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# CO<sub>2</sub>-Based Leaching of Sulfidic Peridotite Drives Critical Mineral Mobilization and Carbonate Precipitation

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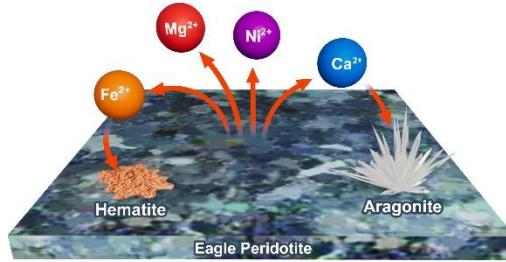
**ABSTRACT:** The transition towards green energy requires both carbon dioxide removal and consistent supplies of energy-critical minerals. Injection and mineralization of supercritical CO<sub>2</sub> at active mafic and ultramafic-hosted mines provides a potential avenue to achieve both, through the stable geologic storage of carbon and subsequent mobilization of critical metals. A sample from the Eagle occurrence, an ultramafic-hosted sulfide deposit in Michigan, USA that is the only active Ni mine in the United States, was characterized both before and after reaction with supercritical CO<sub>2</sub> at elevated pressure and temperature. We present the changes in mineralogy, feature relocation, and potential for carbon mineralization and critical mineral recovery based on the comparison of pre- and post-reaction datasets. Herein, we present evidence of dissolution-precipitation reactions leading to carbon mineralization and critical mineral mobilization driven by water-saturated supercritical CO<sub>2</sub> fluids, including the formation of aragonite and dissolution-reprecipitation of Ni phases. Collectively, these results will improve fate and transport models for carbon storage in ultramafic rocks, increase understanding of new unconventional sources for critical minerals, and provide a foundation for future studies on CO<sub>2</sub> enhanced mineral recovery (CO<sub>2</sub>-EMR).

Synopsis: This experimental study highlights critical minerals mobilization coupled with permanent carbon storage with rocks from the only active nickel mine in the United States.

## INTRODUCTION

Carbon capture and storage (CCS) is foundational to current climate mitigation strategies<sup>1</sup>. Geological storage is a well-studied CCS approach that sequesters carbon emissions into stable carbonate minerals; *in situ* geological storage, or mineral carbonation, has been successful in both laboratory experiments and at the field-scale<sup>2, 3-6</sup>. In this approach, anthropogenic emissions are injected directly into a host rock containing reactive silicates, which provide divalent metal cations to form carbonate minerals. Mafic (i.e. basalt) and ultramafic (i.e. peridotite) lithologies generally contain abundant divalent magnesium, calcium, and iron bound in silicates such as olivine, and are therefore considered excellent host formations for carbon storage via mineralization<sup>7, 8, 9</sup>.

Peridotite carbonation behavior has been extensively studied in the context of natural processes, mine tailings, and anthropogenic carbon mineralization in



the subsurface<sup>7, 10, 11, 12</sup>. Peridotites are predominantly composed of olivine with abundant pyroxene, and typically contain Ca-rich plagioclase feldspar. Olivine has been aggressively studied in the context of carbon mineralization due to its prevalence, simple chemistry, and rapid carbonation kinetics<sup>13, 14</sup>. Olivine dissolution (c.f.<sup>15</sup>) and carbonation<sup>11, 13, 16, 17, 18</sup> behavior, including reactivity in water-bearing supercritical carbon dioxide (scCO<sub>2</sub>) fluids<sup>3, 13, 14, 17, 19, 20</sup> is well-documented, as is the dissolution<sup>21</sup> and carbonation<sup>18, 20, 22, 23</sup> behavior of pyroxene. Plagioclase feldspar dissolution<sup>24</sup> is also well understood, though its carbonation<sup>25</sup> behavior is relatively understudied compared to olivine, pyroxene, or peridotite more generally.

The process of mineral carbonation in peridotites has also been shown to mobilize trace metals in the host rock, largely from the dissolution of olivine<sup>26, 27, 28</sup>. This has important implications for ultramafic lithologies, which are well documented to be

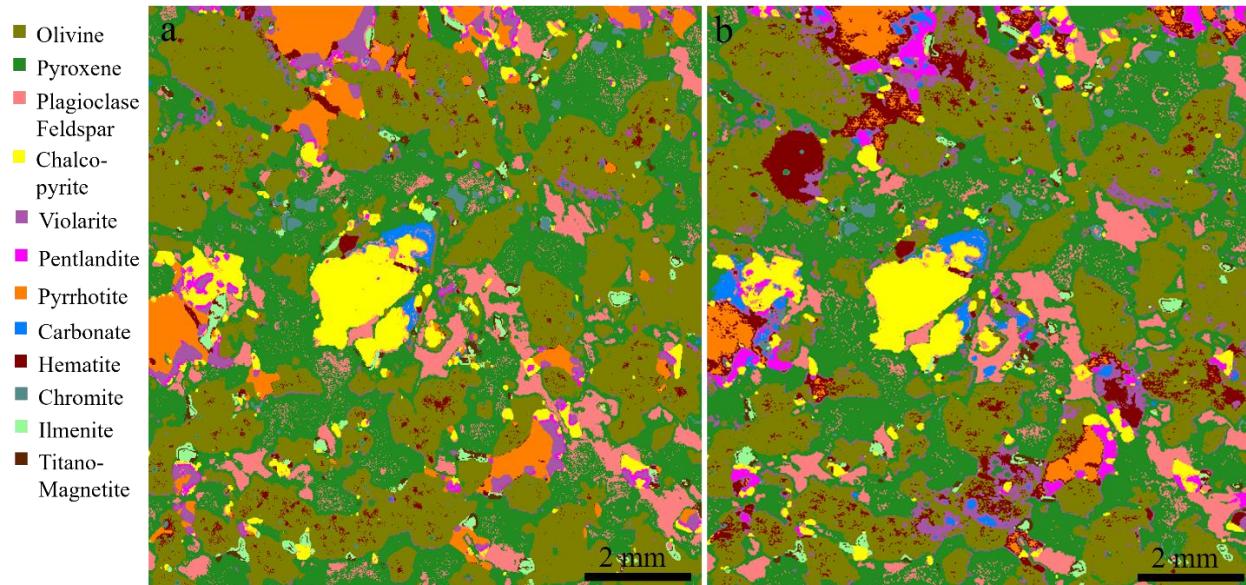
associated with sulfide deposits and are commonly enriched in Ni, Cu, Cr, and platinum-group elements (PGEs).<sup>29, 30</sup> These elements are among those known as energy-critical minerals, designated as such because they are essential to several kinds of existing and emerging technologies, such as those in the green, AI, and aerospace sectors, yet have unstable or depleted supplies. Specifically, Ni is essential in many energy storage batteries and will continue to be a necessary commodity in the wind, solar, nuclear, geothermal, and carbon capture technology fields.<sup>31, 32</sup> Exploitable quantities of these critical minerals occur in ultramafic mines worldwide as sulfide and oxide deposits, with over 150 defined resources of Cu-Ni-PGE sulfides and over 120 of magmatic oxides.<sup>29</sup> However, the prevalence of these energy-relevant resources, specifically Ni and Co, in the olivine structure<sup>33</sup> coupled with the volume of olivine in the gangue and host rock of these deposits, has spurred on the burgeoning research fields of coupling critical mineral recovery with carbon storage in subsurface and subaerial environments that this study contributes to.

