



Measuring silicate mineral dissolution rates using Si isotope doping



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ABSTRACT

New experimental data and quantitative models show that the ²⁹Si doping experimental technique (Gruber, Zhu, and others, 2013, GCA) is robust for measuring silicate mineral dissolution rates even while a Si-containing secondary phase is precipitating. In this study, batch experiments of albite dissolution were conducted under ambient temperature and pH 3–7.5, some seeded with kaolinite. Initial solutions of various Si concentrations were doped with ²⁹Si, resulting in a Si isotopic composition highly anomalous to natural Si isotope compositions. The isotopic contrast and precision of isotope fraction analysis to ± 0.0005 to ± 0.001 allow detection of the dissolution of a minuscule amount of albite in aqueous solutions. Experimental data and quantitative modeling show Si isotope fractionation during albite dissolution ranged from $^{30}\epsilon_{\text{sol-ab}} - 2.870$ to 0.804% , significant for Si biogeochemical cycling, but resulting in only $< \pm 0.04\%$ errors in rate determination. The simultaneous precipitation of secondary phases consumed silica, causing slight changes of Si isotope ratios, but the isotopic fractionation due to secondary phase precipitation is negligible for determining albite dissolution rates. Combination of Si isotopes and Si concentrations, precisely measured with the Si isotope dilution method, allowed determination of secondary phase precipitation rates simultaneously. This means that we can now measure rates at circumneutral pH and near equilibrium conditions, even when secondary precipitates are forming. However, while the isotope doping method has greatly improved the precision and sensitivity of rate measurements, the accuracy of rate measurements is still subject to the vagaries of sample preparation and other unknown effects as shown our data near pH 5.5. When the solution is very close to equilibrium, the backward reaction becomes important and interpretation of the isotope data would be complicated or impossible.

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1. Introduction

The isotopic doping technique used in the present paper introduces an enriched rare isotope of a given element to an experimental solution interacting with a mineral or a suite of minerals that have normal or natural isotopic compositions (Beck et al., 1992; Gaillardet, 2008). Monitoring the isotopic compositions of the solution allows mineral dissolution rates to be determined with the help of the extreme sensitivity of modern mass spectrometer measurements. Because the precipitation of the isotope into secondary phases does not significantly change the isotopic ratios of the fluids, dissolution rates can be measured even when secondary phase precipitation occurs. Therefore, the method allows measurements of

reaction kinetics near equilibrium. This method has been successfully applied using ³⁹K and ⁸⁴Sr simultaneously to measure rates of dissolution of K-feldspar, biotite, and plagioclase during the hydrothermal alteration of a granite in conditions close to equilibrium (Zuddas et al., 1995; Seimille et al., 1998). Also, ⁸⁴Sr/⁸⁷Sr and ⁴⁴Ca/⁴²Ca doping was used to measure rates of calcite recrystallization and conversion from aragonite to calcite (Beck et al., 1992; Berndt and Seyfried, 1999). Finally, ²⁹Si and ³⁰Si were used to find albite dissolution rates (Gruber et al., 2013; Gruber et al., 2014; Zhu et al., 2014).

Although Si isotopes have been measured for over 50 years, the recent advances in high resolution MC-ICP-MS now allow Si isotopes to be analyzed relatively quickly, with minimal sample preparation and with a higher precision (Georg et al., 2006). The main advantage of using Si stable isotopes is that they are part of the silicate mineral structure. Here, we have utilized stable Si isotopes as a way to overcome the sensitivity issues by using “Si isotope spikes” in the initial solution in the batch reactor and by using isotope dilution method to measure the Si

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concentrations with much smaller errors than the conventional chemical analysis.

Feldspars comprise over 50% of the volume of the earth's crust. Establishing reliable rates for low-temperature feldspar dissolution is essential to quantify many fundamental geological and environmental processes. Among these are the functional relationship between silicate weathering and the global climate over geologic time (Berner and Berner, 1997), controls on surface and groundwater quality, global elemental cycling (Lasaga et al., 1994), the availability of inorganic nutrients in soils (Federer et al., 1989; Likens et al., 1998), impacts of acid mine drainage, neutralization of acid precipitation in watersheds (Drever and Clow, 1995), safety of nuclear waste repositories (Spycher et al., 2003), and geological carbon sequestration (White et al., 2003).

One outstanding problem of great significance in modern geochemistry is the apparent discrepancy between laboratory-measured and field derived feldspar dissolution rates (Velbel, 1990; Brantley, 1992; Blum and Stillings, 1995; Drever and Clow, 1995; Zhu, 2005). This discrepancy is significant, up to 2 to 5 orders of magnitude, and can lead to dramatically different modeling results. Obviously, there are several ways to frame this apparent discrepancy, as conditions under which feldspar dissolves in field and laboratory are surely different and we must take pains to ensure comparing equivalent processes and conditions. However, the resolution of this apparent discrepancy is hampered by the experimental challenges at ambient temperatures. Silicate reactions at room temperature are slow for experiments near neutral pH where most reactions occur in nature. In addition, at near equilibrium conditions, the experimental solutions are often supersaturated with secondary phases. Their precipitation depletes Si from solution, causing an apparent lower dissolution rate. New experimental techniques are needed to overcome these obstacles and resolve the apparent discrepancy.

