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Reversible Acidification Enables Closed-Loop Total Separation of Olivine

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Abstract:

Silicate minerals such as olivine are abundant in mineral deposits and mine tailings, and contain alkalinity, Mg^{2+} , Fe^{2+} , and other trace metals. While historically considered waste, the total processing and separation of these components can generate MgO for CO_2 capture and storage, high-grade iron ore, and pozzolanic silica. However, many existing approaches to silicate processing are linear, consuming stoichiometric reagents and generating large volumes of waste. While thermochemical hydrometallurgical approaches to closed-loop silicate processing have been proposed, they typically face incomplete reagent recycling and high enthalpic costs. Herein, we address these challenges by employing a pressure-swing approach with SO_2 , which reversibly modulates the pH and solubility of metal salts. This reversible modulation of pH enables the use of a traditional ‘pH-swing’ approach to separate metal salts but does so without the addition of stoichiometric acid and base. First, we demonstrate that under high SO_2 pressure of 3.5 atm, olivine dissolves rapidly in aqueous solutions. Next, we show that depressurization of SO_2 increases pH incrementally leading to sequential precipitation of Fe^{2+} and then Mg^{2+} sulfite salts. We find that two cycles of pressurization/depressurization are sufficient to enrich Mg^{2+} (92.5% to 99.9%) and Fe^{2+} (8% to 94%). We further show that SO_2 pressure modulation allows one to fully sample the phase space of separation and develop a framework for leveraging SO_2 pressure modulation in counter current ion separations. Finally, we demonstrate that the metal sulfites we produce can be thermally decomposed to recycle SO_2 and form metal oxides. The enthalpic cost of the proposed process is estimated to be 430 kJ/mol MgO, substantially lower than other proposed approaches. This work advances a versatile approach to closed-loop total processing of silicate minerals.

35 Main:

36 Silicate materials such as olivine ($\text{Mg/Fe}(\text{SiO}_4)$) are abundant in natural ultramafic rocks and mine tailings
37 and are vast storehouses of alkalinity, magnesium (Mg^{2+}), iron (Fe^{2+}), and other trace metals¹⁻⁵. These
38 abundant materials can, in principle, be processed to generate valuable pozzolanic silica (SiO_2) and the
39 corresponding metal oxides/hydroxide materials⁶⁻⁸. Specifically, the generated magnesium
40 oxides/hydroxides can serve as alkaline amendments for remediation of acidic soils and are known to
41 capture CO_2 from air on the timescale of months to years to form Mg-carbonates/bicarbonates⁹⁻¹⁴. Thus,
42 magnesium oxides/hydroxides are valuable input materials for agriculture, as well as for surficial
43 mineralization or ocean alkalization schemes for CO_2 mitigation. The generated iron oxides, if sufficiently
44 pure, can serve as precursors to steel production¹⁵. Finally, the generated silica, if sufficiently pure, is of
45 use in the cement, agriculture, and electronics industries¹⁶⁻¹⁸. Thus, the complete extraction and separation
46 of the components of silicate minerals is an attractive approach to generate value from low-value or waste
47 ores.

48 Most extraction and separation in metallurgical processing requires hydrometallurgy^{19,20}.
49 Hydrometallurgy of silicate minerals is typically a linear process that requires stoichiometric chemical
50 inputs and generates large amounts of stoichiometric waste. In particular, the first step of hydrometallurgical
51 processing often begins with strong acid leaching to liberate metal cations into aqueous solution, often using
52 sulfuric acid²¹⁻²³. The sulfuric acid is produced via sulfur burning and contact process, requiring
53 stoichiometric inputs for sulfur sourced, most commonly, from petroleum refining^{24,25}. Likewise, sulfuric
54 acid leaching generates sulfate salt byproducts that are, in some cases, environmentally hazardous¹⁹.
55 Furthermore, stoichiometric addition of base is also commonly used to precipitate metal hydroxide
56 products. This base is commonly sourced from calcination of limestone, ammonia, or electrolysis of
57 brine^{22,26-28}. Thus, the requirement for stoichiometric inputs and the production of stoichiometric waste
58 products from silicate ore processing introduces front and back-end costs and exacerbates environmental
59 impact. However, for many hydrometallurgical processes stoichiometric inputs and wastes are less
60 deleterious, since the aim is to separate minority constituents and to avoid unnecessary mineral dissolution
61 and acid consumption^{29,30}. In contrast, valorization of silicates in their entirety will require much larger
62 quantities of stoichiometric reagents. Thus, sustainable total valorization of olivine and other silicates
63 requires the development of closed-loop, circular processes that recover all or nearly all reagents.

64 There have been several attempts to circularize the hydrometallurgical processing of olivine. In recent
65 years, electrochemical methods have been developed to transform the salt by-products of silicate ore
66 processing into separate acid and base streams for cyclical ore processing(**Fig. 1a**)^{11,31-36}. Specifically, these
67 methods utilize either membrane electrodialysis, and/or proton-coupled redox reactions (e.g. hydrogen
68 evolution/oxidation, oxygen evolution/reduction) to drive the dissociation and separation of water into
69 proton and hydroxide equivalents. The produced acid is used to dissolve magnesium-iron silicates to
70 generate soluble Mg^{2+} and Fe^{2+} , while the base is applied in a subsequent step to sequentially precipitate
71 iron and magnesium hydroxides, separating the ions from solution and each other. Electrochemical
72 approaches, while offering the potential for maximizing thermodynamic efficiency in generating acid and
73 base, face challenges from large overpotentials³⁷, high membrane costs³⁸, limited membrane durability³⁸⁻⁴⁰,
74 and/or low acid-base concentrations^{37,38,41}. Additionally, since electrolytic acid and base production occurs
75 at the 2-dimensional surface of each electrode or membrane, these systems scale in proportion to the total
76 electrode/membrane area^{42,43}. In contrast, thermochemical processes scale in proportion to the volume of
77 the reactor, providing additional economies of scale.

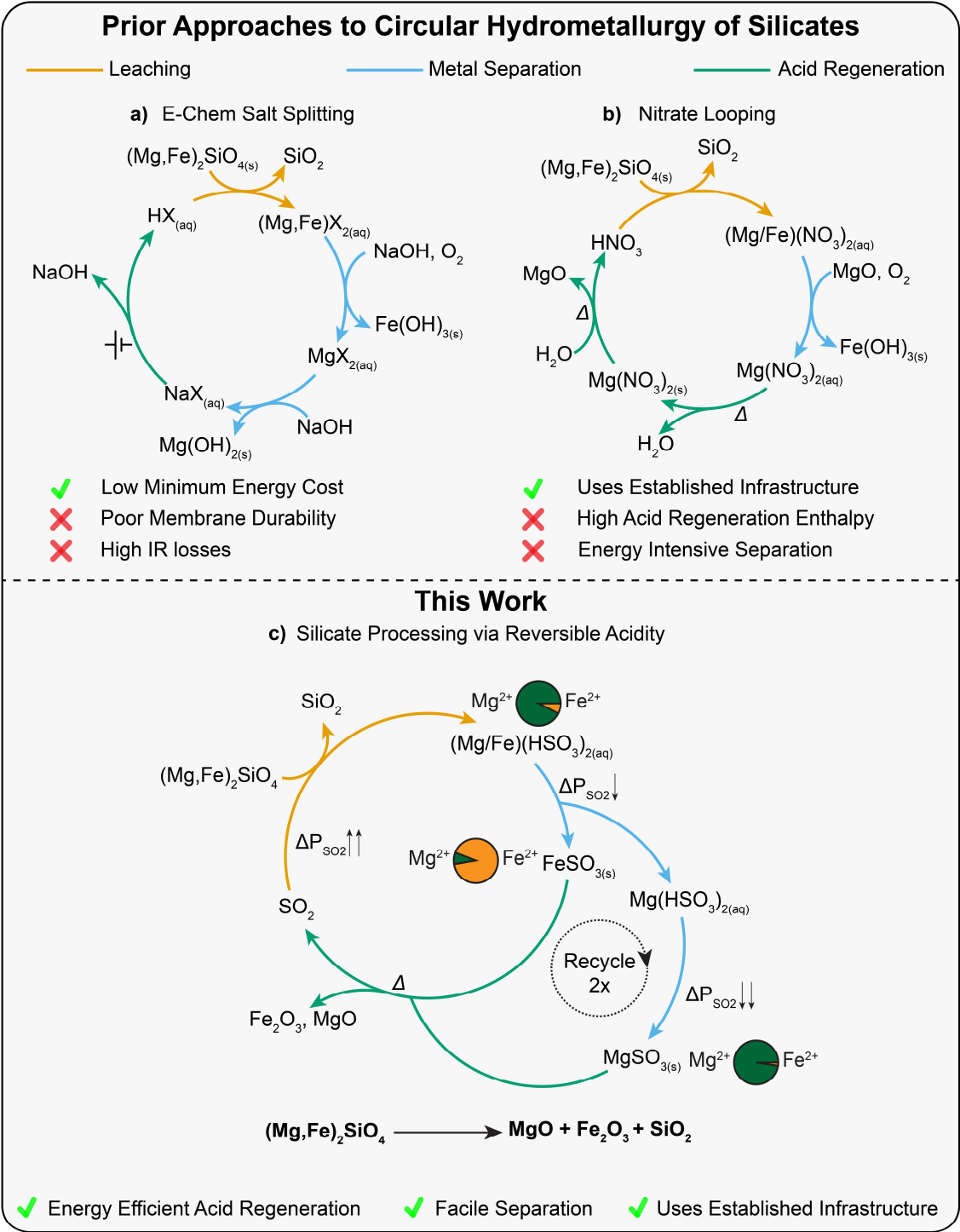


Fig. 1. Schematic illustration comparing this work and prior methods. (a) Electrochemical generation of acid and base for olivine processing, **(b)** ‘nitrate looping’ for thermochemical processing of olivine, **(c)** ‘Reversible Acidity’ SO₂-based processing of olivine (this work).

Thermochemical methods for closed-loop hydrometallurgical processing of silicates have also been proposed^{44–46}. Most prominently, ammonium sulfate roasting has been used to transform serpentine minerals into $\text{Mg}(\text{OH})_2$ ^{47,48}. In this approach, the silicate mineral reacts with molten ammonium sulfate, generating a mixture of SiO_2 and MgSO_4 while releasing NH_3 . The $\text{SiO}_2/\text{MgSO}_4$ mixture is then added to water, dissolving MgSO_4 and enabling separation of insoluble SiO_2 . Finally, the NH_3 released earlier is used as a source of alkalinity to precipitate $\text{Mg}(\text{OH})_2$. The solution is then evaporated to reform $(\text{NH}_4)_2\text{SO}_4$. Although this approach is promising due to the low reaction enthalpy of the initial roast in molten ammonium sulfate, the need to evaporate water to recycle ammonium sulfate and the deleterious losses of ammonium sulfate in the form of SO_2 and NO curtail its viability^{49,50}. Another closed-loop thermochemical approach that has been used for processing nickel laterite ores could also be applied for processing olivine. In this process, which we refer to here as ‘nitrate looping’, leaching occurs with HNO_3 ^{51,52}. After separating SiO_2 from the resulting solution of metal nitrates, MgO addition is used to sequentially precipitate and separate valuable metals as hydroxides. The resulting magnesium-rich nitrate solution must then be evaporated to form solid $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which is thermally decomposed to form MgO , NO_2 , and O_2 , where the gases can be recycled to form HNO_3 through contact with water (**Fig. 1b**). This approach is attractive because reagents are recycled near quantitatively, a challenge in ammonium sulfate roasting methods. In addition, it utilizes well established hydrometallurgical/pyrometallurgical infrastructure. However, the large enthalpy of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decomposition (~ 630 kJ/mol Mg)⁵³ undermines its feasibility for all but the most valuable metals (e.g. Ni) in high grade deposits. Additionally, since the $\text{Mg}(\text{NO}_3)_2$ intermediate in this process is highly water soluble (~ 4.8 m)⁵⁴, isolating the solid $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from the leaching solution requires substantial evaporation of the water, incurring additional energy costs (~ 610 kJ/mol Mg at 4 M concentration). Considering these energy costs, we posit that closed-loop, energy-efficient silicate processing must satisfy the following competing requirements:

- 1) The acid must be strong enough to dissolve the mineral rapidly.
- 2) The generated metal salts must be highly soluble, such that silica and other insoluble components can be separated from the metal ions prior to acid regeneration.
- 3) The generated metal salts must also be *differentially* insoluble, such that they can be separated from solution and each other to enable thermochemical acid regeneration and produce purified outputs.
- 4) Regeneration of the acid (or acid-precursor) and oxide formation must be atom efficient and minimize energy cost.