5, 6, 9, 12, 26, 27, 34, 35, 36

Herein, we examined the carbonation and critical mineral mobilization for sulfidic peridotite exposed to supercritical CO<sub>2</sub> fluids, strategically choosing a sample from the only active Ni mine in the United States. The Eagle and Eagle East intrusions, which host this Ni mine, are two mafic-ultramafic intrusions

situated about 40 kilometers northwest of Marquette, Michigan, USA. Emplaced into Paleoproterozoic black slates, both intrusions are sub-vertical and roughly funnel shaped. They are petrogenetically associated with the early stages of the 1.1 Ga Midcontinent Rift, which is a large igneous province exposed in the Lake Superior region. Both intrusions host economic Ni-Cu-PGE magmatic sulfide mineralization<sup>37</sup> and have been actively mined by the Lundin Mining Corporation since 2014. The dominant silicate minerals in both intrusions are olivine, pyroxene, and plagioclase, while dominant sulfides include pentlandite (Ni-Fe), millerite (Ni), violarite (Ni-Fe), chalcopyrite (Cu-Fe), cubanite (Cu-Fe), and pyrrhotite (Fe). Sulfide minerals make up at least 1-3% of the rock volume in any given portion of both intrusions, and in significant fractions of both intrusions, sulfide minerals make up from 25% to nearly 100% of the rock volume.<sup>38</sup> Traditional mining methods at the Eagle deposit primarily target pentlandite and chalcopyrite.

The goal of this study was to determine reaction outcomes with respect to critical mineral mobilization from olivine and permanent carbon storage via carbonate mineralization in an experimental system that simulates the use of hydrated CO<sub>2</sub> as a leaching fluid. In this work, we reacted an olivine and sulfide-bearing rock chip from the Eagle Intrusion with a water-saturated, CO<sub>2</sub>-dominant fluid at elevated



**Figure 1.** False color mineral maps of the a) unreacted and b) reacted Eagle rock chip. Carbonation-driven dissolution-precipitation reactions are evidenced by the change in distribution and amount of carbonate, hematite, and sulfides. A quantitative comparison of phase distribution can be found in Table S1.

129 pressure and temperature in pressure vessel reactors  
 130 for several weeks. By combining feature-relocation  
 131 imaging, compositional analysis, and spectroscopy to  
 132 compare the sample before and after reaction, we  
 133 gained insights into the critical mineral  
 134 transformations that occur during carbon  
 135 mineralization. This characterization of trace metal  
 136 mobility during simulated *in situ* mineral carbonation  
 137 increases the overall understanding required to  
 138 implement CCS. Coupling the concepts of carbon  
 139 storage and critical mineral transport will provide  
 140 additional carbon storage incentives at active mines  
 141 and related ultramafic targets, forging pathways  
 142 towards carbon-neutral and carbon-negative mining  
 143 strategies and positioning gangue and host rock as  
 144 potential resources

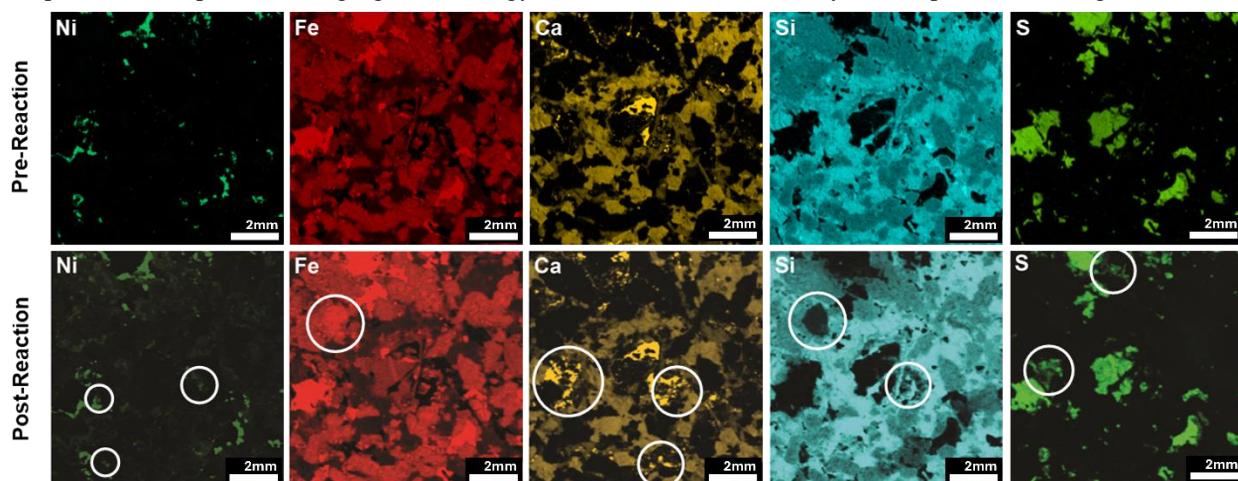
## 145 METHODS AND MATERIALS

146 **Eagle Intrusion Peridotite Sample.** This study  
 147 focused on a ~13×12×4mm chip of peridotite from the  
 148 Eagle Intrusion. The sample was characterized prior to  
 149 reaction with a variety of microscopy techniques and  
 150 micro-X-ray diffraction ( $\mu$ XRD). These methods  
 151 revealed the chip to be composed predominantly of  
 152 olivine and pyroxene, with additional plagioclase and  
 153 Fe-, Cu-, and Ni-bearing sulfides, namely pentlandite,  
 154 violarite, chalcopyrite, and pyrrhotite (**Figure 1**)  
 155 which is consistent with the previously-described  
 156 mineralogy of the sulfide-bearing lithologies at the  
 157 Eagle Mine<sup>38</sup>.  $\mu$ XRF paired with AIMICS determined  
 158 that the olivine composed 38.6% of the sample and  
 159 averaged 3200 ppm Ni; this concentration is consistent  
 160 with other analyses of Eagle deposit olivine<sup>39</sup>. This  
 161 sample does not represent the high-grade lithology that

162 is targeted with traditional mining, but rather is largely  
 163 composed of reactive gangue and host rock silicates  
 164 that can be targeted for metal cation release with  
 165 carbonation-driven dissolution.

