Microbial Acceleration of Olivine Dissolution via Siderophore Production

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Microbial acceleration of olivine dissolution via siderophore production

Mark A. Torres[a]*, A. Joshua West[a], Kenneth Nealson[a]

[a]*University of Southern California - Department of Earth Sciences, 3651 Trousdale Parkway, Los Angeles 90089, United States of America*

Abstract

Silicate minerals represent an important reservoir of essential nutrients at Earth's surface. Due to the slow kinetics of primary silicate mineral dissolution and the potential for nutrient sequestration by secondary mineral precipitation, the bioavailability of many silicate-bound nutrients may be limited by the ability of microorganisms to actively scavenge these nutrients via organic ligand production. In this study, the effectiveness of ligand production as a means to scavenge Fe from Fe-silicates is addressed through targeted laboratory experiments using olivine as a model mineral.

Preliminary results show that microbial Fe-binding ligands (i.e. siderophores) can accelerate olivine dissolution rates stoichiometrically by almost an order of magnitude in experiments buffered at circumneutral pH. In addition to higher reaction rates, organic Fe-binding ligands fostered the accumulation of dissolved Fe in solution, which was below detection in the abiotic experiments due to the precipitation of secondary Fe minerals in the presence of O_2. Accelerated olivine dissolution rates in the presence of microbial Fe-binding ligands is somewhat unexpected because these ligands are known to be highly selective towards Fe^{3+} whereas olivine dominantly contains Fe^{2+}. Spectrophotometric analysis of the ligand complexes produced during reaction with olivine reveals the dominance for Fe^{3+}-ligand complexes in solution.

1. Introduction

The biological demand for Fe and other trace metals despite their low solubility in many Earth surface environments is thought to be met via the production of strong and highly selective ligands known as siderophores[1]. These molecules bind to trace metals, facilitating their biological uptake. The hypothesis that siderophores play a

key role in mobilizing lithogenic nutrients is corroborated by much experimental work showing that the production of these ligands by microorganisms is induced in response to metal deficiencies and that the metal-ligand complexes are actively taken up into living cells[2-3]. Furthermore, siderophores have been measured in natural soils and soil porewaters[4-5].

Understanding the role of siderophores in biogeochemical cycles requires information about how they interact with mineral substrates. To date, most experimental work has focused on the interactions between siderophores and aqueous species[6-7] as well as secondary Fe^{3+}-bearing phases[8]. Comparatively, less is known about the interactions between siderophores and primary Fe-bearing phases (e.g. silicates), especially those that do not contain Al^{3+} (e.g. ref. 9), which is also known to be strongly complexed by siderophores[10]. In this work, olivine $((Mg,Fe)_2SiO_4)$ is used as a model mineral to investigate the interaction between siderophores and Fe-bearing primary silicates in laboratory dissolution experiments.

2. Methods

Large (~1-3 mm) olivine crystals were hand picked underneath a binocular microscope in order to avoid grains with weathered surfaces or mineral inclusions. The un-weathered grains were crushed in an agate mortar and pestle, dry sieved into different grain size fractions, and cleaned ultrasonically with ethanol in order to remove fine-grained particles produced during grinding. Dissolution experiments were preformed in both batch and mixed flow systems with a defined grain size of olivine (75-175 μm) and varying concentrations (i.e. 0 – 280 μM) of the commercially available hydroxyamate siderophore deferoxamine. Batch experiments were buffered to a pH of ~7.5 with a TRIS/HCl buffer (10 mM) and reacted at 30°C in an incubated shaking table that kept the solutions well mixed by rotating at 200 rpm for the duration of the experiments. The batch experiments were sampled regularly for up to 40 hours and analyzed for Mg, Fe, and Si concentrations by MP-OES after acidification with concentrated HCl.

Experiments in mixed-flow reactors were performed using a flow rate of either 0.1 or 0.2 mL/min in order to allow for fluid residence times of 4 or 8 hours respectively. Constant solution volume in the reactors was maintained by pressurizing the reactors with laboratory air so that fluid exited the reactor upon reaching the height of the outlet tubing. The solution pH was held constant at a value of ~7.5 with either a TRIS/HCl buffer (10 mM) or a phosphate/NaOH buffer (500 μM). The mixed flow experiments were performed in an incubated shaking table set at the same temperature and rotation speed as in the batch experiments. The reactors were sampled regularly until a steady state was reached and analyzed for Mg, Fe, and Si concentrations by MP-OES after acidification with concentrated HCl. In addition to concentration measurements, ligand speciation was monitored in selected samples by measuring the solution absorbance at wavelengths between 200 and 600 nm with a spectrophotometer.

