

Evidence of depletion of iron from natural quartzite during laser-driven hydrothermal processing

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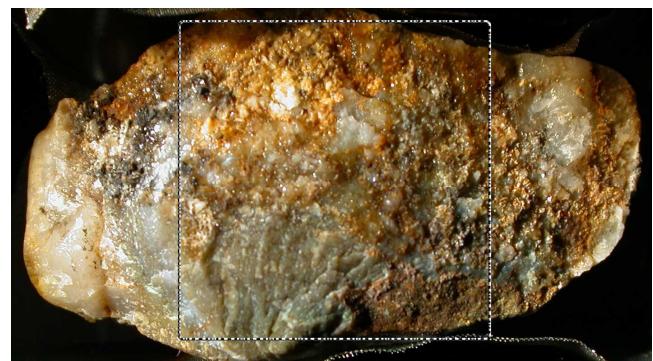
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ABSTRACT: A sample of natural quartzite rock was submerged in deionized water and illuminated with 1.8-J pulses of 527-nm light with 15-ns duration over an area of 3 cm² [fluence = 0.6 J/cm²]. This relatively low fluence and intensity [40 MW/cm²] were far below the threshold needed for direct ablation via plasma formation or thermal evaporation. With each laser pulse, a small cloud of sub- μ m particles was released from the surface and dispersed into the submerging water, forming a long-lived suspension. After one hundred laser pulses, the processing was terminated and the surface of the originally colored quartzite was rendered colorless. The quartzite rock was cut in cross section and the colorless material on the surface was examined with X-ray fluorescence. We report that the transition element Fe was found to be significantly depleted in this colorless layer. This supports the hypothesis that the laser exposure lead to a transient hydrothermal dissolution of the material, followed by a recrystallization process of the SiO₂ that preferentially released iron oxides into the submerging water.

In our first report, we observed \leq 100- μ m colorless particles lining the crater that formed, after directing 351-nm laser pulses onto water-submerged quartzite¹. Although we used an SEM with EDS capability to observe SiO₂ on the inside perimeter of a laser crater [Figure 9 of ref. 1], the starting sample was heterogeneous and clearly started with veins and inclusions of SiO₂. One could argue that colored overlayers had been removed, simply exposing colorless material that was already present. Later, we observed \sim 100- μ m colorless particles decorating the insides of craters that were formed by 248-nm laser pulses at \approx 4 J/cm² on water-submerged quartzite flooring material². Again, no cross-sectional measurements were taken to distinguish between a mechanism that formed colorless material versus a mechanism that simply exposed underlying colorless material [See also, Figure 4 of ref 2]. More recently, we observed enrichment of iron in the sub- μ m particles that were dispersed from 1053-nm laser pulses on water-submerged obsidian, whose crater was again lined with colorless particles after hundreds of laser pulses³. In the present work, after one hundred 1.8-J, 15-ns-duration laser pulses at 1-Hz repetition rate of 527-nm light at 0.6 J/cm² on natural quartzite, we observed a dramatic loss of surface color along with 43 mg of weight loss [\sim 4.2 kJ laser energy/g removed], but no discernable crater. The 0.6 J/cm² laser fluence was so low for this

weakly-absorbed wavelength that the resultant temperature rise was unquestionably far below the melting point of quartzite*. Please see Figures 1 – 4.



* We prepared a 0.34-mm-thick section of the same piece of quartzite shown in Fig. 1, cut parallel to the shot face, and measured its absorbance, “A”, at 527 nm, using a Perkin-Elmer Lambda950 UV-vis spectrometer with integrating sphere to decrease apparent absorption due to elastic light scattering. At four different locations across the quartzite, avoiding any obvious white bands, we measured A = 0.85 to 1.0, corresponding to a bulk absorption of 6.2 \pm 0.5/mm. With a specific heat of 2 J/K^oC³ for quartzite, this means a temperature rise of 12 \pm 1 K in the first 1/6.2 mm of material.

Figure 1. Photograph of surface of quartzite rock, mounted in stainless-steel screen, prior to laser treatment. Sample is roughly 3.3 cm across face. Dotted square roughly indicates location and size of laser beam.

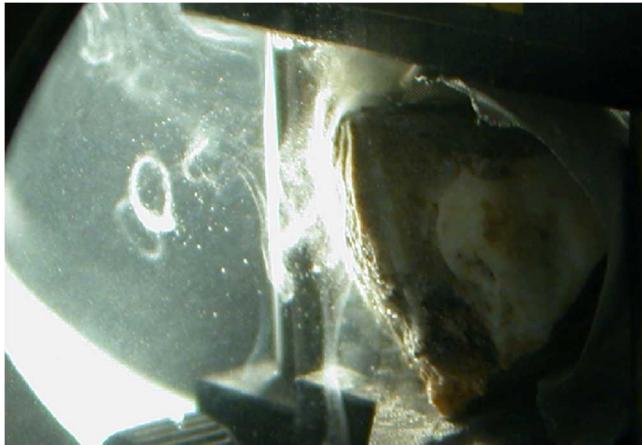


Figure 2. Photograph of side-view of quartzite sample, submerged in deionized water, shortly after laser pulse struck surface, releasing a cloud of sub- μm particles. Laser beam entered from the left, cloud was released towards the left.