166 **Micro X-ray Diffraction ( $\mu$ XRD).** In situ spatially-  
 167 resolved X-ray diffraction analysis was conducted on  
 168 the post-reaction rock chip with our Bruker D8  
 169 Discover TXS-HE XRD system.<sup>23, 40</sup> The Eagle  
 170 sample was mounted on the xyz $\phi\chi$  stage and  
 171 positioned using a laser-video alignment system. The  
 172 XRD is contained in the A25 cabinet and equipped  
 173 with a rotating Cu anode ( $K\alpha \lambda=1.5418 \text{ \AA}$ ), 0.3x3 mm  
 174 cassette tungsten filament, Atlas goniometer, and a  
 175 UMC 1516 motorized stage. The power settings of the  
 176 generator were 45 kV and 120 mA and the source-  
 177 sample distance fixed at 425 mm. The EIGER2 R  
 178 500K detector was used in 2D mode and positioned at  
 179 a 206.8 mm sample-detector distance. The ≤2 mm  
 180 point beam was generated using a Montel mirror optic  
 181 and various collimators.

182 **Scanning Electron Microscopy and Energy  
 183 Dispersive Spectroscopy (SEM-EDS).** The imaging  
 184 and analysis for investigating particle morphology was  
 185 performed using a JEOL 7001F TTLS/LV instrument  
 186 (JEOL USA, Inc.) scanning electron microscopy  
 187 (SEM) configured with a field emission gun capable  
 188 of imaging uncoated, non-conductive specimens in  
 189 low vacuum mode. The SEM is equipped with a  
 190 60 mm<sup>2</sup> silicon drift detector (SDD) energy dispersive  
 191 X-ray spectrometer (EDS; Bruker Quantax 6|60;  
 192 Bruker Nano GmbH) used to determine the elements  
 193 present in specimen areas of interest. Imaging and  
 194 elemental analysis was performed using low vacuum



**Figure 2.**  $\mu$ -XRF false color element maps of the peridotite chip, before and after reaction with water-saturated scCO<sub>2</sub>. Maps are labelled by element, and the top row shows the pre-reaction surface while the bottom row shows the same surface post-reaction. Circled areas indicate sites of clear mineral dissolution and precipitation in the post-reaction maps. Post-reaction maps of Ni, Fe, and Ca show new areas of metal precipitate, while Si and S maps indicate areas of reactivity and coverage by precipitates.

195 backscatter imaging mode at 15kV accelerating  
 196 voltage and a probe current of ~0.3nA. Elemental  
 197 maps were generated on select areas of interest for  
 198 300s with a count rate of ~50kcps. Composition maps  
 199 and point spectra were collected using Bruker Esprit  
 200 2.3 software. Scanning electron microscopy and  
 201 energy dispersive X-ray spectroscopy (SEM-EDS)  
 202 results were used to characterize the mineralogy  
 203 before and after carbonation, as well as to observe  
 204 changes in carbonate minerals, trace metal phases, and  
 205 olivine compositions. Secondary electron mode (SE)  
 206 was also used to collect images of the post-reaction  
 207 surface.

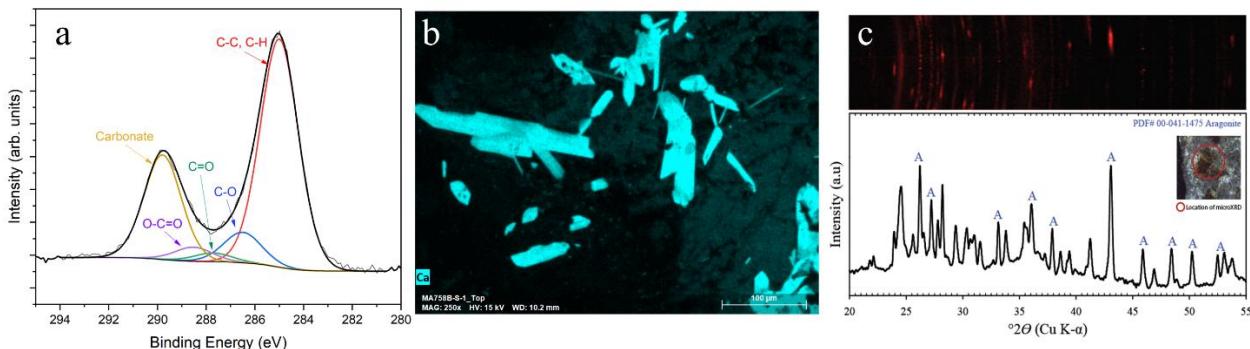
208 **Micro X-Ray Fluorescence Spectroscopy ( $\mu$ XRF).**  
 209 We used  $\mu$ XRF mapping to observe the distribution of  
 210 mineral phases and elements in the rock chip both  
 211 before and after carbonation, as well as to determine  
 212 wt% oxide (**Table S2**) and elemental composition of  
 213 sulfides (**Table S3**).  $\mu$ XRF analysis was performed on  
 214 a Bruker Tornado M4 Plus instrument equipped with  
 215  $2 \times 60 \text{ mm}^2$  silicon drift detectors, and an automated  
 216 XYZ positioner stage. A Rh x-ray source was used for  
 217 data collection operating at 50kV and 600 uA, at a  
 218 chamber pressure of 2 mbar. For chemical mapping, a  
 219 pixel size of less than 20um was used along with an  
 220 acquisition time of at least 25ms/pixel. All data were  
 221 processed using the Bruker Esprit software and  
 222 Bruker Advanced Mineral Analysis and  
 223 Characterization System (AMICS) X-Ray  
 224 microtomography (XMT) was then used to confirm  
 225 the distribution of sulfides and silicates demonstrated  
 226 in the AMICS results (**Figure S5**).