Criteria **1**) and **2**) are typically met simultaneously. Strong acids like HNO_3 and HCl form nitrates and chlorides after leaching, which display high solubility for most mono and divalent metal ions. This means that precipitated SiO_2 or insoluble gangue in the original silicate can be separated after acid leaching, which is particularly important when the aim is to valorize the co-generated SiO_2 . Unfortunately, Criteria **3**) is at odds with **2**), and the nitrate looping process is a clear example of this. To separate the highly soluble nitrate salt from solution, all the water must be evaporated prior to its thermal regeneration, increasing minimum energy costs. Therefore, there is apparently an irreconcilable challenge of needing metal salts that are both soluble (for separation from silica and other gangue) and insoluble (for separation from water and each other prior to acid regeneration and product formation).

Given the foregoing seemingly contradictory criteria, acid gases show unique promise. It is well-documented that the pressure of CO_2 can reversibly modulate the solubility of carbonate species^{55,56}. At higher (lower) pressures, the pH is decreased (increased) thereby generating soluble bicarbonate salts (insoluble carbonate salts). Thus, the pressure-modulated reversible acidification of CO_2 offers a powerful tool to modulate carbonate solubility. Furthermore, the same reversible acidification that enables control of solubility should enable separation of metal cations based on differential solubility. In the same way that metal cations can be separated based on their hydroxide solubilities, with less soluble hydroxides precipitated at lower pH as compared to more soluble hydroxides, progressive modulation of pH through acid gas pressure should enable separation based on differential solubility of the metal salts of the conjugate base of the acid gas. Indeed, control of speciation through CO_2 pressure modulation has proven tremendously useful in the development of CO_2 switchable materials⁵⁷. While CO_2 is incapable of rapidly dissolving olivine^{58,59}, we envisioned that a stronger acid gas that could also elicit changes in anion

speciation and corresponding salt solubility would be an ideal candidate for closed-loop silicate processing. We note that recent work has demonstrated the utility of ammonia pressure modulation in ammonia bifluoride solutions for lithium aluminum silicate processing⁴⁴; however, the recycling of precipitated fluoride salts is energy intensive and is accompanied by hazardous HF formation, curtailing its application here.

Herein, we demonstrate that SO₂ gas, whose acid-base equilibria are analogous to CO₂, enables us to meet Criteria 1)-4) in a thermochemical closed-loop approach for processing olivine that maximizes the ratio of rate to energy input (**Fig. 1c, Table 1**). First, we show that SO₂ gas is acidic enough to enable rapid olivine dissolution and generate pozzolanic silica. Then, we demonstrate that pressure modulation enables precipitation of insoluble sulfites to separate cations from solution without necessitating water evaporation. We also show that through progressive depressurization metal cations can be separated, enriching Mg²⁺ (92.5% to 99.9%) and Fe²⁺ (7.5% to 95%) in just 2 cycles of pressurization/depressurization. Next, we show that SO₂ pressure modulation allows one to fully sample the phase space of separation and we develop a framework for countercurrent precipitation-based separation processes based on SO₂ pressure modulation. Lastly, we show that iron and magnesium sulfites formed through pressure modulation can be thermally decomposed to generate magnesium oxide and iron oxides and recycle SO₂. The overall process maintains high dissolution/processing rate with an energy input for SO₂ recycling that is roughly 50% lower than other proposed thermochemical approaches.

Table 1. Balanced reactions for proposed olivine processing approach. Waters of hydration have been omitted for simplicity.

Silicate Processing Step	Balanced Equation
1. Olivine Dissolution	$\text{Mg}_{1.85}\text{Fe}_{0.15}\text{SiO}_{4(s)} + 2\text{H}_2\text{O}_{(l)} + 4\text{SO}_{2(g)} \longrightarrow$ $1.85\text{Mg}^{2+}_{(aq)} + 0.15\text{Fe}^{2+}_{(aq)} + 4\text{HSO}_3^{-}_{(aq)} + \text{SiO}_{2(s)}$
2. Fe ²⁺ Precipitation	$\text{Fe}^{2+}_{(aq)} + 2\text{HSO}_3^{-}_{(aq)} \rightleftharpoons \text{FeSO}_{3(s)} + \text{SO}_{2(g)}$
3. Mg ²⁺ Precipitation	$\text{Mg}^{2+}_{(aq)} + 2\text{HSO}_3^{-}_{(aq)} \rightleftharpoons \text{MgSO}_{3(s)} + \text{SO}_{2(g)}$
4. FeSO ₃ Calcination	$2\text{FeSO}_{3(s)} + \text{O}_{2(g)} \longrightarrow \text{Fe}_2\text{O}_{3(s)} + 2\text{SO}_{2(g)}$
5. MgSO ₃ Calcination	$\text{MgSO}_{3(s)} \longrightarrow \text{MgO}_{(s)} + \text{SO}_{2(g)}$

Results and Discussion

SO₂ Gas Quantitatively Dissolves Olivine and Generates Pure Silica

To assess if acidification by SO₂ gas would elicit olivine dissolution, we exposed an aqueous slurry of natural olivine to SO₂ at a partial pressure of 3.5 atm SO₂ and 80 °C. All experiments were performed with deaerated solutions. While aerobic oxidation of SO₂ is slow in water, it is accelerated in the presence of aqueous Fe and so this procedure is best performed in absence of O₂ (see **Supplementary Note 1**). The natural olivine employed in this and all subsequent experiments was sourced from Teton Supply Co. This olivine sample contains a pyroxene phase impurity that contributes to ~20% of the total Mg²⁺ content as determined by elemental analysis (**Supplementary Note 2, Fig. S1**). The sample was first sieved to a particle size range of 32-212 µm, then washed thoroughly with reagent grade water to remove fine particles (<1 µm), as confirmed by SEM imaging (**Fig. S2**). The foregoing size range was targeted to more accurately represent the typical size that could be obtained while maintaining CO₂ emissions from comminution to less than about 1% of the CO₂ storage potential of olivine⁶⁰. To quantify the dissolution rate, we periodically extracted aliquots of the liquid phase of the reaction medium and quantified the concentration of dissolved Mg²⁺ and Fe²⁺ ions by ICP-AES. The concentration of dissolved M²⁺ ions over time is plotted in **Fig. 2a**. We observed that the concentration of dissolved Mg²⁺ ([Mg²⁺]) and Fe²⁺ ([Fe²⁺]) increases over time, rising rapidly from 0.58 M Mg²⁺ and 0.05 M Fe²⁺ at 0.5 hours to 1.33 M Mg²⁺ and 0.11 M Fe²⁺ at 3 hours and rising more slowly to 1.73 M Mg²⁺ and 0.14 M Fe²⁺ at 8.5 hours. Importantly, we find that the dissolved Mg²⁺ mole fraction, [Mg²⁺]/([Fe²⁺] + [Mg²⁺]) remains constant at 92.5% for all measured points, close to the 92.3% Mg²⁺ obtained from complete leaching of the sample with HNO₃. This indicates that the dissolution under these SO₂ pressures shows no preferential leaching of Fe²⁺ or Mg²⁺, as shown in **Fig. 2b**. Over the time course of the experiment, the total dissolved M²⁺ concentration rises from 0.63 M at 0.5 hour, 27% dissolution, to 1.87 M at 8.5 hours, 80% dissolution. Extended dissolution of the olivine sample at 3.5 atm SO₂ for 48 hours at 80 C, with 15% solids by mass, led to a total metal concentration, [M²⁺], of 1.90 M M²⁺ corresponding to 100 ± 4.6% dissolution (**Fig. S3**). Furthermore, [M²⁺] was within 2% of the final value within 24 hours, indicating near complete dissolution in that time frame. The foregoing data evince that modest pressures of SO₂ are sufficient to elicit leaching of divalent ions from large particles sizes of natural olivine and pyroxene to molar concentrations over the timescale of hours.

The foregoing dissolution time course displays a pronounced non-linearity, with the rate of olivine dissolution decreasing over time (**Fig. 2a, 2b**). Specifically, we observe about 61% dissolution in the first 3.1 hours, with the subsequent 18% dissolution requiring 5.4 hours. This reflects a decrease in dissolution rate of ~5.5 fold. We hypothesized that this decline in dissolution rate could arise from two main factors. First, during dissolution dissolved SO₂, commonly referred to as sulfurous acid (H₂SO₃), is consumed and the concentration of its conjugate base, bisulfite, [HSO₃⁻], increases, leading to a progressive increase in pH (**Fig. S4**). This pH increase is expected to be more pronounced at the early stages of dissolution, when dissolved SO₂ is in large excess to bisulfite, but this pH change will be attenuated over time as the SO₂/HSO₃⁻ buffering point of 1.8 (1 atm, r.t.) is reached⁶¹. Most silicate dissolution reactions display a weakly positive reaction order in hydronium⁶², thus, this pH increase is expected to attenuate dissolution rates over time. Second, heterogeneity, either in particle size or reactivity could contribute to this decline in rate. Specifically, a decrease in surface area or specific reactivity as dissolution proceeds would yield decreasing dissolution rates. To test the influence of pH on measured dissolution rates, we measured the initial dissolution rates of olivine with and without the addition of ~2 m HSO₃⁻ and observed no significant difference in dissolution rate (**Fig. S5**). To isolate the contributions from particle heterogeneity, we measured the rate of olivine dissolution in a 10-fold molar excess of 1M HNO₃, for which the pH is calculated to shift by a maximum of 0.05 units throughout dissolution. We observe that dissolution rates are roughly 4 times faster during the initial 70% of dissolution as compared to the next 20% of dissolution (**Fig. S6**). Taken together, these observations suggest that the observed rate non-monotonicity results predominantly from heterogeneity in the particle size or reactivity, rather than increasing pH due to increasing [HSO₃⁻].