Figure 3. Photograph of dried quartzite sample, after 100 pulses of 527-nm, 1.8-J/pulse at $\sim 0.6 \text{ J/cm}^2$, showing dramatic loss of color in laser-treated surface.

We used a diamond-imbedded rock saw to cut a cross section through the colorless region, as shown in Figures 4 and 5, and we observed that the original greenish/brownish quartzite bulk material had been transformed into colorless, granular > 10 - to $100\text{-}\mu\text{m}$ -scale particles to a depth of hundreds of μm over the entire irradiated surface. Please see Figure 6.

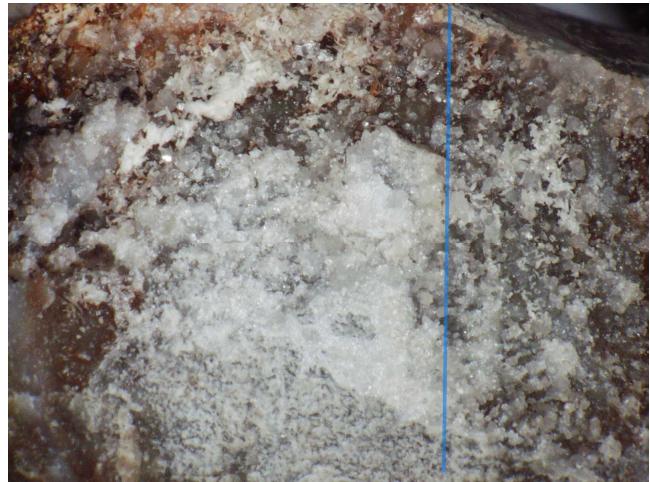


Figure 4. Close-up photo of colorless area shown in Figure 3. Blue line indicates location of cut with rock saw to prepare cross section for XRF studies.



Figure 5. Quartzite rock sample, after cutting with rock saw. XRF measurements were performed perpendicular to the cut surface over an area that included the cut edge of the laser-processed face [facing down in this photograph] and exposed bulk quartzite from the cutting.

We used X-ray fluorescence spectroscopy to measure the silicon and iron concentrations in the bulk and laser-treated regions and observed significant depletion of iron in the laser-treated region. These results are shown in Figure 7. These results are consistent with the hypothesis² that the absorption of the laser pulse produced a pulse of increased pressure and temperature and this pulse may have caused some stress-induced surface fracture⁴ and did produce a transient hydrothermal dissolution of the silica-rich surface material, recrystallizing as purer SiO_2 and

preferentially releasing iron oxides into the submerging water. Although for years materials have been exposed to lasers while submerged in water and other liquids⁵⁻⁷, this appears to be a new regime of conditions that has not previously been studied.



Figure 6. Magnified view of colorless surface particles shown in Figure 5. The granular nature and size of the colorless particles are visible in this image. XRF measurements were made near the center area of this photo. Please see Figure 7.