227 **X-ray Photoelectron Spectroscopy (XPS).** We  
 228 performed XPS on the post-reaction surface of the  
 229 chip to gain insight into the composition and valence  
 230 of the top few nanometers of the rock. XPS is a  
 231 surface-sensitive, non-destructive, quantitative

232 spectroscopic technique capable of definitive  
 233 carbonate identification that also provides insight into  
 234 oxidation state of surface metals. XPS measurements  
 235 were performed using a Thermo Fisher NEXSA  
 236 spectrometer with a 125 mm mean radius, full 180°  
 237 hemispherical analyzer, and 128-channel detector.  
 238 This system uses a focused monochromatic Al K $\alpha$  X-  
 239 ray (1486.7 eV) source for excitation and an electron  
 240 emission angle of 60 degrees. The narrow scan spectra  
 241 were collected using a pass-energy of 50 eV with a  
 242 step size of 0.1 eV. For the Ag 3d $_{5/2}$  line, these  
 243 conditions produced a FWHM of 0.84 eV  $\pm$  0.02 eV.  
 244 The binding energy (BE) scale is calibrated using the  
 245 Cu 2p $_{3/2}$  feature at  $932.62 \pm 0.05$  eV and Au 4f $_{7/2}$  at  
 246  $83.96 \pm 0.05$  eV.

247 **Parr Vessel Experiments.** The peridotite chip was  
 248 reacted in a static batch experiment with wet scCO<sub>2</sub> in  
 249 a 25 mL Parr vessel reactor. Water sufficient to  
 250 saturate the scCO<sub>2</sub> was placed inside of the vessel and  
 251 the chip was set on a Teflon tripod above and out of  
 252 contact with the fluid. The vessel was then sealed and  
 253 kept at temperature in a laboratory oven; trace oxygen  
 254 was not removed from the reactor in order to simulate  
 255 the redox conditions that would exist in field-based  
 256 implementation. Once the vessel had equilibrated to  
 257 90 °C, it was pressurized with CO<sub>2</sub> to 9.0 MPa. These  
 258 elevated conditions relative to typical geothermal-  
 259 geobarometry gradients in the shallow crust were  
 260 chosen to accelerate reaction kinetics for laboratory  
 261 timescales. The chip was reacted under these  
 262 conditions for 56 days, then recovered for  
 263 mineralogical and compositional characterization.

264 **Characterization and Feature Relocation**  
 265 **Workflow Strategy.** We characterized the Eagle  
 266 Mine rock chip with several microscopy and spatially-  
 267 resolved mineral identification methods to understand  
 268 the starting mineralogy prior to carbonation. The chip  
 269 was mapped first with  $\mu$ XRF, then SEM-EDS for



**Figure 3.** (a) XPS spectra of precipitated carbonate (b) EDS map (100  $\mu\text{m}$  scale bar) of Ca-rich aragonite crystals (c) Region probed by  $\mu$ XRD to determine mineralogy of Ca-rich and Si-deficient crystals that appear as clustered translucent crystals in digital optical microscopy image (inset). Two-dimensional detector image showing diffraction rings and spots (top). Integration of the detector image to produce a diffractogram reveals the presence of peaks corresponding to aragonite ( $\text{CaCO}_3$ ). The peak locations match with the International Centre for Diffraction Data powder diffraction file (PDF) entry for aragonite; PDF# 00-041-1475.

comparison and increased resolution of elemental maps. We then performed XPS on several points to gain information on speciation of sulfur, nickel, and carbonate phases on the surface. The chip was then reacted in a water-saturated, CO<sub>2</sub>-dominant fluid in a Parr Vessel reactor for 56 days. The reacted chip was removed from the vessel and dried in an ambient temperature vacuum oven. XPS, the most surface-sensitive technique utilized, was conducted first to mitigate the potential of material deposited on the surface from other microscopy methods. The chip was then mapped with μXRF, then with SEM-EDS. Additional SEM images of neoformed precipitates and other areas of interest on the surface were also collected. Several areas of interest were then analyzed with μXRD. The workflow of pre- and post-reaction analyses developed for this study was the basis of our method development for similar comparison studies and is summarized in **Figure S1**. The relative sample activation volumes for the XPS, and EDS, and μXRF are shown schematically in **Figure S2**, emphasizing the complementary yet distinct nature of the analyses.

## RESULTS AND DISCUSSION

**Post-Reaction Feature Relocation.** The mineralogy of the reacted sample consists of the original sulfide and silicate phases, which underwent partial dissolution, as well as precipitates deposited on the surface (**Figure S3**). Comparison between μXRF element maps (Error! Reference source not found.) reveals changes in the distribution of several elements, specifically metals. Firstly, there are small areas of Ni in the post-reaction map not observed in the original element map. Several areas of Fe and Ca, confirmed with μXRD to be hematite (**Figure S4**) and aragonite (**Figure 3**) respectively, have also precipitated. Cations which formed these precipitates were predominantly released from the partial dissolution of olivine and plagioclase, based on the apparent partial dissolution of the silicates observed in post-reaction microscopy and μXRF maps for Ca and Si. Changes to the S distribution suggests that there was also partial dissolution of sulfide phases.

**Carbon Mineralization.** Initial XPS studies on the recovered Eagle Mine chip indicated that several areas of new precipitate consisted of carbonates (**Figure 3**), the majority of which μXRF mapping and SEM-EDS studies showed to be Ca-dominated. μXRD then confirmed that the Ca-carbonate phases was aragonite. The early formation of aragonite is consistent with previous diopside carbonation studies<sup>20, 41</sup>, in which aragonite precipitation at 9.0 MPa scCO<sub>2</sub> conditions was observed via high-pressure time-resolved X-ray diffraction (50-110 °C) and identical location transmission electron microscopy (50 °C). Previous

field and experimental studies of basalt carbonation paragenesis also indicated that aragonite is one of the first phases to form.<sup>4, 5, 42</sup> The preference for aragonite is expected based on the availability of magnesium in the system, which favors aragonite formation over calcite.<sup>43</sup> Overall, AMICS confirmed that the total amount of carbonate on the surface of the sample increased from 0.29 wt% to 0.83 wt%.

**Fate of Nickel and Other Metals.** Metals that were mobilized during carbonation and reprecipitated as mineral phases on the surface of the rock chip were characterized with XPS, μXRD, and SEM-EDS. Ni, the target critical metal of this study, was observed in precipitates along with Ca and Mn (**Figure 4**) that were not observed in the original mineralogy. These crystals are observed near original sulfides as well as potential dissolved and reprecipitated sulfides. The EDS spectra of these areas are suggestive of a potential carbonate phase but cannot be identified directly due to compositional contribution from the underlying substrate, though this composition would be consistent with divalent substitution in carbonate.

Iron was also readily mobilized in this reaction. Likely released from olivine, it partially precipitated as hematite and was found coating the remnants of original olivine grains (**Figure 2**, Fe and Si false color maps). This phase ID for hematite was also confirmed with μXRD (**Figure S4**). Copper, potentially released in small amounts from original chalcopyrite or as trace amounts from silicate phases, was also observed and mapped using SEM-EDS (**Figure 4**). Cu, with lesser Fe, precipitated with S to form morphologies indicative of rapid growth (dendritic and wire-like precipitates are the most readily observed). Cu precipitation was also spatially related to the potential newly precipitated Ca-Mn-Ni carbonates.

