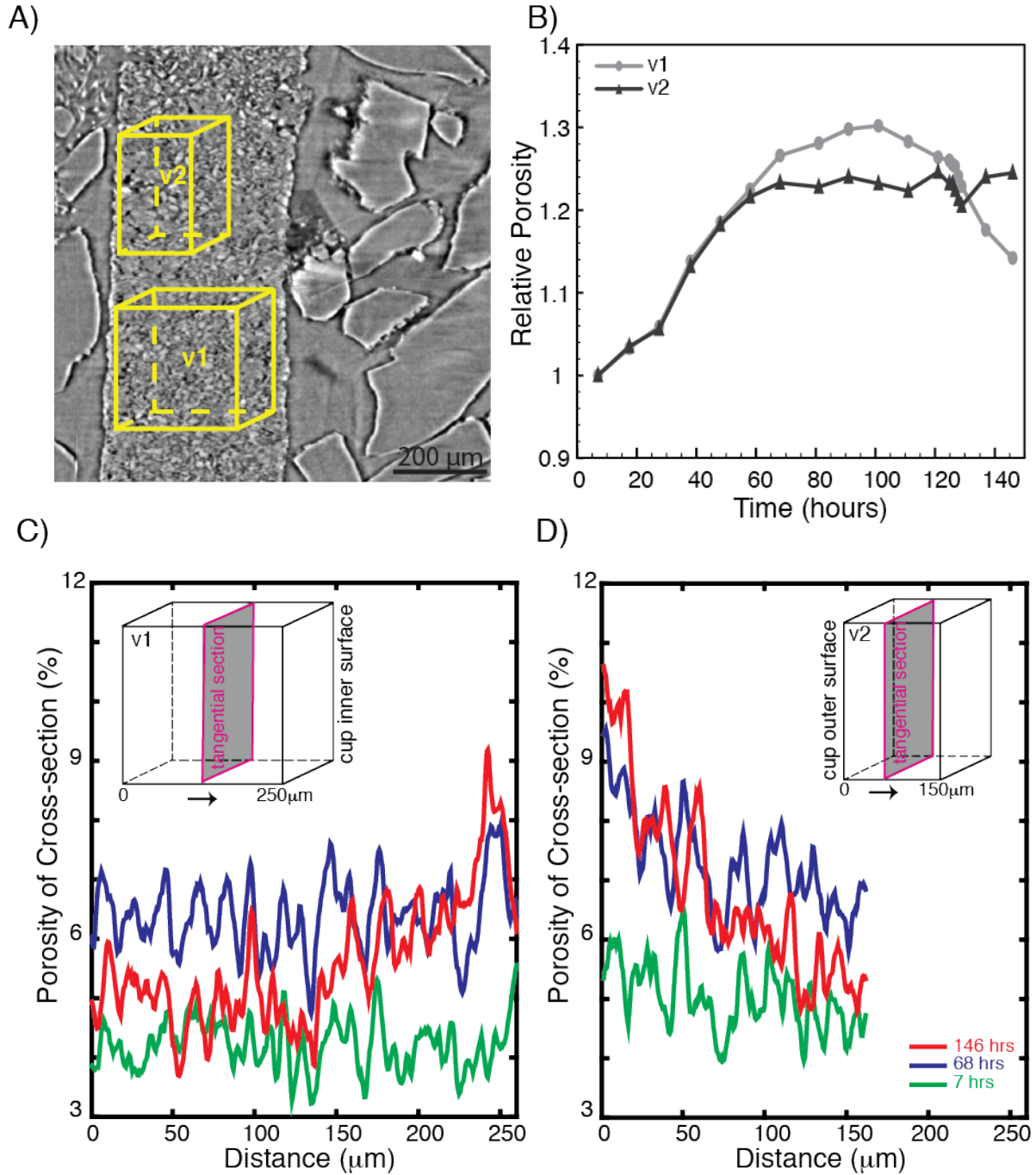
350 Figure 2. Temporal evolution of pore geometry in a tangential section. Microtomographic image
 351 of a tangential section of the olivine cup (magenta outline in Fig. 1A) undergoing A) 8; B) 65; C)
 352 86; D) 118; E) 140 hours of carbonation. Yellow arrows mark an olivine grain in the interior of
 353 the cup wall. Its position change with respect to the top of the image window (fixed) serves as a
 354 strain marker for the volume expansion resulting from reactions. In the tangential section,
 355 polygonal cracks develop along the edge of the reactant clusters (magenta outline). Coalescence
 356 of the polygonal cracks leads to fractures across the aggregate.