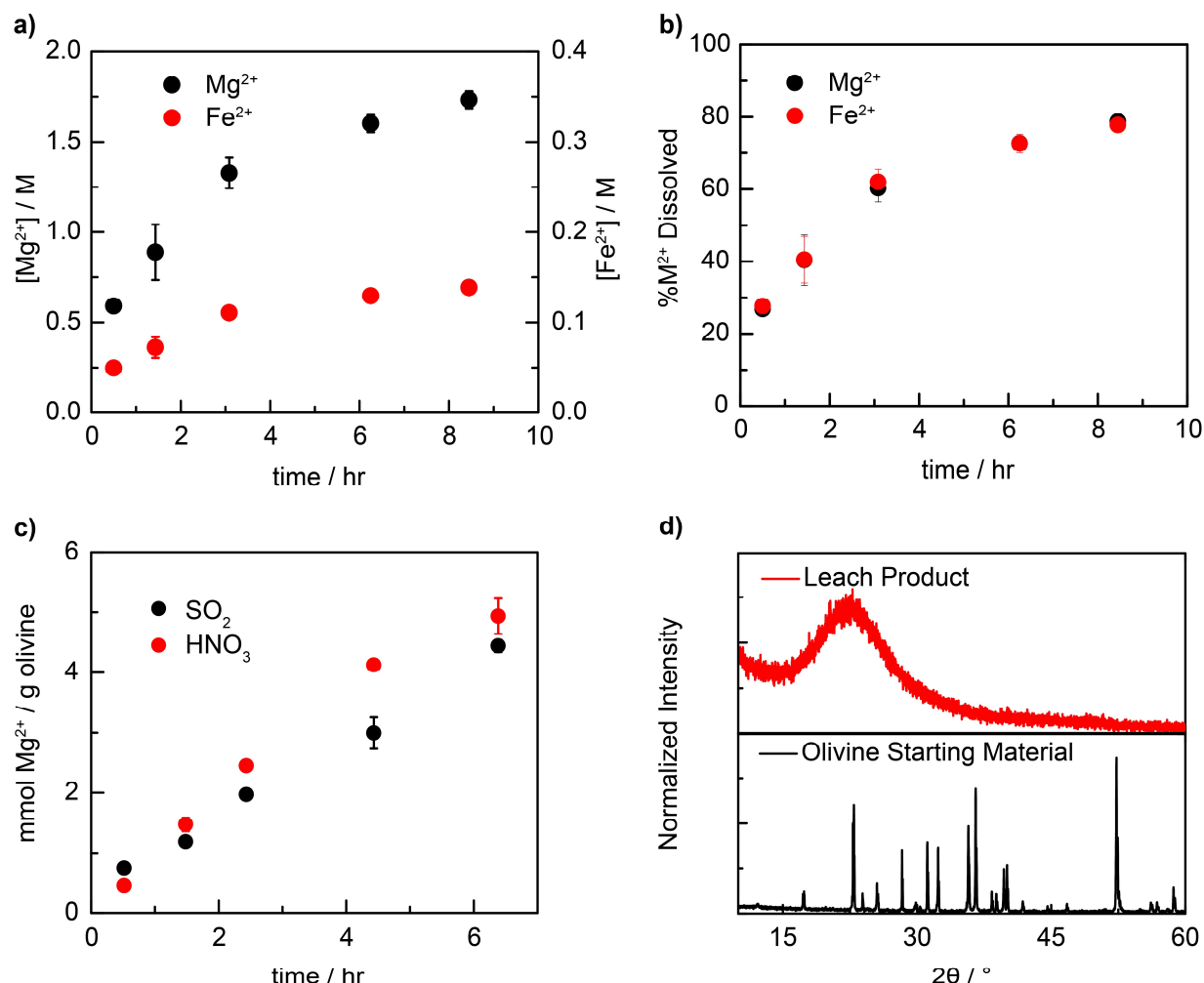


Fig. 2. Dissolution of Olivine in SO_2 and HNO_3 . **a)** Measured concentration of dissolved Mg^{2+} (black) and Fe^{2+} (red) over time during dissolution of olivine in 3.5 atm SO_2 , 80 °C, 18% solids by mass. **b)** Percent dissolution of Mg^{2+} (black) and Fe^{2+} (red) over time during dissolution of olivine in 3.5 atm SO_2 , 80 °C, 18% solids by mass. Percent dissolution is calculated relative to the final measured concentrations of Mg^{2+} and Fe^{2+} after 44 hours of leaching. **c)** Measured moles of Mg^{2+} dissolved per gram of olivine over time during dissolution of olivine in 2.44 m SO_2 (black) and 2.48 m HNO_3 (red), 40 °C, 6.7% solids by mass. To achieve 2.44 m SO_2 , a partial pressure of 2.96 atm SO_2 is maintained. The measured concentrations for the SO_2 leach are corrected for volume expansion of the solution through use of a Cs^+ internal standard (see Methods). The data presented in **a)**, **b)**, and **c)** are the average of two identical trials, with the error bar indicating the range between the two trials. **d)** PXRD of olivine starting material (black) and silica gel leach product (red), after dissolution of olivine in 3.5 atm SO_2 , 80 °C, 15% solids by mass, 48 hours. Performed with Cu X-ray source.

To compare rates of olivine dissolution between SO_2 ($pK_a = 1.8$), an acid weaker than hydronium, and HNO_3 ($pK_a = -1.4$), an acid stronger than hydronium, we measured the initial dissolution rates at low solid/water ratio at common concentrations of dissolved acid (**Fig. 2c**, **Fig. S7**). We set the SO_2 pressure to 2.96 atm leading to an aqueous SO_2 concentration of 2.44 m⁶³, which matches the 2.48 m HNO_3 used for this comparison. In these experiments, the dissolution extent was limited to a maximum of ~50%, so that rates remained linear throughout the experiment (see above). We observe that after 6.4 hours, 4.9 and 4.4 mmol $\text{Mg}^{2+}/\text{g olivine}$ were dissolved in the HNO_3 and SO_2 solutions, respectively. The foregoing data indicate that at common acid concentrations, SO_2 and HNO_3 lead to similar silicate dissolution rates.

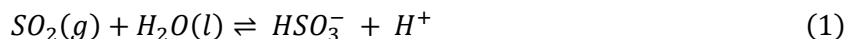
227 To assess the value of the SiO_2 formed during leaching, we analyzed the composition (PXRD and ICP-
228 MS) and reactivity of the solid residue after extended dissolution. The residual solid after extended
229 dissolution contains primarily a white gel, with a minute fraction of dense black particles that are easily
230 separated from the white gel (**Fig. S8**). PXRD analysis of the white gel displayed only a broad feature at
231 near $22^\circ 2\theta$ indicative of amorphous silica (**Fig 2d, red**), and elemental analysis by ICP-MS revealed only
232 Si present, with Mg and Fe concentrations below the detection limit. This indicates that the white gel is
233 highly purified amorphous silica. The powder X-ray diffractogram of the residual dense black particles
234 displayed only a broad feature at near $22^\circ 2\theta$ with weak reflections that could not be identified (**Fig. S9**),
235 indicating that the residual particulates are weakly crystalline, and that some residual SiO_2 was not
236 separated. Critically, there is a complete absence of crystalline olivine or pyroxene. Furthermore, exposure
237 of the isolated silica gel to CaO and water at room temperature for 23 hours revealed the complete
238 consumption of CaO and formation of calcium silicate hydrates, by PXRD analysis (**Fig. S10**). Thus, we
239 conclude that the generated silica is highly reactive and can be used as a pozzolan in cement production⁶⁴.
240 The foregoing data indicate that a highly purified and reactive silica gel can be generated as a solid product
241 from SO_2 leaching of olivine.

242 Taken together, the data evince that the acidity generated at modest SO_2 pressures is sufficient to fully
243 convert olivine to high purity amorphous silica and dissolved metal bisulfites on the time scale of hours,
244 with rates comparable to that of nitric acid, setting the stage for further processing of the leachate solution.

245

SO₂ Pressure Variation Enables Separation of Divalent Cations

Based on the known relationship between SO₂ pressure and metal sulfite solubility⁶⁵, we envisioned that SO₂ pressure modulation could enable closed loop olivine processing. Specifically, decreased SO₂ pressure would cause precipitation of sulfites, and the differential solubility of metal sulfite salts would, in principle enable pressure-induced separation of the metal ions in olivines. To investigate if pressure modulation would elicit changes in sulfite solubility, we measured [Mg²⁺] and [Fe²⁺] as a function of SO₂ pressure. We first suspended a mixture of 8% FeSO₃ and 92% Mg(OH)₂, (all percentages refer to mole fractions unless otherwise stated), in 120 mL of water. We then sequentially exposed the resulting suspension to various pressures of SO₂ and quantified [Mg²⁺], [Fe²⁺], and Mg²⁺/Fe²⁺ solid fraction through ICP-OES. As the Mg(OH)₂ reacts quantitatively with SO₂, this procedure serves to form MgSO₃/Mg(HSO₃)₂, which, in combination with the FeSO₃, constitutes the MgO-FeO-SO₂-H₂O equilibrium system. After each change in SO₂ pressure, the pressure was maintained for at least an hour, although we found that 40 minutes was sufficient to establish time-invariant dissolved ion concentrations (Fig. S11). We observed that between 15.8 atm and 4.2 atm SO₂, [Fe²⁺] decreased by 64% from 0.11 M to 0.04 M (Fig. 3a, red), whereas [Mg²⁺] only decreased 3% from 2.61 M to 2.53 M (Fig. 3a, black). Upon further reduction of SO₂ partial pressure, we observe a decrease in [Mg²⁺] from 2.53 M at 4.2 atm to 2.01 M at 1.28 atm (Fig. 3a, black). Over the same pressure range, [Fe²⁺] continued to decrease from 0.04 M to 0.02 M. In line with the observed differential change in [Mg²⁺] and [Fe²⁺] in solution, the solid products are differentially enriched in Fe²⁺ depending on the SO₂ pressure. For example, we observed that the solid phase at 5.8 atm SO₂ is 66% Fe²⁺, substantially enriched relative to the 8% total Fe²⁺ fraction introduced to the system (Fig. 3b). However, as the SO₂ pressure decreases further to 1.28 atm, the solid phase composition was 20% Fe²⁺, beginning to approach the total 8% Fe²⁺ in the system. PXRD reveals that for almost all solid compositions, only a single crystalline phase is present, with solid products exhibiting the (Fe_x, Mg_{1-x})SO₃·2.5H₂O, (Fe_x, Mg_{1-x})SO₃·3H₂O and (Mg_x, Fe_{1-x})SO₃·3H₂O structures, depending on composition (Fig. S12). These data suggest that the solid phase consists nearly entirely of a solid solution of Mg²⁺/Fe²⁺ sulfites. Binary solid solutions are typically enriched in the less soluble component.⁶⁶ Thus, the observed preferential precipitation of Fe²⁺ over Mg²⁺ is in line with the lower room temperature solubility of FeSO₃ (2 x 10⁻³ mol/kg)⁶⁷ relative to MgSO₃ (5 x 10⁻² mol/kg)⁶⁵. The data suggest that as the SO₂ pressure decreases, the solubility of Mg²⁺ and Fe²⁺ decreases and sulfites are precipitated, which implies that the activity of SO₃²⁻ is increasing. We hypothesize that this results from an increase in pH with decreasing SO₂ pressure, which leads to an increase in sulfite activity through the coupling of the following known acid-base equilibria of SO₂



Indeed, we observe that the pH of sodium bisulfite solutions reversibly varies from pH 1.3 to 2.6 with variations in SO₂ pressure from 1 to 10⁻² atm, respectively (Fig. S13). This is qualitatively in accord with thermodynamic calculations that predict a first order dependence of pH on SO₂ pressure (Supplementary Note 3, Fig. S14-S15). In sum, the data indicate that as the SO₂ pressure over Mg²⁺/Fe²⁺ bisulfite solutions is decreased, the pH and [SO₃²⁻] increases, leading to the precipitation of solid sulfites that are enriched in Fe²⁺, the less soluble component.

Since the solution and solid phases were substantially enriched in Mg²⁺ and Fe²⁺, respectively, we hypothesized that mixtures of Mg²⁺ and Fe²⁺ could be separated and purified through serial application of appropriate SO₂ pressures. This process would ultimately generate a pure FeSO₃ solid and a pure Mg(HSO₃)₂ solution. Upon separation, the Mg(HSO₃)₂ solution could be stripped of SO₂ through dynamic evaporation/crystallization or inert gas sparging to precipitate MgSO₃ and recover SO₂ (Fig. S16)⁶⁸⁻⁷¹. To test this principle, we aimed to separate the Mg²⁺ and Fe²⁺ components of olivine. First, we exposed olivine (92.5% Mg²⁺) to an SO₂ leach at an SO₂ partial pressure of about 2.8 atm for 19 hours. After separating the (Mg/Fe)(HSO₃)₂ solution from insoluble SiO₂, the partial pressure of SO₂ was decreased by flowing N₂ gas. This generated a solid phase containing 89.8% Mg²⁺ and a highly purified solution phase containing 99.9%

Mg²⁺. After solid-liquid separation, the solution was stripped of SO₂ by application of dynamic vacuum, generating a 99.9% pure Mg²⁺ sulfite solid. The 89.8% Mg²⁺ solid was then treated with two more cycles of 1 atm SO₂ and SO₂ stripping to yield a solid product enriched to 94% Fe²⁺ (Fig. S17). This sequence indicates that changes in SO₂ pressure can be used to separate and purify metal cations through precipitation and solid-liquid separation.