**Carbon Mineralization and Critical Mineral Recovery Potential of the Eagle Intrusion.** The volume of the Eagle and East Eagle Intrusion is estimated to be 0.0666 km<sup>3</sup> (Eagle: ~480 m long, ~100-200 m wide, and >300 m vertical extension. East Eagle: ~600m long, ~150m wide, and >500m vertical extension).<sup>44</sup> Using this volume, a conservative estimate of Ni concentration in olivine (3000 ppm), and estimated volume of olivine in the rock (36.8%) (Table S1), , the total potential for carbon storage via mineralization and critical mineral recovery from olivine was calculated. The Eagle Intrusion can produce 27,000 metric tons (MT) of Ni, while storing 5 million metric tons (MMT) of CO<sub>2</sub>. For context, the amount of Ni produced per year at the high grade mine at Eagle (~18,000 MT in 2022,)<sup>45</sup> indicating that CO<sub>2</sub> mineralization and enhanced mineral recovery (CO<sub>2</sub>EMR) could compliment current high grade Ni

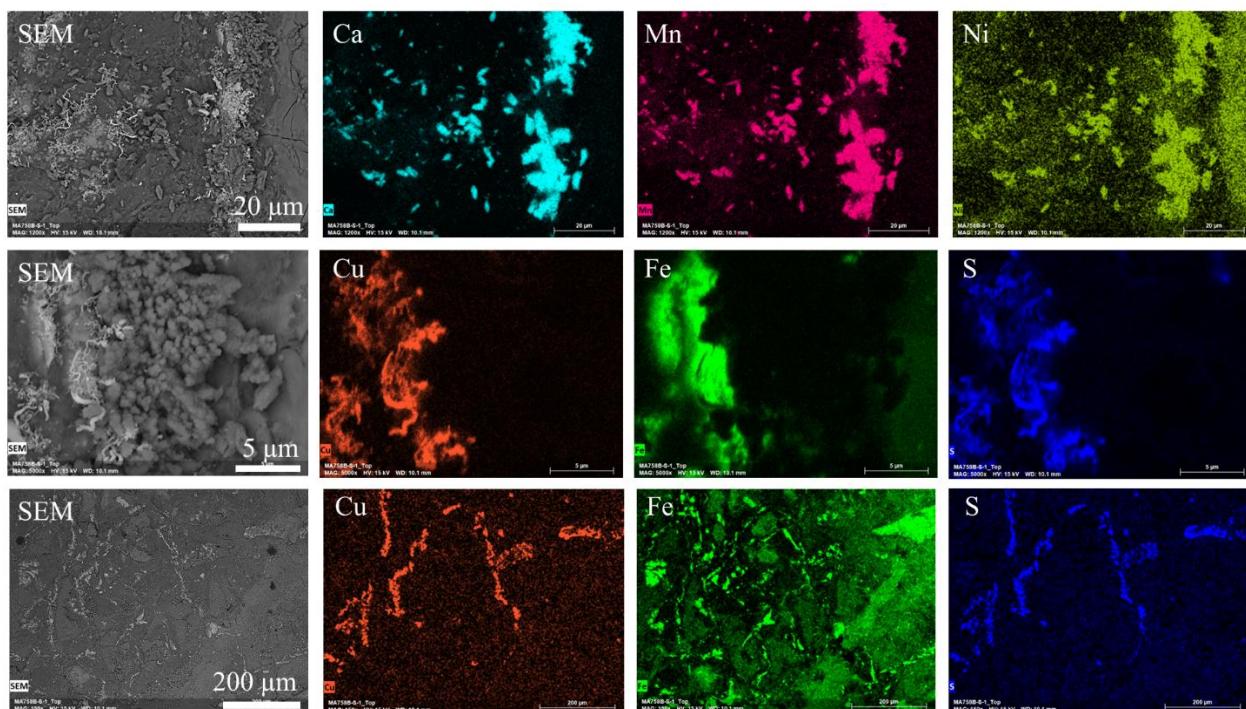
378 mining operations, or serve as an additional source of  
 379 Ni after high grade ore has been exhausted and  
 380 potentially extend life-of-mine

381 **Low-Carbon Mineral Recovery.** This work  
 382 highlights the potential for a coupled carbon  
 383 mineralization-critical mineral recovery process, but  
 384 also reveals some of the key technological  
 385 developments required to advance this technology to a  
 386 pilot and subsequent commercial scale. The injection  
 387 fluid in this experiment used only a H<sub>2</sub>O-bearing CO<sub>2</sub>  
 388 fluid, which resulted in elements of interest (i.e. Ni)  
 389 being incorporated into carbonate phases. To extract  
 390 the Ni for industrial use, the fluid will need to be  
 391 engineered such that Ni remains in the fluid phase and  
 392 is not mineralized, as demonstrated in our study.  
 393 Current work on CO<sub>2</sub>-EMR<sup>36</sup> suggests that the  
 394 addition of Ni-complexing ligands can prevent its  
 395 incorporation into phases such as carbonates.<sup>27, 35</sup>  
 396 Additionally, only the surface of the chip reacted.  
 397 Therefore, it may be necessary in low porosity  
 398 ultramafic rocks to employ injection strategies that  
 399 enhance the reactive surface area of the rock;  
 400 engineered permeability and pore space optimization  
 401 technologies from the mining, oil, and gas industries  
 402 would likely compliment this approach.

## 403 ENVIRONMENTAL IMPLICATIONS

404 The integration of critical mineral recovery and  
 405 carbon dioxide storage at current or former mine sites  
 406 offers opportunities for climate smart mining. Climate  
 407 smart mining involves sustainable extraction and  
 408 processing of minerals to decrease the climate and  
 409 material footprint of mining across the supply chain.<sup>32,</sup>  
 410 <sup>46</sup> The mining industry is currently responsible for 4-  
 411 7% of global greenhouse gas emissions<sup>47</sup>, and the  
 412 approach presented here offers an opportunity for a  
 413 carbon-intensive industry to decarbonize.  
 414 Decarbonized mines, through in situ carbon storage  
 415 and critical mineral recovery, offer an opportunity for  
 416 climate smart mining in the extraction step of the  
 417 mining supply chain while also reducing surface  
 418 impacts and limiting water use.

