A stable isotope doping method to test the range of applicability of detailed balance

Z. Liu1,2, J.D. Rimstidt3, Y. Zhang4, H. Yuan5, C. Zhu2*

Abstract
The principle of detailed balance (PDB) has been a cornerstone for irreversible thermodynamics and chemical kinetics for a long time (Wegscheider, 1901; Lewis, 1925; Onsager, 1931), and its wide application in geochemistry has mostly been implicit and without experimental testing of its applicability. Nevertheless, many extrapolations based on PDB without experimental validation have far reaching impacts on society’s mega environmental enterprises. Here we report an isotope doping method that independently measures simultaneous dissolution and precipitation rates and can test this principle. The technique reacts a solution enriched in a rare isotope of an element with a solid having natural isotopic ratios. Dissolution and precipitation rates are found from the changing isotopic ratios. Our quartz experiment doped with 29Si showed that the equilibrium dissolution rate remains unchanged at all degrees of undersaturation. We recommend this approach to test the validity of using the detailed balance relationship in rate equations for other substances.

Introduction
The principle of detailed balance (PDB) arose from statistical and quantum mechanics in the early twentieth century to become a foundation of modern chemical kinetics (Wegscheider, 1901; Lewis, 1925; Onsager, 1931), and its wide application in geochemistry has mostly been implicit and without experimental testing of its applicability. Nevertheless, many extrapolations based on PDB without experimental validation have far reaching impacts on society’s mega environmental enterprises. Here we report an isotope doping method that independently measures simultaneous dissolution and precipitation rates and can test this principle. The technique reacts a solution enriched in a rare isotope of an element with a solid having natural isotopic ratios. Dissolution and precipitation rates are found from the changing isotopic ratios. Our quartz experiment doped with 29Si showed that the equilibrium dissolution rate remains unchanged at all degrees of undersaturation. We recommend this approach to test the validity of using the detailed balance relationship in rate equations for other substances.
for high-level radioactive waste disposal (Grambow, 1985) and geological CO₂ sequestration (Johnson et al., 2004; Marini, 2007). The operational periods of these repositories extend beyond 10,000 years and span geochemical conditions far from equilibrium to equilibrium. Failure of the detailed balance assumption would invalidate these important models (see Supplementary Information). Nevertheless, the ad hoc applications continue because of the lack of experimental techniques to test the valid range of extrapolation for the principle of detailed balance.

Here we show that recent advancements in stable isotope analysis by MC-ICP-MS and enriched isotopic standards make it possible to use an isotope doping method to determine the simultaneous dissolution and precipitation rates independently at any degree of saturation so we can validate rate equations and also test the range of applicability of the principle of detailed balance. Although our isotope doping method is applicable to many solid dissolution reactions, we demonstrate it by reacting a saturated H₄SiO₄ aqueous solution with predominantly ²⁸SiO₂ (quartz).

Quartz makes up about 20 % of the earth’s crust and there are many implications for its rate of reaction with aqueous solutions. The simultaneous dissolution and precipitation reactions that occur as solids equilibrate with solution are typically modelled with a two-term rate equation. For example, quartz dissolves in water by the reaction

\[ \text{SiO}_2(\text{qz}) + 2 \text{H₂O}(l) = H_2\text{SiO}_4(\text{aq}) \]  

(Eq. 3)

and the rate of change of silica concentration can be expressed as.

\[ r = k_4 a_{\text{SiO}_2} a_{\text{H}_2\text{O}}^2 - k_5 a_{\text{H}_4\text{SiO}_4} = k_4 - k_5 a_{\text{H}_4\text{SiO}_4} \]  

(Eq. 4)

where the activities of SiO₂ and H₂O equal one. The two rate constants cannot be uniquely defined by measuring only the rate of change of elemental silica concentration. This problem is typically circumvented by using the principle of detailed balance to recast the rate equation in terms of one rate constant and the known equilibrium constant \( K = k_4/k_5 \) (Rimstidt and Barnes, 1980).

\[ r = k_4 \left( 1 - \frac{a_{\text{H}_4\text{SiO}_4}}{K} \right) \]  

(Eq. 5)

However, this approach is valid only if the rate-limiting step (and therefore \( k_4 \) and \( k_5 \)) remains unchanged when the reaction departs from equilibrium. Etch pits (Bantley et al., 1986; Lüttge, 2006) and “leached or re-precipitated layers” (Hellmann et al., 2003), which are not present at equilibrium, suggest that the extrapolation of equilibrium rate constants to highly undersaturated solutions may not be justified. Testing the applicable range for the PDB in cases affected by these and other complications will be difficult. Quartz was chosen for this test of the utility of the isotope doping method because there is good evidence that the PDB is valid over the entire range of undersaturation. Berger et al. (1994) showed that quartz dissolution rates fit Equation 5 and Rimstidt and Barnes (1980) showed that they also fit Equation 4.