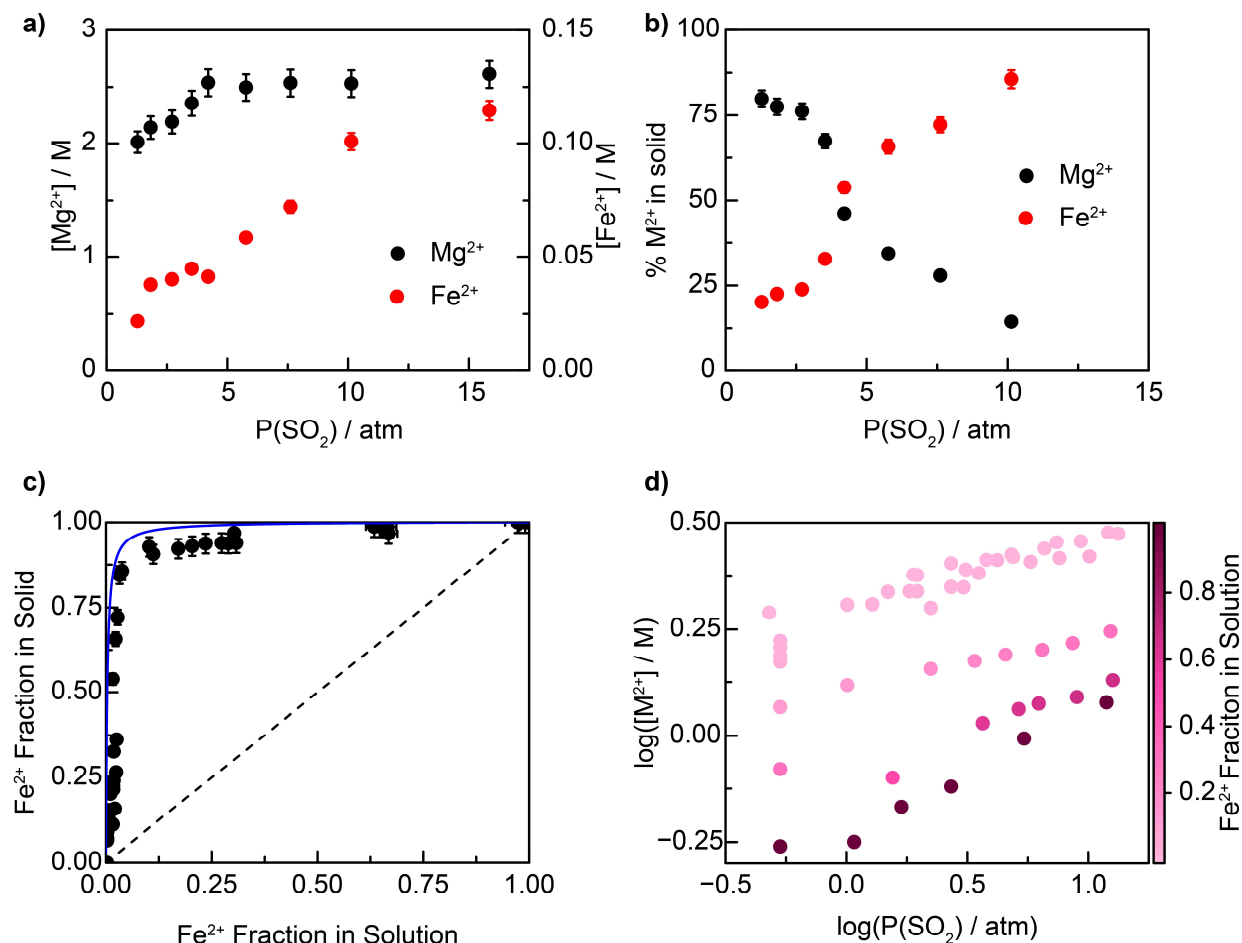


Fig. 3) SO₂ Pressure Reversibly Determines Cation Solubility and Solid/Liquid Phase Fractionation
a) Measured concentrations of soluble Mg²⁺ (black) and Fe²⁺ (red) as a function of SO₂ pressure at 80° C. The initial ionic solution was produced by leaching a Mg(OH)₂ and FeSO₃·3H₂O mixture containing 8% Fe²⁺ and 92% Mg²⁺ by mole at 3 atm SO₂, then exposing the system to varying SO₂ pressures. **b)** Measured percent Mg²⁺ (black) and Fe²⁺ (red) in the precipitate as a function of SO₂ pressure at 80° C. **c)** Measured Fe²⁺ fraction in the precipitated phase as a function of measured Fe²⁺ fraction in solution for a range of pressures and Mg²⁺/Fe²⁺ ratios between 0-100% Fe²⁺ at 80° C. The dotted line indicates the parity line, if no differential solubility was exhibited for either Mg²⁺ or Fe²⁺. The blue line indicates the ideal Roozeboom plot in the absence of non-ideal mixing enthalpy and entropy. **d)** Measured log(P(SO₂) / atm) versus log([M²⁺] / M), where M²⁺ is the sum of Mg²⁺ and Fe²⁺ concentrations, measured at 80° C. Points are colored to represent the Fe²⁺ mole fraction in solution, with light pink representing 0.0 fraction Fe²⁺, and dark purple representing 1.0 fraction Fe²⁺.

In most precipitation-based metal separations, the extent of water evaporation or pH adjustment by base addition are the main control levers for generating differential solubility of the component ions in a mixture. To the best of our knowledge, the use of acid gas pressure to control speciation and generating differential metal ion solubility has not been demonstrated. Thus, the foregoing findings motivate the development of the basic principles and systematic workflow for optimized separations based on reversible acid gas pressure swings. In particular, an optimized acid gas-based separation requires a methodology for predicting the appropriate series of SO₂ pressures to effect high separation yield with minimal separation stages. Multi-stage countercurrent separation processes such as solvent extraction and distillation are workhorses of chemical industry due to their high purity and yield of products⁷². Therefore, we aimed to develop a methodology for acid gas pressure swings based on a countercurrent precipitation, although in principle any separation scheme could be chosen. To realize this ultimate goal, using the Mg²⁺/Fe²⁺ separation as a test case, we break down the problem into three steps. (1) Map the phase partitioning in MgO-FeO-SO₂-H₂O aqueous system, (2) calculate steady-state material flows using mass balance and Mg²⁺/Fe²⁺ equilibrium distributions as constraints, and (3) extract optimized SO₂ pressures from experimental solubility data. Each of the steps are detailed below to furnish a general predictive framework for optimizing reversible acidity-based ion separations. Given the substantial non-idealities in solid-solution formation and dissolved ion activities in concentrated solutions⁶⁶, the desired SO₂ pressures cannot be calculated from tabulated solubility data for FeSO₃ and MgSO₃ solubility. Instead, the full phase partitioning in the MgO-FeO-SO₂-H₂O aqueous system must be mapped experimentally to account for these non-idealities. To map this phase space, the solubility of (Fe/Mg)(SO₃) solids were measured as a function of SO₂ pressure for a variety of total %Fe²⁺ fractions ranging from 0 to 100%, using the same methodology described above for **Fig. 3a,b**. Integrating data from all these experiments, we plot the measured solid phase Fe²⁺ fraction vs the solution phase soluble Fe²⁺ fraction, to generate a Roozeboom plot⁶⁶ (**Fig. 3c**) that illustrates the distribution of Fe²⁺ and Mg²⁺ between the solid and solution at equilibrium. This plot shows the extent to which one cation is preferentially precipitated over the other, irrespective of the conditions of the precipitation (i.e. total metal concentration or SO₂ pressure). The diagonal ‘parity line’ indicates where data would lie if no preferential precipitation of Mg²⁺ or Fe²⁺ took place. Instead, we observe that the data points trace a curve close to the top and left axis indicating that Fe²⁺ is preferentially enriched in the solid under all conditions. As quantitative examples, we observe that 4% and 64% Fe²⁺ in solution are in equilibrium with 85% and 98% Fe²⁺ in the solid, respectively. The blue line in **Fig. 3c** indicates the calculated Roozeboom plot based on the MgSO₃ and FeSO₃ endmember solubilities assuming ideal mixing enthalpy and entropy. We observe that the experimental Roozeboom data is displaced relative of the blue line, indicating that the non-idealities of Mg²⁺/Fe²⁺ solid solution formation drive further mixing. The Roozeboom data thus quantitatively captures the non-idealities in the precipitation of (Mg/Fe)SO₃ solid solutions, and demonstrates a clear preference for Fe²⁺ in the solid phase in line with our intuition from the lower solubility of FeSO₃ relative to MgSO₃.

While the foregoing Roozeboom plot provides quantitative insight into the Fe²⁺ fractionation between solution and solid, it omits information about the absolute concentrations of ions in solution phase. Indeed, the data points in this plot arise from a wide variety of ion concentrations and SO₂ pressures (**Fig. S18**). To determine the number of variables that must be defined to fully characterize the system, we performed Gibbs Phase Rule Analysis (**Supplementary Note 4**). This analysis reveals that for the FeO-MgO-SO₂-H₂O system, 3 independent system variables must be defined to fully constrain the equilibrium. Taking easily measurable variables, this implies that at a fixed temperature (80 °C) and a given total metal ion concentration, any desired Fe²⁺ fraction in solution will correlate uniquely to an SO₂ pressure. Thus, SO₂ pressure modulation allows one to adjust ion concentration and Fe²⁺ fraction in solution across the entire phase space. We represent this graphically in **Fig. 3d**, which plots the measured solubilities as log([M²⁺]) versus log(P_{SO2}) where [M²⁺] is the total concentration of Mg²⁺ and Fe²⁺. The Fe²⁺ fraction in solution is shown as a colormap with light pink representing 0% Fe²⁺, and dark purple representing 100% Fe²⁺. We observe that for a given pressure the total ion solubility increases with decreasing Fe²⁺ fraction in solution, or equivalently in the solid (**Fig. 3c**). As an example, at log(P) of -0.27, the total ion solubility increases from log(M) of -0.26 to 0.22 in going from 1.0 to 0.03 fraction Fe²⁺ in solution, respectively. This is in line

with the lower solubility of FeSO_3 than MgSO_3 , such that higher soluble ion concentrations are obtained at a common pressure as the fraction of the less soluble component decreases. When coupled with mass balance constraints, the data indicate that SO_2 pressure, which can be tuned reversibly, can be used as a powerful control lever to traverse a range of soluble ion concentrations and fractionations, analogous to traditional pH adjustment.

The above phase mapping provides the inputs for developing a protocol for multistage pressure swing separation of the Fe^{2+} and Mg^{2+} in olivine. Using methodology analogous to those used in well-established countercurrent techniques⁷², we proceed to develop a workflow to describe how an SO_2 pressure driven countercurrent precipitation can be implemented. The workflow takes process parameters (number of stages, feed stream composition, precipitation model) as inputs, solid-liquid equilibrium data (**Fig. 3c**) and mass balance as constraints and calculates as outputs the $\text{Fe}^{2+}/\text{Mg}^{2+}$ fractionation and total ion concentration at each stage of separation. The $\text{Fe}^{2+}/\text{Mg}^{2+}$ fractionation and total ion concentration will subsequently be used to define the SO_2 pressure required to achieve the desired separation (**Fig. 3d**). The flow of solids and solution in a countercurrent precipitation scheme is shown in **Fig. 4a** for the example of a 3-stage $\text{Fe}^{2+}/\text{Mg}^{2+}$ separation process. In each stage, a fraction of the total cations is precipitated. Next, the solids, enriched in Fe^{2+} , will move in one direction (i.e. from stage 2 to 3), while the solutions, enriched in Mg^{2+} , will move countercurrent (i.e. from stage 3 to 2). After each cycle of precipitation and solid-liquid separation, a new feed stream is added to stage 2 and water is added to the final stage on the solid output side. For this analysis we chose to have a total of 3 separation stages and set the feed stream composition to 7.5% Fe^{2+} , 92.5% Mg^{2+} , 2.65 M solution to mimic olivine after leaching with high pressure SO_2 . We kept these constraints constant as they are less tunable in a practical application. The final input parameter is the extent of precipitation at each stage i.e. the fraction of total cations precipitated into the solid phase. The extent of precipitation is a key parameter in all countercurrent precipitation processes that affects the purity, number of stages, water requirement, enthalpic cost and more⁷³. For this illustrative example, we set the extent of precipitation in each stage as proportional to the amount of Fe^{2+} in the stage and varied the proportionality constant, κ , between calculations (see **Methods, General Countercurrent Precipitation Analysis, κ -Designation, Supplementary Note 5**, for details and script). We performed the countercurrent analysis for a variety of κ varying from (1,1,1) to (6,1,0.166), in a symmetric fashion. The notation ($\kappa_1, \kappa_2, \kappa_3$) refers to the values of κ at stages 1, 2, and 3, respectively, and will be used hereafter. We observe that the purities of the Mg^{2+} (Fe^{2+}) products increase from 0.979 (0.927) to 0.992 (0.990) between the (1,1,1) and (6,1,0.166) precipitation models (**Fig. 4b**). However, the total holdup, in terms of metal cations, increased from 2.12 to 3.39 (**Fig. 4b**). This calculation illustrates that, as in all separations, the optimal extent of precipitation is a tradeoff between product purity and the material holdup in the system at steady-state, with higher product purities being accompanied by larger process volume. Proper optimization of the extent of precipitation would depend on the costs associated with gas pressurization/depressurization, solid movement, and capital costs, which is beyond the scope of this work. However, this does not influence subsequent steps of this analysis. Taking precipitation model (4,1,0.25) as a specific example, we calculate that at steady-state the solution phase Fe^{2+} fraction is 1.1%, 4.3%, and 80.3% for stages 1, 2, and 3, respectively, yielding the output streams as 98.9% Mg^{2+} solution and 98.7% Fe^{2+} solid. The corresponding total soluble ion concentrations are 1.67 M, 1.96 M, and 1.19 M for stages 1, 2, and 3, respectively. In sum, the preceding workflow uses cation fractionation data and mass balance to calculate the steady state purity and soluble ion concentrations in each stage of the pressure-modulated countercurrent precipitation system.