3. Results

In batch experiments, measured olivine dissolution rates increase non-linearly with increasing deferoxamine concentrations in a similar manner to that seen with the mineral hornblende (Fig. 1; ref. 9). However, a greater enhancement in dissolution rate at lower deferoxamine concentrations is seen for olivine relative to hornblende. Additionally, olivine Mg, Si, and Fe release rates are all increased stochiometrically by deferoxamine, which is not seen for the constituent ions of hornblende[9]. At deferoxamine concentrations of ≥200 μM, dissolution rates appear to plateau at a value that is almost an order of magnitude greater than the dissolution rate measured in the absence of any ligands (Fig. 1).

Generally, the rates measured in the mixed-flow experiments are consistent with those derived from the batch experiments (Fig. 1). Ligand speciation analysis of the outlet fluids from the mixed flow reactors reveals the dominance of Fe^{3+} complexes due to the presence of an absorbance peak at around 430 nm that can be re-produced when Fe^{3+} is added to the initial solution, but not when either Mg^{2+} or Si^{4+} are added (Fig. 2).

4. Discussion

The ability of the siderophore deferoxamine to appreciably accelerate olivine dissolution rates at circumneutral pH is interesting in that olivine dominantly contains Fe^{2+} whereas deferoxamine is highly selective towards binding Fe^{3+}. Three mechanisms could potentially explain this observation. If secondary Fe-oxide phases inhibit olivine dissolution by armoring the mineral surface, then the presence of a strong Fe^{3+} binding ligand could remove these phases and act to increase the reactive surface area of olivine. In the ligand-free batch experiments, secondary Fe-oxides are likely precipitating as the concentration of Fe is below the analytical detection limit. However, the removal of secondary Fe-oxide phases is unlikely to be the dominant mechanism contributing to the accelerated olivine dissolution rates measured in our system as ligand-free dissolution rates do not decrease with time after stoichiometric dissolution with respect to Mg and Si is reached.

Another possibility is that adsorbed deferoxamine accelerates the oxidation of Fe^{2+} at the mineral surface and then the strong capacity for deferoxamine to bind Fe^{3+} leads to the accelerated dissolution by facilitating bond breakage. This is similar to the mechanism proposed by ref. 11 to describe the effect of Mg^{2+} complexation by oxalate on olivine dissolution rates. This mechanism would explain the observed production of Fe^{3+} - ligand complexes (Fig. 2). Alternatively, the lower affinity (i.e. 10^{10} v.s. 10^{30}; ref. 7) of deferoxamine for Fe^{2+} may still be high enough to accelerate olivine dissolution rates by binding Fe^{2+} and facilitating bond breakage. If this is the case, then the oxidation of Fe^{2+} to Fe^{3+} must occur in solution in order to produce the observed Fe^{3+} complexes. While subtlety different, these mechanisms have implications for how siderophores react with ferrous silicates in natural environments, because variations in pO_2 strongly affect Fe oxidation kinetics[12]. Further work will seek to identify which mechanism dominates the interaction between olivine and deferoxamine.

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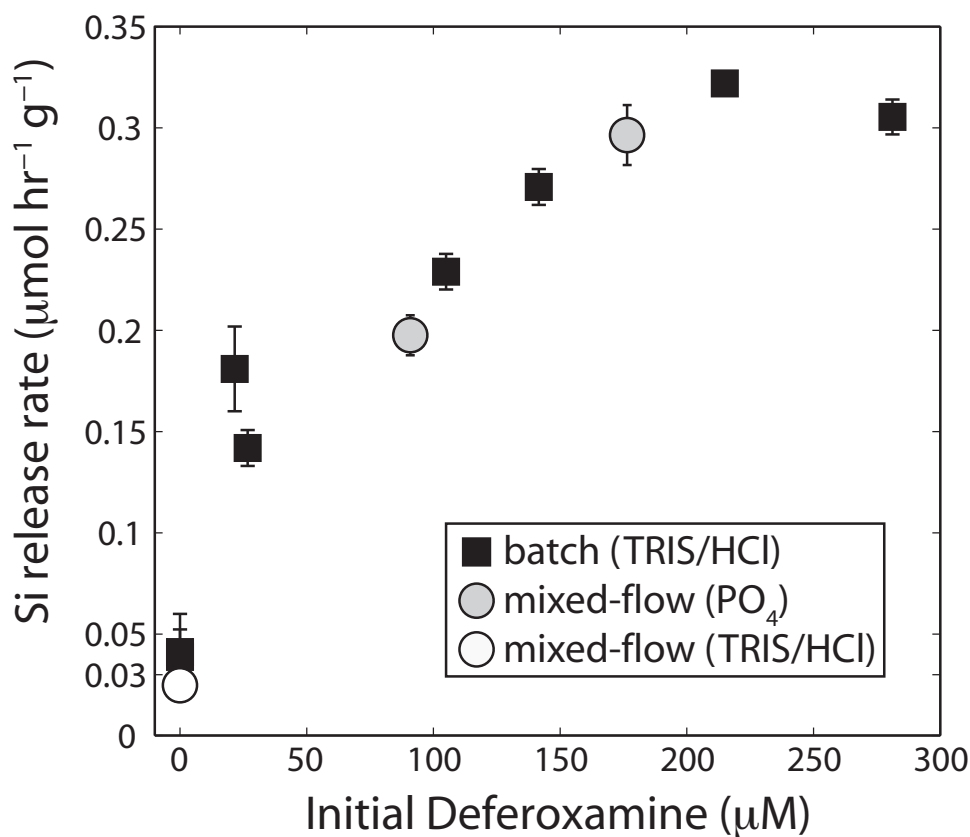