### Methods

We tested the validity of Equations 4 and 5 using a stable isotope doping experiment. The silicon in quartz has three stable isotopes and the natural quartz used in our experiments has an isotopic composition of 91.232 % ²⁸Si, 5.410 % ²⁹Si, and 3.3585 % ³⁰Si. In our Type 1 equilibrium experiments a solution initially containing nearly 100 % ²⁸Si was maintained at or near equilibrium with quartz and sampled periodically to find the ²⁸Si and ²⁹Si concentrations. We used the initial rate method (Rimstidt, 2013) to find the rate of appearance of ²⁸Si in solution, which gives the dissolution rate at equilibrium, and the rate of disappearance of ²⁹Si, which gives the precipitation rate at equilibrium. The Si isotope abundances in the experimental solutions evolved significantly over the course of experiments but the initial rate method determined the rate at zero time thereby avoiding complications associated with minor but measurable isotopic fractionation.

Two types of experiments were carried out in this study. Type 1 experiments were conducted at equilibrium conditions where the solution was saturated with respect to quartz and Type 2 experiments were performed at far from equilibrium conditions where the initial solution contained no dissolved silica. Type 1 and Type 2 dissolution experiments were both batch reactor experiments conducted at 50 ± 1 °C. The starting solution for Type 1 experiments contained 340 μM ²⁸SiO₂, which is the solubility of quartz at 50 °C (Rimstidt, 1997), and the solution was reacted with an ion exchange resin to remove cations that would catalyse the quartz dissolution rate. These solutions remained within ±0.3 kJ/mol of equilibrium throughout the experiments. The starting solution for the Type 2 dissolution experiments was deionised water. The pH of the starting solutions was near 5.5 for both types of experiment. More detailed analytical methods are described in the Supplementary Information section.

### Results

Figure 1 shows the fractional Si isotope concentrations versus time for the Type 1 equilibrium experiments and Table 1 gives the rates derived from all of the experiments. Figure 2 shows that the dissolution and precipitation rates are essentially the same, thus demonstrating that we have measured the dissolution rate constant at equilibrium. Furthermore, Figure 2 shows that the Type 2 far from equilibrium (no dissolved silica) dissolution rates (Q₂ experiments) were essentially the same as the equilibrium (saturated solution) rates. The dissolved silica activity in the Type 2 experiments was zero for the initial rate. Inserting that
value into either Equation 4 or 5 shows that the initial rate equals the dissolution rate constant. This means that the dissolution rate constant ($k_+$) is the same at zero silica concentration as it is at equilibrium.

**Figure 1** Si isotope fractional abundances in experimental solutions over time. The solution was saturated with quartz and doped with nearly 100% $^{29}$Si. The first sample was taken after 15 minutes. The increase of $^{28}$Si concentration (fractional abundance times dissolved elemental Si concentration) is due to the dissolution of quartz while the decrease of $^{29}$Si abundances and concentrations is due to the precipitation of quartz. The reaction rates given in Table 1 are based on the slopes of the trends extrapolated to zero time.