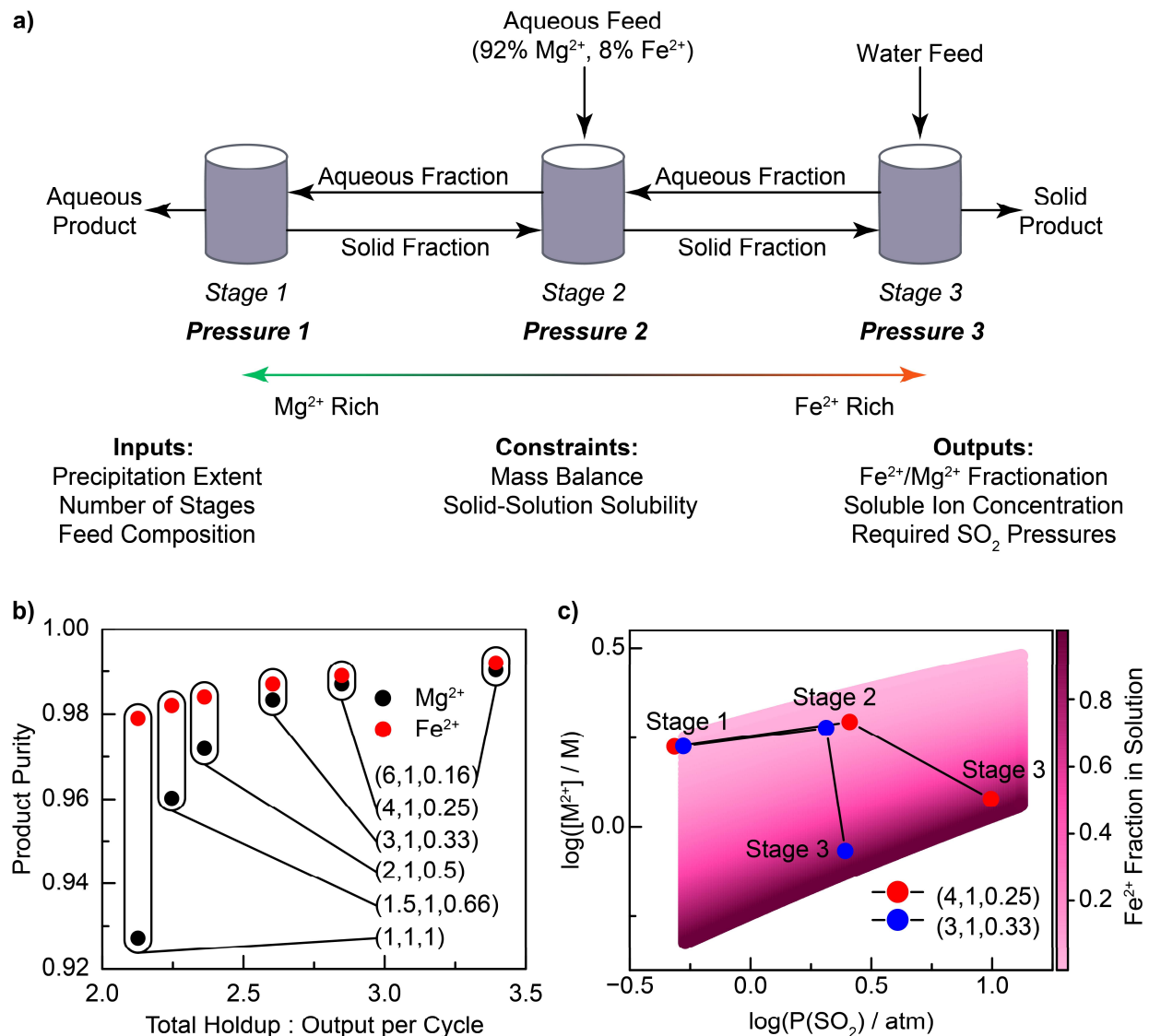


Fig. 4) SO_2 Pressure Controls Extent of Precipitation in Countercurrent Precipitation. a) Schematic of SO_2 pressure modulated countercurrent precipitation, indicating material flow, inputs and constraints, and outputs in the calculations performed. b) Plot of output product purity for the Fe^{2+} (red) and Mg^{2+} (black) products, versus the Total Holdup : Output per Cycle, which is the ratio of the quantity of cations in the system to the quantity of purified cations leaving the cascade each cycle. The various points represent, as indicated by the connecting lines, precipitation models of (6,1,0.166), (4,1, 0.25), (3, 1, 0.33), (2, 1, 0.5), (1.5, 1, 0.66), and (1,1,1), using the notation for precipitation model described in the text. c) Heatmap for pressure-concentration-composition phase space, with equilibrium compositions at steady-state of each stage indicated in the plot for countercurrent precipitation schemes of (4,1,0.25) (red) and (3,1,0.33) (blue). The heatmap is colored to represent the Fe^{2+} fraction in solution, with light pink representing 0.0 fraction Fe^{2+} , and dark purple representing 1.0 fraction Fe^{2+} .

Armed with the Fe^{2+} fractionation and soluble ion concentration calculated above, we can then use the relationship between SO_2 pressure, ion concentration, and Fe^{2+} fractionation shown in Fig. 3d to determine the necessary SO_2 pressure to achieve the desired extent of precipitation at each stage. To do this for the

420 full range of possible concentrations and Fe^{2+} fractionations, we interpolated the solubility data in **Fig. 3d**
421 (**Fig. 4b**, see **Supplementary Note 5** for details and error analysis). Inputting the calculated soluble ion
422 concentration and Fe^{2+} fractionation into this interpolation allows us to calculate the pressures required to
423 achieve the precipitation model (4,1,0.25). We calculate that if 0.5, 2.6, 9.9 atm SO_2 are applied to stages
424 1, 2, and 3, respectively, the requisite Fe^{2+} fraction in solution and total soluble ion concentration will be
425 generated (**Fig. 4c, red**). Performing the same analysis, but changing the precipitation model to (3,1,0.33),
426 yields slightly less pure products of 98.7% Mg^{2+} and 98.3% Fe^{2+} and requires pressures of 0.5, 2.1, and 2.5
427 atm SO_2 for stages 1, 2, and 3, respectively (**Fig 4c, blue**). Comparing the results for the two precipitation
428 models, we observe that by applying a distinct series of pressures in the countercurrent cascade, two
429 different precipitation models with different purities, yields, and holdups can be achieved. As noted above,
430 the optimal choice of precipitation extent, and thus SO_2 pressure cascade, is an important area of future
431 work. Taken together, the methodology developed here describes how countercurrent precipitation
432 processes based on reversible acid gas pressure swings can be achieved, which can in principle be applied
433 to a range of cation separations and acid gases.

434 We briefly note that while the separation of Mg^{2+} and Fe^{2+} described here relied on thermodynamic
435 differences in solubility at 80 °C, we hypothesized that at lower temperatures where precipitation is slower,
436 separation based on precipitation *kinetics* may be possible. Indeed, we find that the differential precipitation
437 of Mg^{2+} and Ni^{2+} at 45 °C is strongly dependent on the rate of SO_2 depressurization (**Fig. S19**). While the
438 origin of this effect remains unclear, the data suggest that optimization of depressurization conditions could
439 enable separation of metal cations based on precipitation kinetics, rather than thermodynamics. In sum, the
440 data strongly indicates that stepwise and reversible depressurization of SO_2 from mixed bisulfite solutions
441 can enable separation of metal cations in the form of purified sulfite solids. This approach, which utilizes
442 acid gas pressure to modulate pH and precipitating anion speciation, functions analogously to traditional
443 pH-swing methodologies utilizing bases like NaOH or CaO, but without the need for stoichiometric
444 reagents.

445

Thermal Decomposition of Sulfites Generates Pure Oxides and Recycles SO₂

The final stage in our proposed process consists of thermal decomposition of the purified metal sulfites to regenerate the SO₂ and form the desired purified metal oxides. MgSO₃ decomposition to form MgO and SO₂ has been industrially practiced in the flue gas desulfurization and pulp industries for several decades, with temperatures of decomposition typically near 1000 °C^{74–76}. We also observe by PXRD that calcination of MgSO₃•3H₂O at 950 °C yields an MgO solid product (**Fig 5a, Fig. S20**). We note that, as has been previously reported, elemental sulfur gas can form as an intermediate, necessitating appropriate gas/solid contact times to yield high sulfur recovery as SO₂ (**Supplementary Note 6**)^{77–79}. To investigate if MgO produced from olivine using our proposed process can rapidly react with CO₂, we exposed MgO, generated by calcination of (Mg_{0.993}Fe_{0.007})(SO₃)•3H₂O, to 1 atm CO₂ and water at ambient temperature. Measuring the concentration of Mg²⁺ in solution, we observe that ~60% of Mg²⁺ dissolved from the MgO in 30 min, dramatically larger than the negligible dissolution measured for the olivine starting material in the same conditions (**Fig. S21**). This data suggest that MgO should rapidly react with CO₂ to form magnesium carbonate/bicarbonate to capture and store CO₂. Indeed, exposure of the MgO product to 1 atm of CO₂ at ambient temperature for 6 hours yields MgCO₃•3H₂O quantitatively (**Fig. S22**). In line with the established reactivity of MgO^{11,13}, these data also indicate that the MgO produced from olivine through this SO₂ recycling approach is competent for CO₂ capture and storage. We also investigated the calcination of FeSO₃•3H₂O by thermogravimetric analysis (TGA) and PXRD. We observe that calcination of FeSO₃•3H₂O in air yields a constant weight above 700 °C (**Fig. S23**). By PXRD we identify the solid products of calcination at 800 °C to be Fe₂O₃ (**Fig. 5b**). We observe that calcination of FeSO₃•3H₂O in N₂ yields a constant weight above 500 °C (**Fig. S24**). By PXRD we identify the solid products of calcination at 600 °C to contain mostly Fe₃O₄, with a small amount of non-stoichiometric FeS (**Fig. S25**), in accord with previous reports⁸⁰. This data indicates that FeSO₃ can be decomposed to generate iron oxides and SO₂, although calcination in oxygen is needed to maximize SO₂ recovery (**Supplementary Note 7**). Taken together, the data and the industrial precedent of sulfite decomposition for SO₂ recovery strongly indicates that calcination can effectively be used to generate purified metal oxides and recycle SO₂.

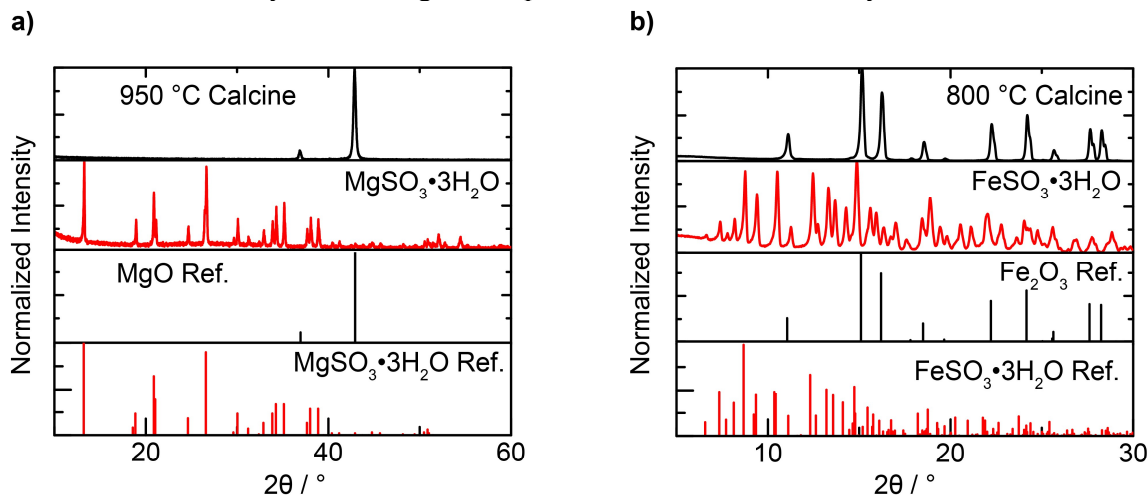


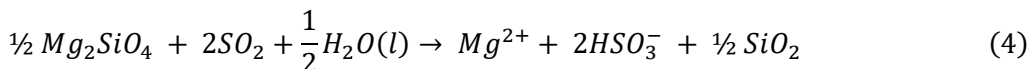
Fig. 5. Thermal Decomposition of Sulfites to Generates Metal Oxides. **a)** PXRD patterns of MgSO₃•3H₂O (red) and after calcination of MgSO₃•3H₂O at 950 °C in N₂ for 20 minutes (black). Reference patterns for MgO and MgSO₃•3H₂O are shown below. PXRD performed with Cu source. **b).** PXRD patterns of FeSO₃•3H₂O (red) and after calcination of FeSO₃•3H₂O at 800 °C in N₂ for 1 hour (black). Reference patterns for Fe₂O₃ and FeSO₃•3H₂O are shown below. PXRD performed with Mo source.