Figure 1. Silicon release rates from olivine in the presence of deferoxamine at pH ~7.5.
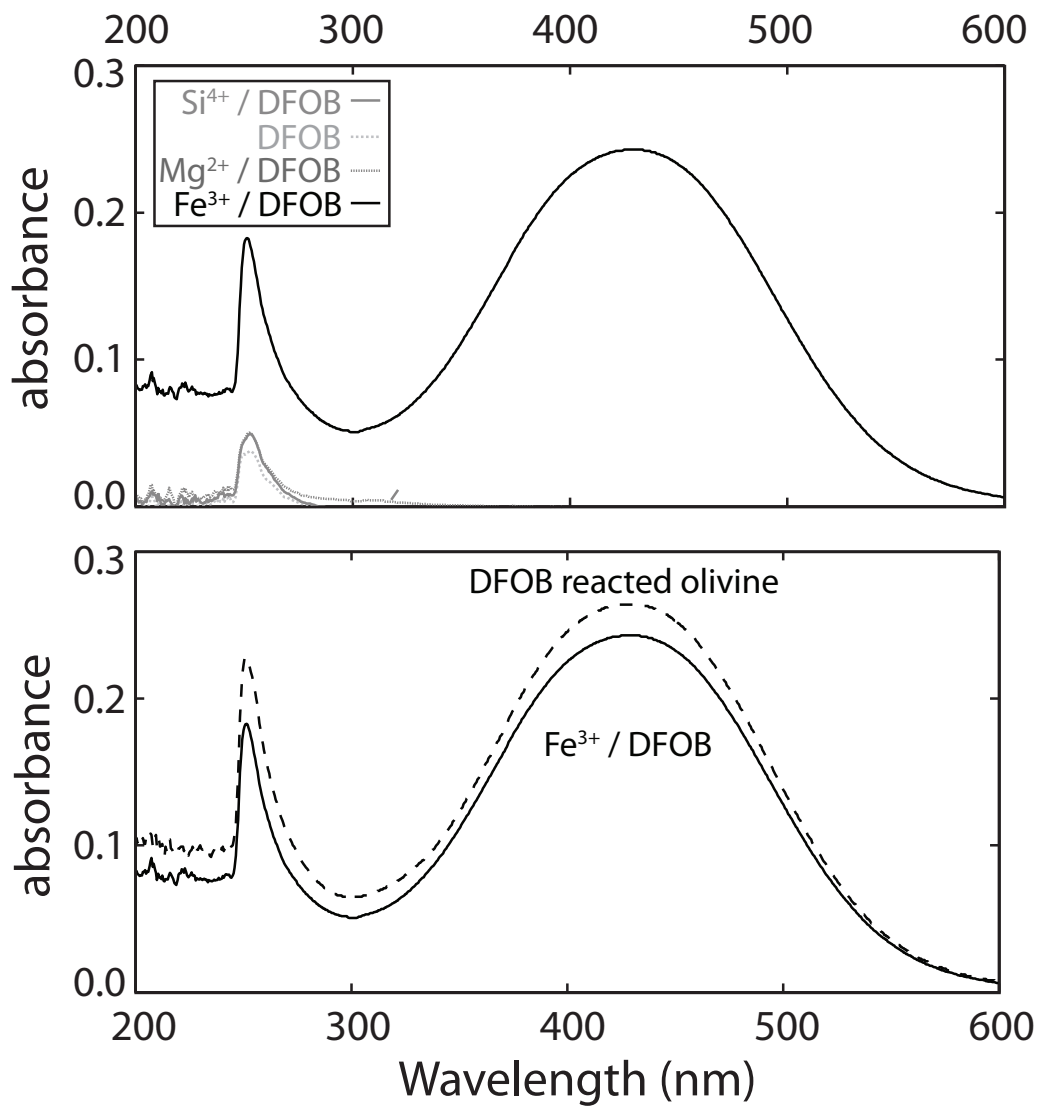
Figure 2. Absorbance spectra of Si^{4+}-DFOB, Mg^{2+}-DFOB, Fe^{3+}-DFOB, and DFOB reacted with olivine