419 The CO<sub>2</sub> for this climate-smart mining technology can  
 420 either be sourced through point source capture or  
 421 direct air capture (DAC) sources. This could either be  
 422 sourced at the mine site or transported to the mine site  
 423 via pipelines. Capturing and storing CO<sub>2</sub> underground  
 424 at mines will offset carbon emissions associated with  
 425 various stages of the supply chain including  
 426 processing, refining, smelting, and transportation,



**Figure 4.** SEM images of three areas precipitated during carbonation, imaged with secondary electrons (greyscale) and then elementally mapped with EDS (false-color images). Scale bars present in greyscale images are consistent across rows. (d) Ca-Mn-Ni-bearing phase, likely carbonate. (e) Cu-Fe-S mineralization, interpreted as chalcopyrite based on elemental mapping. The morphology of this phase is indicative of quick growth, and this is interpreted as sulfide dissolution-reprecipitation. (f) Additional area of Cu-Fe sulfide that is not observed in the pre-reaction chip, which is indicative of sulfide reactivity.

427 potentially leading to carbon-neutral and carbon-  
428 negative mining.

## 429 ASSOCIATED CONTENT

430 **Supplemental Information.** This material is available  
431 free of charge on the ACS Publications website at  
432 <http://pubs.acs.org>. Characterization and experimental  
433 methodology workflow chart, schematic of  
434 XPS/EDS/XRF sample excitation volumes, pre- post-  
435 reaction optical images of reacted chip, microdiffraction  
436 data for reacted rock chip

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### 444 Notes

445 The authors declare no competing financial interests.

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1445

*Supporting Information*

# CO<sub>2</sub>-Based Leaching of Peridotite Drives Critical Mineral Mobilization and Carbonate Precipitation

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10 Pages

5 Figures

3 Tables

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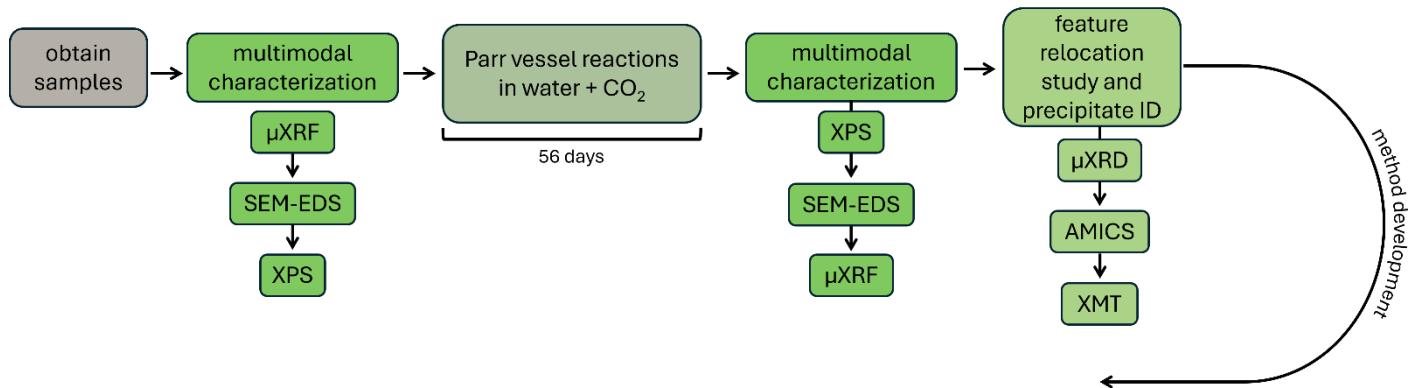
## METHODS

**X-Ray Microtomography (XMT).** In this study, we adopted high-resolution X-ray microtomography (XMT) technology and image analysis on the reacted sample. The XMT scanning of reacted sample was conducted with Bruker's Skyscan 1273, with a pixel resolution of 8  $\mu\text{m}$ . The energy level was at 130 kV and 57  $\mu\text{A}$  and two radiographies were collected every 0.3° of a 360° rotation. After the XMT scanning, we reconstructed the three-dimensional model of the entire sample using the Bruker NReconn software package. Then, we applied Avizo 3D software and Dragonfly 3D software for image processing, segmentation, and extraction of the geometrical information of the sample. The reconstructed digital surface of the reacted sample is shown in Figure S5a. Further analysis focused on the center portion shown in Figure S5b, to match the  $\mu\text{XRF}$  analytical region. Three phases of material were segmented and labeled in Figure S5c based on the intensity histogram. Yellow areas represent highest density material, sulfide. Green areas are pyroxene and the remaining material represents the less dense silicate phases, olivine and plagioclase.

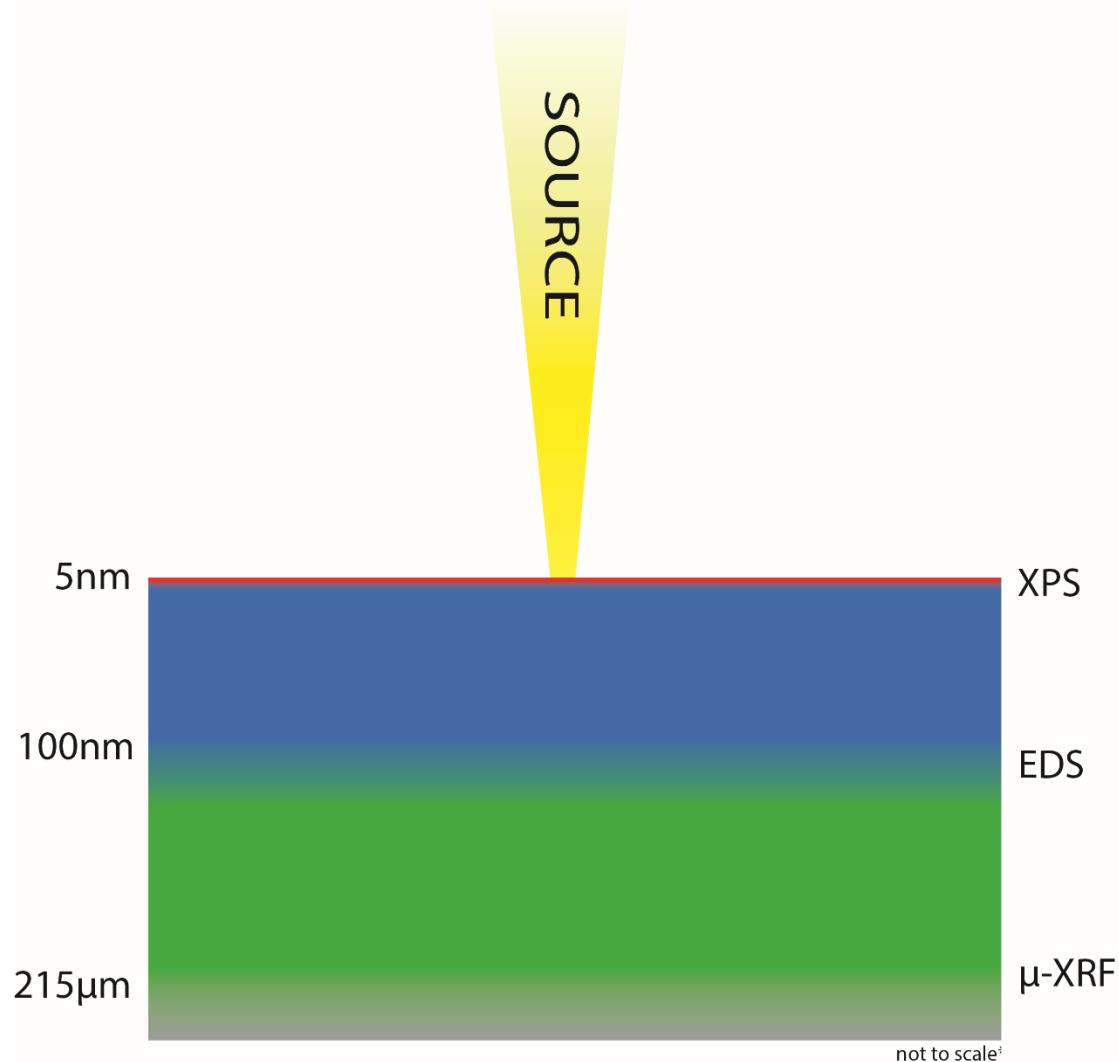
Three-dimensional reconstructed model also provided geometrical data of this reacted sample. The total volume is 508.31  $\text{mm}^3$ , 8.77% of which is sulfide, which is 44.60  $\text{mm}^3$ .