The Moderate Acidity of SO₂ Enhances the Efficiency of Closed-Loop Olivine Processing

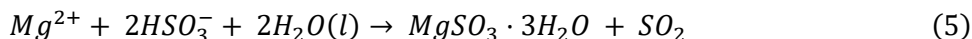
To evaluate the energetic efficiency of our proposed closed-loop acid recycling process, we estimated the enthalpic cost of acid recycling (Table 2). To calculate the enthalpic cost, we analyzed the net reaction of



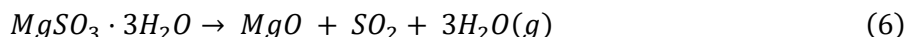
In terms of three sequential steps. The first step is the exothermic leaching of olivine in SO₂:



The second step is the slightly endothermic precipitation of MgSO₃:



And the third step is the endothermic calcination of MgSO₃



We then calculated the enthalpy of each stage at room temperature, assuming negligible variation with temperature. The total reaction is slightly endothermic, at 40 kJ/mol MgO. We find that the dissolution is exothermic (−210 kJ/mol MgO), precipitation is slightly endothermic (60 kJ/mol MgO), and calcination of MgSO₃·3H₂O is endothermic (310 kJ/mol). The balance in the endothermic costs is closed by considering the exothermic condensation of water vapor (−130 kJ/mol MgO) (Supplementary Note 8.1). We make the assumption that minimal heat can be recovered from the exothermic dissolution step and water vapor condensation, since these will occur at low temperatures (< 100 °C), resulting in low-grade waste heat that will not meaningfully contribute to reducing total energy costs. In addition, we estimate the minimum thermodynamic work required to pressurize 2 moles of SO₂ gas (for processing 1 mole of Mg) by 5 orders of magnitude is 60 kJ/mol (Supplementary Note 8.2). We therefore calculate the minimum enthalpic cost of acid recycling will be the sum of the enthalpies of the precipitation, calcination, and pressurization, leading to total energy cost of 430 kJ/mol Mg (Table 2).

To benchmark this energetic cost to that of other acids, we performed a similar analysis for the proposed ‘nitrate looping’ approach. We calculate that dissolution of olivine in nitric acid is more exothermic (−310 kJ/mol MgO) than for SO₂. The precipitation of Mg(NO₃)₂·6H₂O is slightly exothermic (−30 kJ/mol MgO), but unfavorable in aqueous solutions. Therefore, we estimate the cost of water evaporation for a Mg(NO₃)₂ solution at industrial concentrations (e.g. 4 M Mg²⁺) of 610 kJ/mol MgO. The thermal decomposition of Mg(NO₃)₂·6H₂O is significantly endothermic (630 kJ/mol MgO). The energy balance is closed by considering the condensation of water vapor from the precipitation and calcination steps. This leads to an estimate for the minimum enthalpic cost of 1,240 kJ/mol MgO (Supplementary Note 8.1). Based on the foregoing analysis, we conclude that the minimum enthalpic cost of the SO₂ recycling process is dramatically lower than acid-recycling processes with a strong acid such as HNO₃.

Table 2. Summary of enthalpic costs of each stage of olivine processing. Total Input combines all endothermic costs.

Acid	Leaching	Evaporation	Precipitation	Pressurization	Calcination	Total Input
SO ₂	−210	—	60	60	310	430
HNO ₃	−310	610	−30	—	630	1,240

518 Considering the similar leaching rates (**Fig. 2c**) between SO_2 and HNO_3 , this implies that there is a
519 superior energy cost-rate tradeoff for SO_2 as compared to the stronger acid HNO_3 . We posit that the leveling
520 effect of water and the weak dependence on pH of mineral dissolution rates contribute to this. Since the
521 pK_a of HNO_3 , -1.7 , is less than that of hydronium, its acidity is limited to the acidity of hydronium in water.
522 As a result, it does not generate solutions that are as acidic as its intrinsic acidity should engender. However,
523 during thermal decompositions to regenerate the acid precursors (i.e. NO_2 , O_2), the intrinsic acidity of the
524 acids contributes to the endothermicity of that reaction. As a result, the endothermic cost of acid recycling
525 is much larger for strong acids than for SO_2 , but the acidity generated in water is not proportionally larger.
526 Furthermore, it is well established that mineral dissolution rates typically have a suppressed dependence on
527 proton activity (~ 0.5 for olivine)⁶². Therefore, while acidity is needed as a stoichiometric reagent, increasing
528 the proton activity does not substantially increase dissolution rates. In sum, we propose that the leveling
529 effect and the weak proton dependence of dissolution rates cause closed-loop processing with stronger acids
530 to have significantly larger enthalpic costs, but the additional acidity does not result in significantly faster
531 dissolution rates. This in turn leads to the superior energy cost-rate tradeoff for SO_2 .
532

533 Conclusion and Outlook

534 In this work, we develop a proof-of-concept approach to closed-loop processing of alkaline silicate
535 minerals. Using olivine as a test case, we demonstrate that using SO_2 as an acid gas with moderate acidity
536 enables separation and isolation of high purity MgO , Fe_2O_3 , and SiO_2 while minimizing the energy cost of
537 recycling SO_2 . The fundamental advance of this work is the modulation of acid gas pressure (SO_2 in this
538 instance) to generate a ‘pH-swing’ without the addition of stoichiometric acid and base. This approach
539 enables reversible modulation of counter anion speciation and metal ion solubility which creates
540 opportunities for separation of metal cations from solution and from each other based on differential
541 solubility. While these studies focused on olivine processing, this work establishes the foundational
542 understanding for separation based on acid gas pressure that could, in principle, be used for other ion
543 separations and with other pH-modulating gases. For separations that require many sequential stages of pH
544 modulation, control of pH through reversible pressure modulation creates an opportunity for substantial
545 decreases in reagent use. Thus, this work establishes principles for more efficient closed-loop hydrothermal
546 processing of multicomponent minerals.

548 **Materials and Methods**

549 **Materials**

550 *General Chemicals*

551 The following chemicals were used as received; any chemicals or materials requiring additional preparation
552 are described in their own subsection below: sulfur dioxide (SO₂, Linde, 99.9%); argon (Ar, Linde,
553 99.995%); 68-70% nitric acid for dissolution (HNO₃, Avantor, ACS Grade); nitric acid for ICP (HNO₃,
554 Avantor, ARISTAR® ULTRA), magnesium hydroxide (Mg(OH)₂, Sigma Aldrich, ≥99.0%), iron chloride
555 tetrahydrate (FeCl₂·4H₂O, Sigma Aldrich, ≥99.0%), sodium metabisulfite (Na₂S₂O₅, Sigma Aldrich,
556 ≥99.0%), sodium hydroxide (NaOH, Sigma Aldrich, 99.99%), magnesium sulfate (MgSO₄, VWR
557 International, ≥98.0%), nickel chloride hexahydrate (NiCl₂·6H₂O, Sigma Aldrich, 99.9%), carbon dioxide
558 (CO₂, Linde, 99.9%). MilliQ water (Millipore Type 1, 18.2 MΩ·cm) was used as the source of ultrapure
559 water for all experiments.

560 *Preparation of Olivine*

561 Olivine (Teton-Black, 120 Mesh) was first dry sieved to a fraction of 32-212 μm, then wet sieved with
562 copious water for about one hour. During this process, fine black particles in the original product were
563 separated. This procedure was performed to remove any fines that may artificially enhance dissolution rates.
564 The wet olivine was then dried at 200 °C. PXRD confirms that the majority phase is olivine (**Fig. S1**), and
565 SEM imaging confirms that olivine grains are 32-212 μm and contain no visible fine particles on the surface
566 (**Fig. S2**).

567 *Preparation of MgSO₃·6H₂O*

568 1.8g (31 mmol) of Mg(OH)₂ were added to 10 mL of milliQ water, then oxygen was removed by sparging
569 with Ar for 40 minutes. Subsequently, 1 atm of SO₂ was introduced for ~30 minutes, at which point all the
570 solid Mg(OH)₂ had dissolved. Ar was then introduced by sparging to strip SO₂, which led to precipitation
571 of MgSO₃·6H₂O as a white powder. After sparging Ar for ~90 minutes, the solid product was filtered
572 through cellulose filter paper and stored in an N₂-filled glovebox.

573 *Preparation of FeSO₃·3H₂O*

574 28.28 g (148 mmol) of Na₂S₂O₅ and 26.92 g (135 mmol) of FeCl₂·4H₂O were dissolved in about 400 mL
575 of deaerated water in an N₂ glovebox. Next, 6.92 g (173 mmol) of NaOH was added while stirring
576 vigorously. This led to the precipitation of a yellow-orange solid. After 10 minutes, the precipitated yellow-
577 orange solid was filtered with cellulose filter paper and dried at 100 °C in an N₂ atmosphere. The final
578 product upon drying was a white-yellow solid, confirmed by PXRD to be FeSO₃·3H₂O.

579 *Preparation of amorphous NiSO₃*

580 1.18 g (5 mmol) of NiCl₂·6H₂O and 0.967 g (5 mmol) of Na₂S₂O₅ were dissolved in about 5 mL of deaerated
581 water in an N₂ glovebox while stirring rapidly. 0.46 g (12 mmol) of NaOH was added while stirring
582 vigorously. After 10-30 minutes, the precipitated blue solid was filtered with cellulose filter paper and dried
583 at 100 °C in an N₂ atmosphere. The final product was a light blue solid, that was determined to be
584 amorphous by PXRD

585 *Preparation of (Mg/Fe)SO₃*

586 MgSO₃ containing varying amounts of Fe was synthesized by leaching olivine in SO₂ for at least 12 hours.
587 Then, an aliquot of the resulting slurry was transferred to a 50 mL centrifuge tube and centrifuged for 2
588 minutes at 4180 rcf (relative centrifugal force). Subsequently, the centrifuge tube was transferred into an
589 N₂ glovebox and the supernatant decanted. Next, the supernatant was exposed to dynamic vacuum, which

led to the vigorous generation of bubbles, and after less than 2 minutes, a white solid precipitated. By varying the length of exposure to dynamic vacuum, the composition of the solid phase was altered. Products enriched in Fe were obtained by very short depressurization, while products enriched in Mg were obtained from longer depressurization, or by depressurization of the filtrate after a solid enriched in Fe was separated. After depressurization, the product was heated to 80°C for about 20 minutes, filtered, rinsed briefly with deaerated water, then dried at 80 °C in an N₂ glovebox. The composition of the product was determined by ICP as described below, and the structure confirmed by PXRD and TGA to be (Mg/Fe)SO₃ of various degrees of hydration.

Experimental Methods

Olivine Dissolution Experiments, SO₂

All olivine dissolution experiments with SO₂ were performed in a 300 mL stainless steel pressure reactor (Parr) equipped with overhead stirring, a heating mantle, a pressure gauge, an internal thermocouple, a gas outlet valve, and a stainless steel tube immersed in the reaction solution connected to two valves used as a gas inlet and a solution sampling port, respectively (**Fig. S27**). To the pressure reactor was added 100 mL milliQ water, 7.15-22.22 g olivine, and any Mg(OH)₂ as needed. The vessel was then sparged with Argon for at least 30 min, then sealed and heated to the desired temperature. Experiments with Mg(OH)₂ present were initially equilibrated to 10 °C lower than the desired temperature because the reaction of Mg(OH)₂ with SO₂ is exothermic and would rapidly raise the temperature to the desired temperature. Once the reaction was initiated by injection of SO₂, the temperature was set to the desired temperature. To initiate the reaction, SO₂ was injected into the reactor. The reactor was pressurized and vented 10 times to ensure that all Ar in the headspace was replaced with SO₂, then the outlet of the reactor was sealed while leaving the inlet open to the SO₂ tank to maintain pressure. Aliquots were obtained by sealing the inlet temporarily, opening the valve associated with the solution sampling port, and collecting 6-8 mL of the slurry in a 50 mL centrifuge tube. The first 5 mL were always discarded, then an additional 1-3 mL were collected. Aliquots were either centrifuged (2 min at 4180 rcf) or filtered with a 0.22 µm PTFE filter, then a 50 µL aliquot of the solution phase was diluted in HNO₃ for analysis by ICP-OES. We found that both centrifugation and filtration for various times between taking the sample and diluting in HNO₃ (between 10s to 3 min) resulted in identical measurements within error of ICP-OES. The solid residue after 48 hours of leaching was centrifuged and rinsed 4 times, then the white gel was decanted and dried at 120 °C. This methodology was used to generate **Fig. 2a, 2b, 2c – black, 2d, S3, S5, S7 – black, S9**.