In this paper we first present new experimental data on Si isotope doping and isotopic fractionation during albite dissolution. Then we evaluate possible interferences on determining the rates, namely (A) isotopic fractionation during albite dissolution, (B) precipitation of a Si-containing secondary phase, and (C) Si isotope fractionation during the precipitation of the secondary phase. Three conceptual models were developed, progressively including above three interferences (termed Model A, B, C), and these models were applied to the experimental data. Our results show that all three interferences have negligible effects on determination of albite dissolution rates, which makes this new experimental method particularly useful for measuring albite dissolution rates while a Si-containing secondary phase is precipitating. We further demonstrate that, together with silicon concentration data—particularly the more precise silicon concentration data from the isotope dilution method, the rate of secondary phase precipitation can also be determined from the isotope data. Finally, based on our experimental data and the above conceptual models, we predicted optimal experimental conditions for measuring silicate mineral dissolution over a wide range of rates.

2. Materials and methods

Part of the isotope doping methodology described below was described in earlier publications (Gruber et al., 2013; Lu et al., 2013). For completeness, we repeat some essential details.

2.1. Albite grains preparation

Research grade albite crystals (from Amelia Court House, Virginia, USA and from Evje, Norway) were purchased from the Ward's Natural Science Establishment, Inc. The crystals were handpicked, ground with a clean agate mortar and pestle, and subsequently dry sieved through clean copper mesh to retain the 53–106 μm fraction. For the freshly ground material, there were a large number of submicron-to-micron

particles that adhered to the surface of large grains. Dissolution of these ultra-fine particles will result in initially non-linear rates of reaction or parabolic kinetics (Holdren and Berner, 1979; Lu et al., 2013). To remove these particles, the ground feldspar sample was ultrasonically rinsed with ethanol eight times for about 20 min per treatment. The cleaned feldspar grains were then rinsed with deionized (DI) water and freeze-dried. They were examined under SEM to observe the particle morphology, size distribution, and cleaned surface (Fig. 1a). Finally, the cleaned feldspar samples were kept in an oven at 100 °C overnight to exclude all possible organic contamination and were then stored in a desiccator. See below (Section 2.7) for X-ray diffraction analysis of the samples.

2.2. Kaolinite pre-treatment

Florida kaolinite from Ward's Natural Science Establishment, Inc. and a sample of Georgia kaolinite were filtered through a 38 μm sieve using deionized water to eliminate any possible coarse grained contaminants. The remaining mixtures were then dried in an oven overnight at 100 °C. They were then mounted in separate titanium 1.5 cm front pack mounts for X-ray diffraction to determine the purity of the sample. The analysis revealed the Florida sample to be 88.12% kaolinite and 11.88% dickite and the Georgia sample to be 82.97% kaolinite and 17.03% dickite. Based on these results the Florida kaolinite was used in the experiments.

The treatment of the Florida kaolinite sample in this study followed the method described in Yang and Steefel (2008). The sample was first cleaned in order to remove amorphous oxy-hydroxide material before

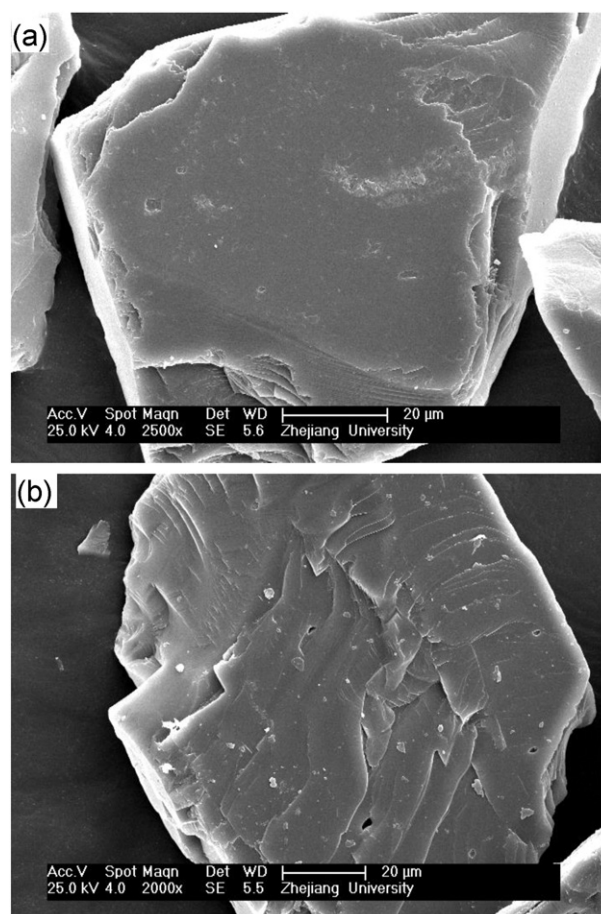


Fig. 1. FEI-SEM micrographs of albite grains pre (a) and after (b) after 60 day's reaction in pH ~5 solutions.

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