## FIGURES

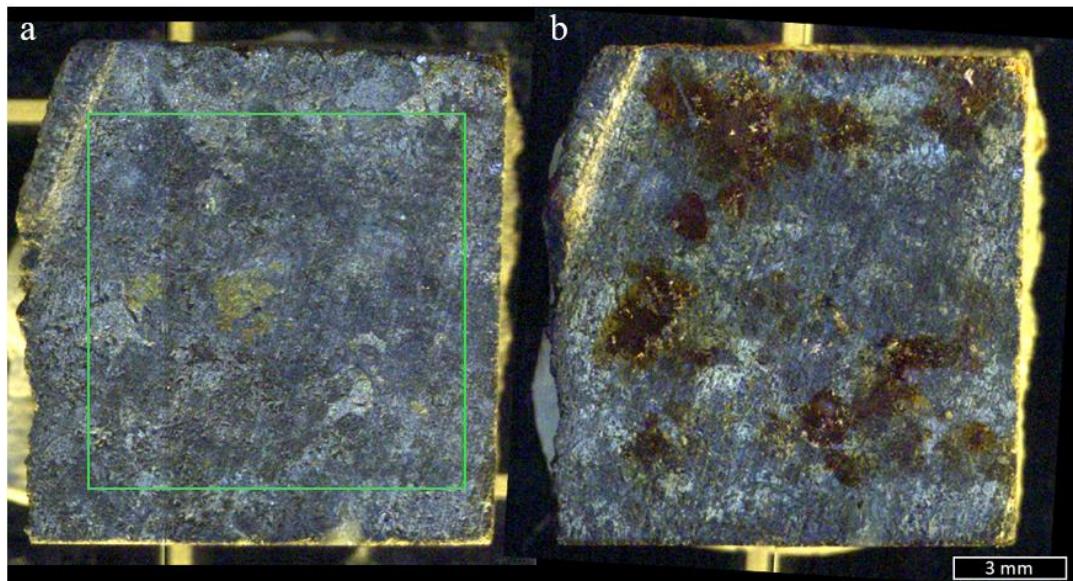
**Figure S1:** Flow chart depicting the process of examining, carbonating, and re-examining the peridotite chip via multimodal characterization techniques including micro-XRF ( $\mu$ XRF), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), micro-XRD ( $\mu$ XRD), advanced mineral analysis and characterization system (AMICS), and X-ray microtomography. The process contributed towards method development for similar future experiments.



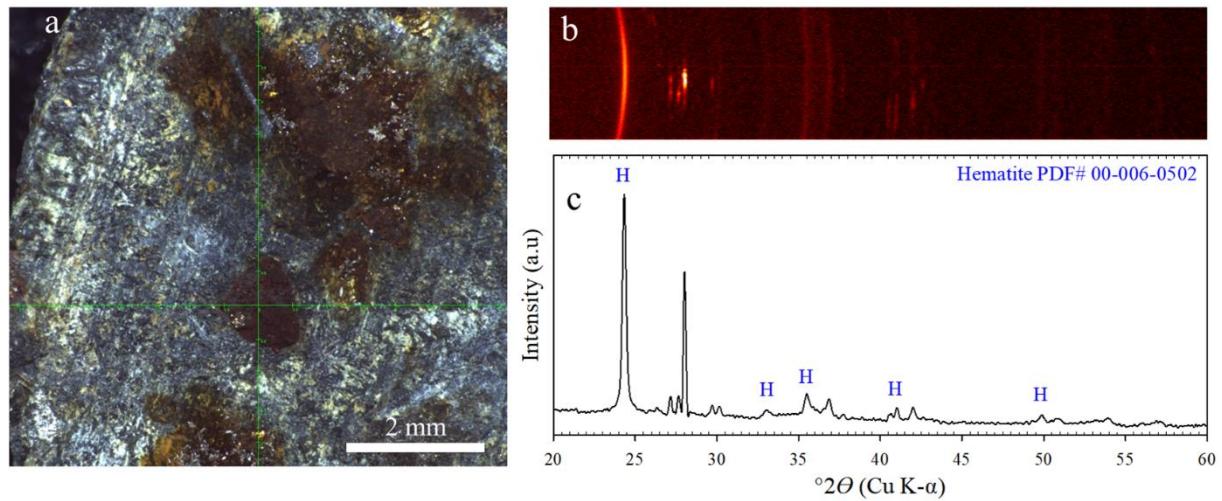
**Figure S2:** Schematic showing the portion of sample probed with each method and relative excitation volume of the corresponding analysis (not to scale).