**Table 1** Rate of quartz dissolution and precipitation at equilibrium based on the rate of appearance of $^{28}$Si and disappearance of $^{29}$Si respectively, and the far from equilibrium dissolution rate for solutions containing no dissolved silica.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Dissolution rate</th>
<th>Precipitation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol/m²/sec</td>
<td>mol/m²/sec</td>
</tr>
<tr>
<td><strong>Type 1 Equilibrium experiments</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q1-1</td>
<td>$7.05 \times 10^{-13}$</td>
<td>$8.40 \times 10^{-13}$</td>
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<tr>
<td>Q1-2</td>
<td>$6.83 \times 10^{-13}$</td>
<td>$7.75 \times 10^{-13}$</td>
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<td>Q1-3</td>
<td>$7.65 \times 10^{-13}$</td>
<td>$9.39 \times 10^{-13}$</td>
</tr>
<tr>
<td>Q1-4</td>
<td>$3.95 \times 10^{-13}$</td>
<td>$5.64 \times 10^{-13}$</td>
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<td>Q1-5</td>
<td>$6.12 \times 10^{-13}$</td>
<td>$7.51 \times 10^{-13}$</td>
</tr>
<tr>
<td>Average</td>
<td>$6.32 \times 10^{-13}$</td>
<td>$7.74 \times 10^{-13}$</td>
</tr>
<tr>
<td>±std dev</td>
<td>$±1.43 \times 10^{-13}$</td>
<td>$±1.38 \times 10^{-13}$</td>
</tr>
<tr>
<td><strong>Type 2 Far from equilibrium experiments</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q2-1</td>
<td>$8.32 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>Q2-2</td>
<td>$6.11 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>Q2-3</td>
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<td></td>
</tr>
<tr>
<td>Q2-4</td>
<td>$6.66 \times 10^{-13}$</td>
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</tr>
<tr>
<td>Q2-5</td>
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<td>Average</td>
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</tr>
<tr>
<td>±std dev</td>
<td>$±0.88 \times 10^{-13}$</td>
<td></td>
</tr>
</tbody>
</table>

**Discussion and Conclusions**

Our results show that $k_+$ at zero silica concentration is the same as at equilibrium so we conclude that the $k_+$ determined at equilibrium is valid at all degrees of undersaturation. This has important implications for predicting rates over a wide range of conditions as explained by Schott *et al.* (2009).

Another application of our experimental results is the validation of equilibrium constants for quartz solubility. Rimstidt (1997) measured quartz solubility at 25, 50, 75, and 96 °C in experiments up to 4917 days. These long-term experimental data formed the basis for establishing quartz solubility as a function of temperature, and also for deriving the standard thermodynamic properties for aqueous species $H_4SiO_4$(aq) (Rimstidt, 1997; Stefansson, 2001). However, all experiments approached the quartz solubility from undersaturation and the reverse experiments – precipitation from oversaturation is far more complicated experimentally. Applying Equation 1, we found that the log $K$ value for reaction (3) at 50 °C in pure water is -3.50, which is within the experimental uncertainties in Rimstidt (1997).
Applying our isotope doping method to quartz reaction rates and solubility is an obvious first step, and the results are confirmatory rather than contradictory to experimental data from conventional methods, which give us confidence to apply the $^{29}$Si method used in this study to investigate reactions of the other silicate minerals. Experiments for multicomponent silicate minerals often involve changes of reaction schemes in response to departure from equilibrium (Beig and Lützge, 2006), and a poorly understood “leached” or “re-precipitated” layer can be developed (Hellmann et al., 2003). Aluminium may inhibit dissolution (Oelkers et al., 1994), and other non-equilibrium surface features may occur so that the far from equilibrium dissolution and precipitation reaction paths can involve different pathways. However, Zhu et al. (2014) showed that this method was promising to measure albite dissolution rates very close to equilibrium, and the interferences of secondary phase precipitation and isotope fractionation was negligible. Detailed investigation of these multicomponent silicate minerals that make up the majority of Earth’s crust is the logical next step.

In theory, our isotope doping method can be applied to many solids to test the range of validity of the near equilibrium rate constants. ICP-MS technology eases the analytical problems associated with using this experimental design for a wide range of non-silicate minerals and solids using the increasing number of non-traditional stable isotopes (such as Mg, Fe, Li). Therefore, the application of this method is not limited to geochemistry, but can be used in chemistry, chemical engineering, and environmental sciences as well.

The utility of the principle of detailed balance does not only rest on predicting rate constants or equilibrium constants. Lasaga (1981) gives examples of predicting rate laws, the Arrhenius pre-exponential constants, and activation energy. Our experiments on quartz show the potential for harnessing the power of PDB for obtaining more kinetic parameters in geochemistry. Equally important is that the legitimacy of the extrapolation of PDB rate constants now can be experimentally tested for reactions where the PDB extrapolation has been used to model geological and environmental processes without due reckoning of its applicability.

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Author Contributions

JDR and CZ developed the concept, designed the study, interpreted the data, and wrote the manuscript. ZYL carried out the experiments, YLZ participated in the interpretation of the data, and HLY developed method and performed the Si isotope analysis.

Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1608
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References


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Supplementary Information

The Supplementary Information includes:

- Supplementary Methods and Results
- Supplementary Information References

Supplementary Methods and Results

Derivation of the $K = k_+ / k_-$ and $R = f(\mu)$ relationships

Aagaard and Helgeson (1982) derived a rate equation that relates the time rate of change of reaction progress ($\xi$) to the reaction affinity ($A$), where reaction affinity equals negative chemical potential ($\mu$).

$$\frac{d\xi}{dt} = k s \left( \prod_i \frac{a_i - \xi}{a_i} \right) \left( 1 - \exp \left( -\frac{A/\sigma}{RT} \right) \right)$$

(Eq. S-1)

where $k$ denotes the rate constant (mol m$^{-2}$ s$^{-1}$), $s$ the surface area (m$^2$ mol$^{-1}$), $R$ the gas constant, $T$ temperature (K), and $\sigma$ the Tomkin’s average stoichiometric number. Both the chemical potential $\mu$ and chemical affinity $A$ have the unit of J mol$^{-1}$. This equation is sometimes called a “transition state theory rate law” even though the Aagaard and Helgeson (1982) paper makes only a passing mention

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of transition state theory and the derivation is actually based on the principle of detailed balance and Temkin’s average stoichiometric number (see Equations 18 and 20 in Aagaard and Helgeson, 1982).

This section shows how Equation S-1 is related to the principle of detailed balance. A key, but underappreciated, assumption in this derivation is that the reaction mechanism for the rate-determining step does not change when the reaction departs from equilibrium. As long as that assumption is true, the $K = k_+/k_-$ relationship derived below, can be used in rate equations for reactions that are not at equilibrium. However, if the reaction mechanism changes when the reaction departs from equilibrium then $k_+/k_-$ $\neq$ $K$ (see for example p. 287 in Laidler, 1987) and Equation S-1 is not valid.

The principle of detailed balance recognises that at equilibrium the rates of the forward and backward reactions must be equal. The consequences of this relationship are illustrated here by considering a simple reaction between two species: A and B (e.g., quartz and H$_3$SiO$_4$(aq)).

$$A \xrightarrow{r_+} B$$

The forward reaction rate ($r_+$) is the product of the forward rate constant ($k_+$) and the activity of species A.

$$r_+ = \frac{dA}{dt} = k_+ a_A$$

The backward reaction rate ($r_-$) is the product of the backward rate constant ($k_-$) and the activity of species B.

$$r_- = \frac{dB}{dt} = k_- a_B$$

The overall reaction rate ($R$) is the difference between these two rates.

$$R = r_+ - r_- = k_+ a_A - k_- a_B$$

At equilibrium the forward reaction rate exactly equals the backward reaction rate so that the net rate ($R$) is zero. If $r_+$ = $r_-$ then $k_+ a_A,eq = k_- a_B,eq$ and because $K = a_A,eq/a_B,eq$ we find that $K = k_+/k_-$. This equation is analogous to Equation 30 in Aagaard and Helgeson (1982) except that in their equation the activity of A is raised to a power due to their incorporation of the Temkin average stoichiometric number. That allowed them to generalise to a chain reaction rather than a single step reaction as shown here. See Boudart (1976) and Hollingsworth (1957) for very similar derivations.

Many rate equations assume that the reaction mechanism for the rate-determining step for the equilibrium reaction remains the same at non-equilibrium conditions and that means that $k_+$ and $k_-$ are the same at non-equilibrium conditions. This allows Equation S-5 to be written in terms of the activity ratio, Q ($= a_A/a_B$).

$$R = k_+ a_A \left(1 - \frac{k_- a_B}{k_+ a_A}\right) = -k_+ a_A \left(1 - \frac{Q}{K}\right)$$

(Eq. S-7)

The differential rate equation for silica dissolution (Equation 33 in Rimstidt and Barnes, 1980) has this form. This equation can be further transformed by expressing the chemical potential driving the reaction as a function of $Q/K$.

$$\Delta \mu_r = RT \ln \left(\frac{Q}{K}\right)$$

(Eq. S-8)

$$Q = e^{\Delta \mu_r / RT}$$

(Eq. S-9)

Substituting Equation S-9 into Equation S-7 gives the reaction rate as a function of the chemical potential driving the reaction.