Olivine Dissolution Experiments, SO₂ – atmospheric pressure

Olivine dissolution experiments at atmospheric pressure with SO₂ were performed in a 40 mL glass vial with magnetic stirring and heated with an aluminum heating block. A pH probe (Vernier) was inserted through the septum cap of the 40 mL vial, generating an air-tight seal. The pH probe was calibrated directly before use at 80 °C. To the vial was added 15 mL milliQ water and 3.33 g olivine. The reactor was then heated to 80 °C. The vessel was then sparged with argon for at least 30 min. To initiate the reaction, SO₂ gas was flown through the reactor. The pH was monitored throughout this process. This methodology was used to generate **Fig. S4**.

Olivine Dissolution Experiments, HNO₃

All olivine dissolution experiments with HNO₃ were performed in a 20 mL glass vial with magnetic stirring and heated with an aluminum heating block. To the vial was added 8.56-9.37 mL milliQ water and 0.0358-0.715 g olivine. The vessel was then sparged with nitrogen for at least 30 min at 10 mL/min with a water prebubbler to avoid water loss. The vessel was maintained under an anoxic atmosphere by flowing 10 mL/min nitrogen throughout dissolution. This procedure was employed to ensure consistency with the anoxic conditions during dissolution with SO₂. The reactor was then heated to the desired temperature. To initiate the reaction, concentrated HNO₃ was added into the reactor, such that the total volume was equal to

10 mL. Aliquots were obtained by removing 0.3-0.5 mL of the slurry. Aliquots were subsequently filtered with a 0.22 μm PTFE filter, then a 50 μL aliquot of the filtrate was diluted in HNO_3 for analysis by ICP-OES. This methodology was used to generate **Fig. 2c – red, S6, S7 – red.**

Correction for Volume Expansion During SO_2 Leaching

We observed that upon exposure of water to elevated pressures of SO_2 , the solution volume would expand by 10-20%, reflecting the large solubility of SO_2 in water. As a result, calculations of the fraction of dissolved olivine based on converting measured concentration using the volume of added water were similarly inaccurate by about 10-20% (i.e. 100 mL of added water is actually ~115 mL of water with dissolved SO_2). To correct for this volume expansion when making quantitative comparisons, we performed leaching reactions with ~0.02 M CsCl present as an internal standard. First, we measured the concentration of Cs^+ by ICP-MS, prior to the introduction of SO_2 , then compared all other ion concentrations measurement in subsequent aliquots to the concentration of the Cs^+ internal standard. This methodology was applied for the following experiments: the 48 hour leach of olivine to accurately calculate total dissolution extents (**Fig. S3**), for calculating the dissolved moles of Mg^{2+} and Fe^{2+} during low-conversion kinetic analysis to compare between HNO_3 leaching (**Fig. 2c.**), and to compare between leaching with and without added $\text{Mg}(\text{HSO}_3)_2$. (**Fig. S5**)._{_}

Sulfite Solubility Experiments, Supra-Atmospheric SO_2 Pressure

All sulfite solubility experiments with SO_2 at pressures greater than atmospheric pressure were performed in a 300 mL stainless steel pressure, as described above in the section ‘Olivine Dissolution Experiments, SO_2 ’. The reactor was loaded in an air-free nitrogen glovebox with <0.1 ppm oxygen. To the pressure reactor was added 8.5 – 24.0 g $\text{Mg}(\text{OH})_2$ and 5.73 – 20.0 g $\text{FeSO}_3 \cdot 3\text{H}_2\text{O}$. Then 100-150 mL of deaerated milliQ water was added, the reactor was sealed and then removed from the glovebox. SO_2 was then injected into the reactor, which caused rapid heating of the reactor due to the exothermic reaction with $\text{Mg}(\text{OH})_2$. The reactor was left exposed to SO_2 for several hours, then the headspace was cleared at least 10 times to ensure there was no residual nitrogen inside the reactor. The reactor was then sealed, cooled with a water/ice mixture to ~10 $^\circ\text{C}$, then pressurized with SO_2 . The reactor was sealed again, then heated to 80 $^\circ\text{C}$, which would allow for the pressure to be larger than can be provided by the SO_2 tank (around 45 psi). Aliquots were obtained by sealing the inlet temporarily, opening the valve associated with the solution sampling port, and collecting 6-8 mL of the slurry in a 50 mL centrifuge tube. The first 5 mL were always discarded, then an addition 1-3 mL were collected. Aliquots were subsequently centrifuged (2 min at 4180 rcf) or filtered with a 0.22 μm PTFE filter, then a 50 μL aliquot of the solution phase was diluted in HNO_3 for analysis by ICP-OES. In between aliquots, the reactor was depressurized by releasing SO_2 gas through the gas outlet valve. The pressure within the reactor was allowed to stabilize for at least 40 minutes, and aliquots were only taken if the pressure was stable within 1 psi for at least 30 minutes. We separately confirmed that the concentrations of Mg and Fe would equilibrate within 20 minutes after a pressure change at 80 $^\circ\text{C}$. To confirm that solubility changes with pressure were reversible, the reactor would sometimes be repressurized by injecting SO_2 from the tank. However, this could only be performed for pressures up to 45 psi. Pressures are reported as partial pressures of SO_2 , so the vapor pressure of water at 80 $^\circ\text{C}$ (6.87 psi) was subtracted from the measured value of the pressure. This methodology was used to generate data in **Fig. 3, 4, S11, S18**, except for data shown at sub-atmospheric pressure.

Sulfite Solubility Experiments – Solid Solutions, Atmospheric Pressure SO_2

A set of 7 sulfite solid solution solubility measurements with varying compositions of Mg and Fe were performed at atmospheric pressure. These were performed in a 40 mL glass vial. The reaction slurry was prepared in an N_2 -filled glovebox with <0.1 ppm oxygen. To the glass vial was added 1.5 g of $\text{FeSO}_3 \cdot 3\text{H}_2\text{O}$. Then 10 mL of deaerated milliQ water was added, the vial was sealed, then removed from the glovebox. 1 atm SO_2 in the headspace was then introduced into the vial by flowing SO_2 . The vial was then heated to 80 $^\circ\text{C}$ in an aluminum heating block. The systems were maintained at this temperature for 1 hour to allow for

full equilibration. Aliquots of the solution composition were taken by removing 0.2-0.5 mL of the slurry, filtering with a 0.22 μm PTFE filter, then a 50 μL aliquot of the filtrate was diluted in HNO_3 for analysis by ICP-OES. Aliquots of the solid phase were taken by removing 0.2-0.5 mL of the slurry, filtering through a cellulose filter, rinsing the solid residue twice, then dissolving a small quantity of solid in HNO_3 for analysis by ICP-OES. After each measurement, 2-4 mL of a deaerated, 2g $\text{Mg}(\text{OH})_2$ in 15 mL milliQ water slurry was added to change the total ratio of $\text{Mg}:\text{Fe}$. As for solubility measurements performed above 1 atmosphere, we waited for one hour after changing the partial pressure of SO_2 prior to taking an aliquot. Pressures are reported as partial pressures of SO_2 , so the vapor pressure of water at 80 $^\circ\text{C}$ (6.87 psi/0.47 atm) was subtracted from atmospheric pressure, leading to a partial pressure of SO_2 of 0.53 atm. This methodology was used to generate 7 data points in **Fig. 3c, 3d, 4c**.

Sulfite Solubility Experiments – Mg^{2+} only, sub-Atmospheric Pressure SO_2

A set of experiments to measure the MgSO_3 solubility as a function of SO_2 pressure were performed. These were performed in a 40 mL glass vial. To the glass vial was added 2.63 g of $\text{Mg}(\text{OH})_2$. Then 15 mL of milliQ water was added. The water was degassed by flowing 100 mL/min N_2 for ~30 min. 1 atm SO_2 in the headspace was then introduced into the vial by flowing SO_2 . The vial was then heated to 80 $^\circ\text{C}$ in an aluminum heating block. The systems were maintained at this temperature overnight to allow for full equilibration. Aliquots of the solution composition were taken by removing 0.2-0.5 mL of the slurry, filtering with a 0.22 μm PTFE filter, then a 50 μL aliquot of the filtrate was diluted in HNO_3 for analysis by ICP-OES. After each measurement, a mixture of SO_2 and N_2 with varying ratios were flown through the reactor to set a new SO_2 partial pressure. Gas flow rates were controlled by mass flow controllers. As for solubility measurements performed above 1 atmosphere, we waited for one hour after changing the partial pressure of SO_2 prior to taking an aliquot. Pressures are reported as partial pressures of SO_2 , so the vapor pressure of water at 80 $^\circ\text{C}$ (6.87 psi/0.47 atm) was subtracted from atmospheric pressure, leading to a partial pressure of SO_2 of 0.53 atm. This methodology was used to generate **Fig. S16**.

pH Measurements in NaHSO_3 as a Function of SO_2 Pressure

For the following experiments, a 50 mL glass reactor with 2 14/20 joints, 2 screw cap openings, and 1 24/40 joint was employed. The 24/40 joint was fitted with a septa that contained a hole just large enough for a pH probe (Vernier). The pH probe was calibrated directly before use. The two screw caps were sealed with rubber septa, and the two 14/20 joints were also sealed with rubber septa. Needles were used to puncture the 14/20 septa to be used as gas inlets and outlets. First, about 27.5 mL of 1M NaOH was added to the reactor, then the reactor was sparged with Ar . Then, SO_2 was introduced by flowing at 1 atmosphere while monitoring the pH. Once the pH stabilized near 1.4, the flow rate of SO_2 was lowered to about 5-20 mL/min, then measured with a bubble flow meter. To set different partial pressure of SO_2 , a known flow rate of N_2 was also flown through the vial to dilute the SO_2 gas in the headspace. The pH was recorded once the pH did not vary by more than 0.05 units for 5 minutes. This methodology was used to generate **Fig. S13**.

Olivine Processing Tests – Leaching and $\text{Mg}^{2+}/\text{Fe}^{2+}$ Separation

The pressure reactor described above in ‘Olivine Dissolution Experiments, SO_2 ’ was used for olivine processing tests. 150 mL milliQ and 33g olivine were added to the reactor. The reaction was sparged with Ar for 30 minutes, then sealed and heated to 80 $^\circ\text{C}$. SO_2 was then injected to initiate the reaction, then the reactor was pressurized and vented 9 times to remove any remaining Ar . The gas inlet was then left open to maintain SO_2 pressure and allowed to react for 19 hours. Then, the reactor was depressurized and the resulting slurry was immediately filtered through cellulose to isolate solid silica. About 100 mL of the aqueous filtrate was collected. The filtrate solution was then exposed to 1000 mL/min N_2 to strip SO_2 , causing a yellow-white, Fe^{2+} -enriched solid to precipitate. Then the solution and solid were separated by filtration over cellulose. The filtrate solution was then exposed to dynamic vacuum for about 30 minutes, which resulted in rapid precipitation of a Mg^{2+} -enriched white solid. The white solid was subsequently separated from the solution by filtration over cellulose. The solid was then rinsed twice for subsequent

analysis. The first precipitated yellow-white solid was subsequently introduced to deoxygenated water, exposed to 1 atm SO₂ until it all dissolved, then exposed to 50 mL/min N₂. After about 10 min, a yellow-brown solid, further enriched in Fe²⁺, was precipitated. After filtration over cellulose, the new solid was again introduced to deoxygenated water, exposed to 1 atm SO₂ until complete dissolution, then exposed to 50 mL/min N₂. After about 10 min, a brown precipitate, even further enriched in Fe²⁺, formed and was filtered over cellulose. Although the temperature was allowed to deviate from 80 °C during processing, solid-liquid slurries were always equilibrated to 80 °C prior to any filtration steps. 50 µL aliquots of the solutions were diluted in HNO₃ for analysis by ICP-OES. In addition, 1-10 mg of each solid was dissolved in HNO₃ for analysis by ICP-OES. This methodology was used to generate **Fig. S17**.

Calculation of Ideal Roozeboom plot

Using reported solubilities (in mol/kg) of MgSO₃⁶⁵ and FeSO₃⁶⁷ at 80 °C, we calculate the K_{sp} of each endmember by assuming that upon mixing sulfite solids with water, sulfite is the dominant form of S(IV), since the pH will likely be greater than 8. Through this assumption, we square the reported value of the solubility in mol/kg to obtain the K_{sp}. We then plot the Roozeboom plot using the standard equations⁶⁶. We used solubilities of 0.061 mol/kg for MgSO₃ and 0.0034 mol/kg for FeSO₃, which yields a K_{sp} of 3.8 x 10⁻³ for MgSO₃ and 1.15 x 10⁻⁵ for FeSO₃. This methodology was used to generate the blue curve in **Fig. 3c**.