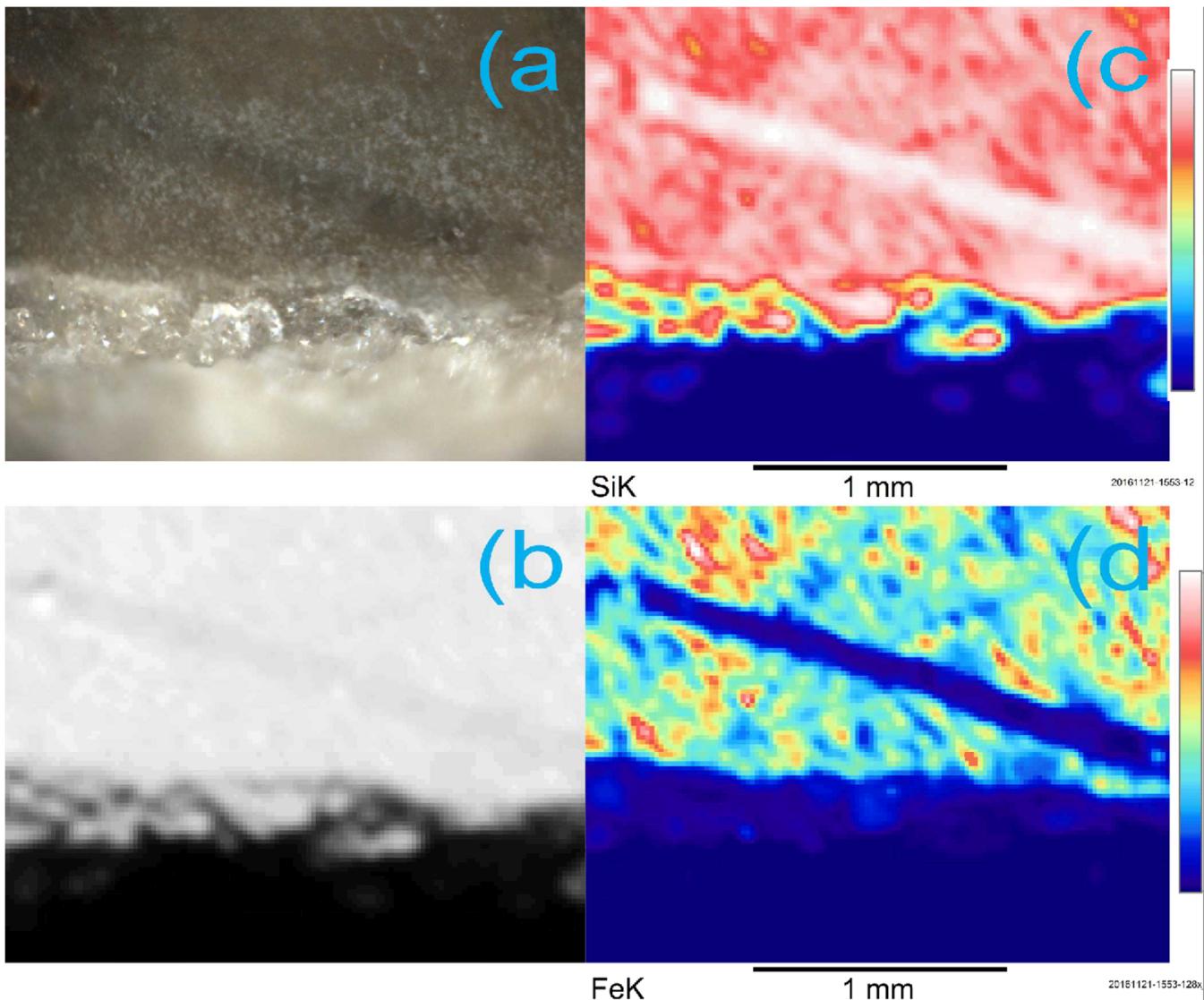


Figure 7. Area of cut quartzite Q4 sample examined with XRF spectroscopy. [Sample orientation is the same as in Figures 5 and 6] 7a) [upper left] Monochrome optical image. 7b) Map of total X-rays emitted from area. 7c) Linear “heat map” [color scale is on right-hand side of image: white denotes maximum signal, dark blue minimum signal] of Si K_{α} X-ray signal from the bulk and colorless layer. Note that the Si is not depleted in the colorless, laser-processed layer, compared with the bulk. We ascribe the diagonal white band to a silica-rich vein. 7d) Linear “heat map” [color scale is on right-hand side of image: white denotes maximum signal, dark blue minimum signal] of Fe K_{α} X-ray signal for bulk and colorless layer of quartzite Q4 sample. Note that the Fe is depleted in the colorless, laser-processed layer, compared with the bulk.

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Author Contributions

The manuscript was written through contributions of all authors.

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REFERENCES

1. Mariella Jr., R., Rubenchik, A., Norton, M. & Donohue, G. Laser comminution of submerged samples. *Journal of Applied Physics* **114**(2013).
2. Mariella Jr., R., *et al.* Laser-driven hydrothermal process studied with excimer laser pulses. *Journal of Applied Physics* **122**(2017).
3. Menon, S., Camargo, A., Wu, W., Mariella Jr, R. & Luhrs, C. Characterization of Particles Created By Laser-Driven Hydrothermal Processing. *Materials Characterization* (accepted for publication).
4. Dingus, R.S. & Scammon, R.J. Ablation of material by front surface spallation. in *Laser Ablation Mechanisms and Applications: Proceedings of a Workshop Held in Oak Ridge, Tennessee, USA 8–10 April 1991*, Vol. 389 (eds. Miller, J.C. & Haglund, R.F.) 180-190 (Springer New York, New York, NY, 1991).
5. Bäuerle, D. *Laser Processing and Chemistry*, (Springer, 2000).
6. Kruusing, A. Underwater and water-assisted laser processing: Part 1—general features, steam cleaning and shock processing. *Optics and Lasers in Engineering* **41**, 307-327 (2004).
7. Kruusing, A. Underwater and water-assisted laser processing: Part 2—Etching, cutting and rarely used methods. *Optics and Lasers in Engineering* **41**, 329-352 (2004).