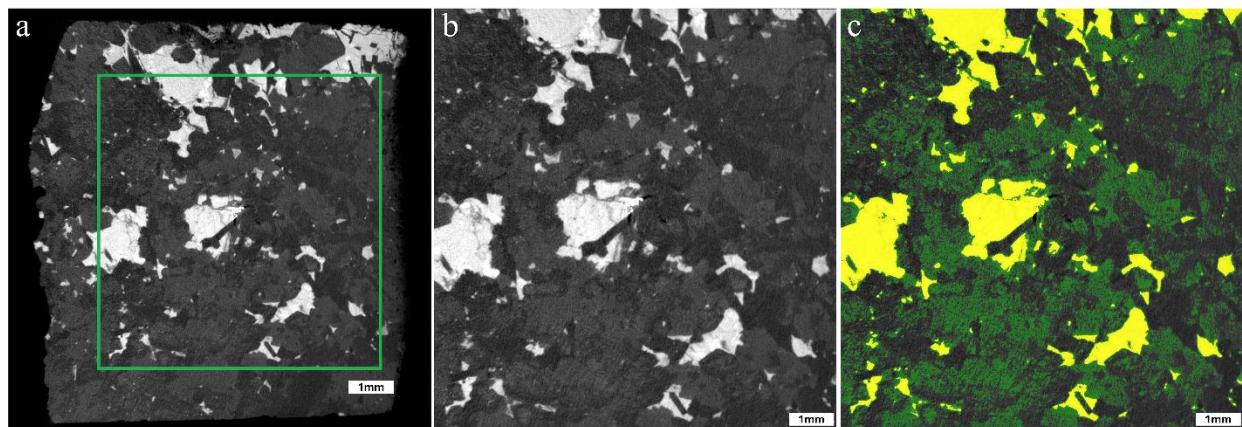
**Figure S3:** Optical photos of the Eagle Mine peridotite chip. (a) Unreacted rock chip. Green area represents the portion of chip analyzed with  $\mu$ XRF. (b) Reacted rock chip.



**Figure S4:** a) Digital microscopy image of the post-reaction chip probed by micro XRD to determine mineralogy of Fe-rich and Mg- and Si-deficient feature that covers up a portion of olivine in the unreacted rock. b) Two-dimensional detector image showing diffraction rings and spots. c) Integration of the detector image to produce a diffractogram reveals the presence of peaks corresponding to hematite ( $\text{Fe}_2\text{O}_3$ ). The peak locations match with the International Centre for Diffraction Data powder diffraction file (PDF) entry for hematite; PDF# 00-006-0502.



**Figure S5:** a) Reconstructed digital surface of reacted sample resulting from XMT analysis. Analytical area marked in green. b) Reconstructed digital surface of the analytical area b) Mineral phases segmented based on intensity histogram. Yellow areas represent sulfides, the highest density material in the chip. Green areas are pyroxene, and the rest represents the other less dense silicates, olivine and plagioclase.



## TABLES

**Table S1:** Wt% and area % of mineral phases for both the unreacted and reacted sample, based on  $\mu$ XRF results analyzed with AMICS

Mineral Phase	Unreacted Sample		Reacted Sample	
	Wt%	Area %	Wt%	Area %
olivine	35.86	38.60	29.94	32.63
augite	31.39	32.08	30.64	32.87
plagioclase	6.15	8.01	5.61	7.45
diopside	0.58	0.61	0.51	0.54
titano-magnetite	0.65	0.72	0.55	0.61
carbonate	0.29	0.38	0.83	1.10
pyrrhotite	7.74	5.63	3.75	2.95
pentlandite	1.25	0.93	2.54	1.92
violarite	4.43	3.40	7.50	5.84
chalcopyrite	5.89	5.01	5.73	4.94
ilmenite	1.59	1.20	1.27	0.97
chromite	1.21	0.90	1.16	0.87
hematite	2.50	1.69	9.50	6.49
unknown	0.47	0.84	0.41	0.74

**Table S2:** Oxide composition (wt%) from  $\mu$ XRF for the bulk sample, olivine (3200 ppm Ni), plagioclase feldspar, pyroxene, and sulfide.

<b>Oxide</b>	<b>Composition (oxide wt%)</b>				
	<b>Bulk</b>	<b>Olivine</b> Fo80 (forsteritic olivine)	<b>Plagioclase</b> An70 (labradorite)	<b>Pyroxene</b> Wo29En54Fs17 (augite)	<b>Sulfide</b>
SiO <sub>2</sub>	37.50	38.57	48.38	48.31	6.30
TiO <sub>2</sub>	0.69	0.64	0.26	0.53	0.16
Al <sub>2</sub> O <sub>3</sub>	5.02	3.55	23.91	9.25	1.03
CaO	5.11	2.63	7.99	11.61	1.28
Fe <sub>2</sub> O <sub>3</sub>	19.47	21.63	6.85	10.28	31.62
MgO	22.08	27.95	6.21	16.45	4.84
MnO	0.23	0.25	0.23	0.22	0.03
K <sub>2</sub> O	0.29	0.28	1.02	0.39	0.05
Na <sub>2</sub> O	0.87	0.89	3.88	1.55	0.45
NiO	0.47	0.41	0.04	0.07	2.57
Cu <sub>2</sub> O	0.54	0.24	0.09	-	4.87
Cr <sub>2</sub> O <sub>3</sub>	0.38	0.31	-	0.52	-
SO <sub>3</sub>	7.35	2.65	1.15	0.83	46.78

**Table S3:** Normalized elemental composition (wt%) from  $\mu$ XRF for the bulk sulfidic peridotite sample, along with the sulfide compositions for pyrrhotite, chalcopyrite, and pentlandite.

Element	Composition* (normalized elemental wt%)			
	Bulk	Pyrrhotite $\text{Fe}_{1-x}\text{S}$ ( $\text{Fe}_7\text{S}_8$ to $\text{Fe}_9\text{S}_{10}$ )	Chalcopyrite $\text{CuFeS}_2$	Pentlandite $(\text{Fe},\text{Ni})_9\text{S}_8$
S	2.94	36.27	31.55	28.76
Fe	13.62	59.76	30.16	33.82
Mg	13.31	1.40	2.14	4.40
Si	17.53	1.54	2.53	3.62
Al	2.66	0.31	0.53	0.32
Ca	3.65	0.19	0.70	1.28
Ni	0.37	0.22	0.08	27.54
Na	0.64	0.08	1.51	-
Cu	0.49	0.17	30.65	0.17
K	0.24	0.03	0.03	0.01
Ti	0.41	0.03	0.04	0.08
O*	43.64	-	-	-
Mn	0.18	-	0.08	0.01
Cr	0.26	-	-	-
Cl	0.06	-	-	-

\* Oxygen abundance is calculated, not directly measured