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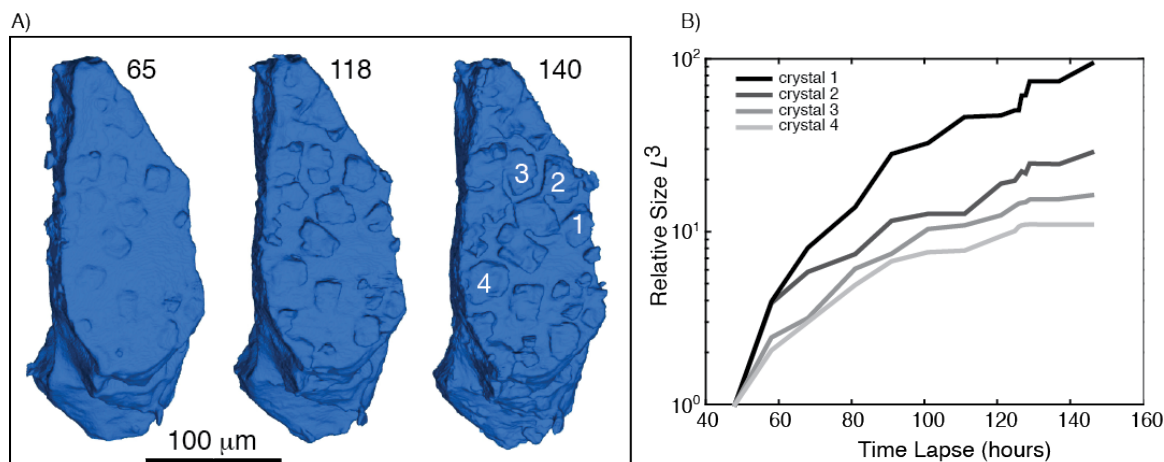
359 Figure 3. Segment of the post-reaction cup wall. A) A 2D nanotomographic image shows that new
 360 phases (mgs, dark grey) precipitate in the pore space between olivine grains (ol, light grey) of the
 361 olivine aggregate; B) EDS data of the post-reaction cup wall. The weak carbon signal in the
 362 spectrum of olivine grains results from carbon coating. In contrast, the spectrum of the regions
 363 filled with precipitants (mgs+ol) shows significant carbon content, which suggests epitaxial
 364 magnesite (mgs) growth on the olivine grains (ol).



365

366 Figure 4. Porosity evolution of subvolumes. A) Subvolumes v1 and v2; B) Relative porosity
 367 change of v1 (light grey) and v2 (dark grey) during 146 hours of olivine carbonation. C) Porosity
 368 evolution of 2D tangential sections (magenta slice) taken from C) subvolume v1; D) subvolume
 369 v2 after 7 (green), 68 (blue), 146 (red) hours of reactions. Note that the leftmost edge of subvolume
 370 2 is at the outer surface of the olivine cup wall, the rightmost edge of subvolume 1 is at the inner
 371 surface of the cup wall. Porosity at the interior first increases and then decreases during
 372 carbonation, whereas porosity near both the outer and inner surfaces increases.

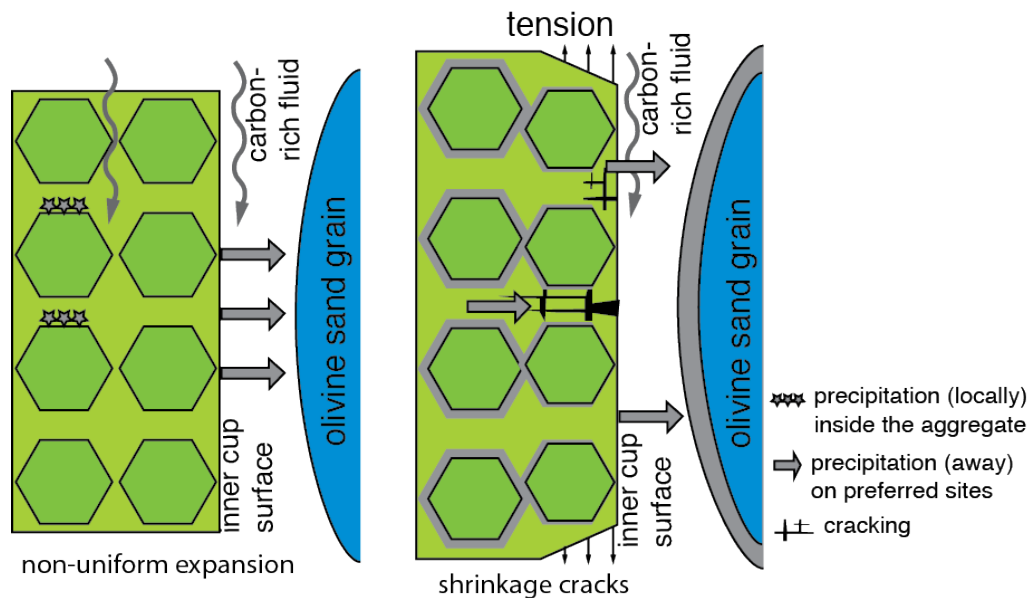
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375 Figure 5. Nucleation and growth of new crystals. A) Surface of a representative olivine sand grain
376 (blue outline in Fig. 1) in the olivine cup; B) Cubic circumferential length L (normalized to that at
377 48 hours of carbonation when most of the new crystals first appeared) of several new crystals as a
378 function of time.

379



380

381 Figure 6. Schematic diagram for shrinkage cracking during mineral carbonation. At the surface of
382 the fine-grained olivine aggregate (green), reactants (grey) preferentially precipitate on the large
383 olivine sand grains (blue). Beneath the surface of the cup wall, reactants precipitate locally (grey
384 stars), leading to non-uniform volume expansion. As the reaction continues, cracks form in
385 response to increasing strain.

386