General Countercurrent Precipitation Analysis

A total of 51 solubility measurements (i.e. [Mg²⁺], [Fe²⁺], and Fe²⁺ fraction in solid) for a range of SO₂ pressures from 0.5-13.3 atm and the complete range of Mg²⁺/Fe²⁺ compositions were used in the analysis here. First, the data was compiled to generate Roozeboom plots (Fe²⁺ fraction in solid versus Fe²⁺ fraction in solution). The Roozeboom data (**Fig. 3c**) was fit as a piecewise function of two linear segments, although in principle a wide variety of fitting functions have been used historically. Next, we performed a non-linear fit of an empirical function for log([M²⁺]) as a function of log(P(SO₂)) and Fe²⁺ fraction in solution (**Fig. 3d. Supplementary Note 5**). This fit was performed solely for the purpose of interpolating between measured values of solubility, and the non-linear fit is required to capture the non-idealities in both the aqueous solution and solid solution. We performed a validation procedure wherein 15% of the data (8 data points) were removed, the remaining data was fit to the empirical non-linear function, and finally the 8 removed points were used as test cases to determine the error in the non-linear fit (~4%). Ultimately, the non-linear function utilized was chosen due to the similar average error as our experimental error and the absence of sharp discontinuities in calculated values.

The fitting of the Roozeboom data and log([M²⁺])-log(P)-Fe²⁺ solution fraction were then utilized in a Mathematica script designed to model a countercurrent precipitation process, which are included in the Supplementary Information as an associated .zip file (**Reversible_Acidity_CCA_Script.zip**). The script is developed to model a 3-stage countercurrent process, wherein the solid fraction (Fe²⁺ enriched) progresses towards stage 3, while the liquid fraction (Mg²⁺ enriched) progresses towards stage 1. The script is a loop wherein moles of M²⁺, Fe²⁺ aqueous fraction, Fe²⁺ solid fraction, moles of sulfite solid, and moles of water are determined in each cycle. These values are determined based on the inputs for each of these values from previous cycles, Roozeboom data, and the desired precipitation fraction, which is set by the precipitation model. At the end of each loop, the input values for the next cycle are set to mimic countercurrent movement of solids and liquids. To simplify the countercurrent movement of water, it was assumed that for each mole of solid, 3 moles of water were associated, although only 2 or 2.5 waters of hydration are present in highly purified Fe²⁺ solids (>96% Fe²⁺). ChatGPT was used in developing and editing syntax for the script.

The outputs of the script are the moles of M²⁺, Fe²⁺ aqueous fraction, Fe²⁺ solid fraction, moles of sulfite solid, and moles of water in each stage after each cycle. Using the non-linear fit for log([M²⁺])-log(P(SO₂))-Fe²⁺ solution fraction, we calculated log(P(SO₂)) from log([M²⁺]) and Fe²⁺ solution fraction. To do this, we assumed a molar concentration of water of 48.17 mol/L, which was chosen instead of 55.5 mol/L to account for the roughly 15% volume expansion observed upon exposure to high pressure SO₂. However, this assumption is not perfect as the extent of volume expansion is dependent on both the pressure of SO₂ and

dissolved ion concentration, and a more accurate countercurrent precipitation analysis will require a feedback loop between the SO_2 pressure, total water volume, and resulting M^{2+} concentration. This methodology was used to generate **Fig. 4b, 4c**.

κ -Designations for Countercurrent Precipitation Model

In designing a model for countercurrent precipitation, various extents of precipitation at each stage can be selected. In this work, we chose to set the extent of precipitation in each stage as proportional to the amount of Fe^{2+} in the stage and varied the proportionality constant, κ , between calculations. In other words, if a given stage contains a total of 1 mole of M^{2+} , with 5% Fe^{2+} , 0.05 moles of the total M^{2+} would be precipitated into the solid phase if $\kappa = 1$ was used in the model. Analogously, 0.1 moles of M^{2+} would be precipitated if $\kappa = 2$ was used. Precipitating in excess of the fraction of Fe^{2+} ($\kappa > 1$) yields a less pure solid as more Mg^{2+} is precipitated but leaves the solution phase purer as more Fe^{2+} is removed from the solution. The opposite is true for $\kappa < 1$. We performed the countercurrent analysis for a variety of κ : (1,1,1), (1.5,1,0.66), (2,1,0.5), (3,1,0.33), (4,1,0.25), (6,1,0.166), in a symmetric fashion. The notation ($\kappa_1, \kappa_2, \kappa_3$) refers to the values of κ at stages 1, 2, and 3, respectively. In principle, non-symmetric precipitation factors, or precipitation extents chosen based on entirely different parameters can also be used.

Separation of $\text{Mg}^{2+}/\text{Ni}^{2+}$ solutions through SO_2 Depressurization

For the following experiments, a 50 mL glass reactor with 2 14/20 joints, 2 screw cap openings, and 1 24/40 joints was used. The 24/40 joint was fitted with a septa that contained a hole just large enough for a pH probe (Vernier). The pH probe was calibrated directly before use. The two screw caps were sealed with rubber septa, and the two 14/20 joints were also sealed with rubber septa. Needles were used to puncture the 14/20 septa to be used as gas inlets and outlets. First, $\text{Mg}(\text{OH})_2$ and water was added to the reactor, then the reactor was sparged with Ar. Then, against a flow of fast Ar, amorphous NiSO_3 was added to the reactor. Then, the reactor was heated to 45 °C in a water bath and SO_2 was introduced. Once complete dissolution of $\text{Mg}(\text{OH})_2$ and NiSO_3 had occurred, an aliquot was obtained. Then, the depressurization process was initiated by replacing the SO_2 flow with a known flow rate of N_2 (20 or 300 mL/min). Throughout depressurization, aliquots were obtained by puncturing a septa with a needle and removing 0.2-0.4 mL of the slurry with a 1 mL pipette. Then, each aliquot was filtered through a 0.22 μm PTFE filter, and 50 μL of the filtrate were immediately diluted in HNO_3 for analysis by ICP-MS. This methodology was used to generate **Fig. S19**.

MgO – CO_2 Reactivity Tests

To quantify the reaction rate of MgO with CO_2 , two tests were performed. The first test was performed in dilute conditions where no precipitate would form. To a 20 mL glass scintillation vial was added 10 mL of MilliQ water, then the vial was sparged with 1 atm CO_2 for 20 minutes while agitated by rapid stirring. To initiate the reaction, 4 mg of the solid calcination product of 99.3% MgO (generated by calcination of 99.3% MgSO_3 at 950 °C in an argon atmosphere) was added, and the concentration of Mg^{2+} was monitored by taking 0.2 mL aliquots, diluting 50 μL of each aliquot in HNO_3 for analysis by ICP-OES. The second test was performed in concentrated conditions where $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ would precipitate. To a 4 mL vial was added 1.12 mL of milliQ; then the vial was sparged with 1 atm CO_2 for 20 minutes while agitating the solution with rapid stirring. To initiate the reaction, 45 mg of the solid calcination product were added, then the reaction was allowed to proceed for 6 hours under a flow of 1 atm CO_2 . The final solid product was then centrifuged and the supernatant decanted. The solid product was then analyzed by PXRD. This methodology was used to generate **Fig. S21, S22**.

Error Analysis for Measured Concentrations

Unless otherwise stated, the error for measured concentrations was calculated based on propagating the error associated with dilution with micropipettes and error in the ICP-OES/ICP-MS measurements. All ICP-OES measurements were carried out by either single or double dilution of 50 μL into 3.95 mL of 2% HNO_3 .

The error for the micro-pipetting procedure, reported as 1 standard deviation by the manufacturer's specifications, is 0.2% for dispensing 3.95 mL, and 2.55% for dispensing 50 μ L. ICP-OES calibration curves typically exhibited a relative standard error near 3% for Mg^{2+} measurements and 1% for Fe^{2+} . Errors in concentrations and dissolved solid compositions were propagated from these measurement errors using standard procedures.

Calcination of MgSO_3 and FeSO_3 materials

Most calcination experiments of MgSO_3 and FeSO_3 solids were performed using a TA Instruments SDT-650 to allow for simultaneous thermogravimetric analysis and analysis of the calcination product (**Figs. S23, S24**). Occasionally, calcinations were performed in a Lindberg Blue M horizontal tube furnace, with the solid product held in an alumina vessel (**Fig. S25**). Analysis of MgSO_3 calcination during rapid heating was performed by loading MgSO_3 into an alumina crucible and sealing a lid with a small pinhole to the crucible with ceramic paste. Subsequently, the crucible was placed upright inside of a quartz tube held in a vertical tube furnace such that the crucible was held outside of the heating zone. The crucible was held in place by small permanent magnets inside and outside the quartz tube, such that the crucible was resting on the magnets inside the quartz tube. The vertical tube furnace was heated to 890 $^{\circ}\text{C}$ and cleared of oxygen by flowing Ar. Finally, the calcination was initiated by removing the permanent magnet from the outside of the quartz tube, allowing the crucible to fall into the heating zone. Heating was retained for 20 min. After the quartz tube was removed, the crucible was opened and the solid removed for subsequent analysis. This methodology was used to generate **Fig. S20**.

General Analytical Methods

Powder X-Ray Diffraction (PXRD)

To determine the crystal structure of solid powders, PXRD was performed. Samples were prepared on a Si Zero Background Plate (Malvern Panalytical) by placing a small amount of sample on the holder, then achieving a flat surface by pressing the powder with a microscope slide. Both Cu (PANalytical X'Pert PRO MPD) and Mo (PANalytical_Empyrean) X-ray sources were used during this work. For samples containing Fe in large proportion, the Mo X-ray source was used to minimize fluorescence background. The following reference patterns were obtained from the International Center for Diffraction Data (ICDD) database⁸¹: Fe_3O_4 (04-001-7822), $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (04-011-2636), MgO (04-012-3469), MgSO_4 (04-014-7920), $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ (04-001-0473), $\text{Fe}_{0.94}\text{S}$ (04-004-7981), Fe_2O_3 (00-075-0647), MgSiO_3 (04-008-5424), Mg_2SiO_4 (04-007-7321), $\text{FeSO}_3 \cdot 2.5\text{H}_2\text{O}$ (04-011-6889), $\text{FeSO}_3 \cdot 3\text{H}_2\text{O}$ (04-012-8821), $\text{Ca}(\text{OH})_2$ (04-006-9147), CaCO_3 (04-006-9147). The reference patterns for $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ ⁸², $\text{FeSO}_3 \cdot 2\text{H}_2\text{O}$ ⁸³, and calcium silicate hydrate⁸⁴, which were not designated with ICDD card numbers were obtained elsewhere from literature.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

To measure solution phase concentrations of ions, ICP-OES (Agilent 5100 Inductively Coupled Plasma – Optical Emission Spectroscopy) was used. 2% high-purity HNO_3 (ARISTAR® ULTRA) was used as the diluent. A total of 4 mL of solution were used for each sample. A 1.25 ppm Sc internal standard was used for all measurements to account for plasma drift. Samples were diluted such that the expected concentration was between 1 and 10 ppm (typically diluted 6400-fold). The optical emission lines used were 234.350 nm (Fe), 279.553 nm (Mg), and 361.383 nm (Sc). Mg and Fe standards of 1-10 ppm were prepared immediately prior to measurement from a 100 ppm stock standard solution. Concentrations are reported as molarities (M), as the measured concentrations are directly measured as a function of volume, not solvent mass. Where relevant and measurable, molality (m) is reported.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

The same procedure as described above for ICP-OES was used for analyzing solutions containing trace Ni with ICP-MS (Agilent 7900 ICP-Mass Spectrometer). The masses analyzed were 58 (Ni), 45 (Sc), and 24 (Mg).

Thermogravimetric Analysis (TGA)

Samples were analyzed by TGA using a TA Instruments SDT-650. The total gas flow rate during all experiments was 100 mL/min. Samples were held in a 90 μ L alumina pan during heating.

Scanning Electron Microscopy (SEM)

To analyze the morphology of olivine starting materials and confirm the removal of fines, a small amount of olivine was added to carbon tape on an SEM stub. No conductive material was added since charging of the sample was not excessive. SEM analysis was performed on a Sigma HD VP SEM (Zeiss).

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Competing interests

The authors declare the following competing financial interest(s): A.A.B. and Y.S. are inventors on patent application WO2026147820, submitted by the Massachusetts Institute of Technology, that covers the process of metal ion separation through reversible pressure modulation described in this work.

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