$$R = k_+ a_A \left(1 - e^{\Delta \mu_r / RT}\right)$$

(Eq. S-10)

This relationship can also be written in terms of affinity ($A = -\mu$).

$$R = k_+ a_A \left(1 - e^{-A / RT}\right)$$

(Eq. S-11)

Analytical Methods

The Iota STD quartz (106–180 μm) from Unimin Corporation, New Canaan, CT, USA was used in the experiments. All of the peaks visible on the X-ray diffraction patterns were from quartz. The quartz grains were washed with deionised water to remove fine particles and then the disturbed surface layer was removed by leaching in 65°C deionised water for 4 weeks. The leaching bottle was stirred twice a day by inverting and the water was changed once a week. After 4 weeks, the quartz was recovered and washed four times with deionised water and then rinsed twice with ethyl alcohol. The quartz was air dried on aluminium foil at room temperature. The specific surface area of the quartz powder was determined using the N$_2$ BET method (Brunauer et al., 1938).
The NaOH fusion method was used to prepare the $^{29}\text{SiO}_2$ solution. We mixed $0.0488 \pm 0.001$ g of $^{29}\text{SiO}_2$ powder ($0.04\%$ $^{28}\text{Si}$, $99.90\%$ $^{29}\text{Si}$, and $0.06\%$ $^{30}\text{Si}$ from Isoflex, San Francisco, CA, USA) and $0.3200 \pm 0.001$ g of NaOH in a silver crucible and then fired the crucible at $730 \degree\text{C}$ in a muffle furnace for 10 min. After slight cooling, the crucible contents were dissolved into 30 mL deionised water and washed with 470 mL deionised water into a Teflon bottle. This solution was diluted to produce a solution with $97.6$ ppm $^{29}\text{SiO}_2$. Sodium was removed from this solution using a Bio-Rad cation exchange resin AG 50W-X8 (100–200 mesh) in H$^+$ form distributed as a 1.8 mL resin bed in each of seven Bio-Rad columns. The resin was prepared by rinsing it with 50 mL of 1 M HCl. Before loading the sample on the resin, the pH was adjusted to near 5.5 to ensure complete removal of any acids. Each column treated 31 mL of the $97.6$ ppm $^{29}\text{SiO}_2$ solution. Then an additional 4 mL of deionised water was passed through each column. The effluent solution was diluted to 1 L so that the final cation free solution with a pH of 5.28 had a $^{29}\text{SiO}_2$ concentration of 21 ppm.

Each experiment consisted of 10 leak-proof 30 mL polyethylene bottles each containing 30 g of quartz grains and either 15 mL of the 21 ppm $^{29}\text{SiO}_2$ solution or deionised water. The bottles were stirred twice per day by inverting. Five replicates of each experiment type were run. At the predetermined sampling time, a bottle was opened and the solution was recovered using a vacuum filter system ($0.45 \mu\text{m}$ nitrocellulose sterile analytical filter). Part of the solution was used for a pH measurement and the remainder was stored in a refrigerator at $4.0 \degree\text{C}$ until analysis. The silica concentration of the solution samples was measured using the molybdate blue method (Govett, 1961). The precision of this method in our laboratory is about $\pm 4\%$.

The Si isotope abundances were measured using high-resolution multiple-collector inductively coupled plasma mass spectrometry (HR-MC-ICP-MS, Nu Plasma II, Wrexham, UK) at Northwest University, China. Blank samples were filled with ultrapure deionised water, and acidified with ultrapure HNO$_3$. The $^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$ abundances were measured using Faraday cups under static mode. Instrumental sensitivity was $-11\text{V}/\mu\text{g g}^{-1}$ for $^{28}\text{Si}$ in high-resolution mode. Sample solution was introduced into MC-ICP-MS using a dry aerosol system (Aridus II, Cetac, USA) and a 100 $\mu\text{L min}^{-1}$ PFA micro-flow nebuliser. We used standard bracketing method (Alfa Aesar Si, Stock# 38717, LOT 591543G) to calculate $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ and every sample was measured three times using the Time-Resolved-Analysis (TRA) method. The relative standard deviation (RSD) of the three ratios was used to evaluate the data quality. Only those analyses with RSDs ($\delta^{29}\text{Si}$) < 10% were reported and samples with RSDs ($\delta^{30}\text{Si}$) > 10% were re-measured.

**Supplementary Information References**


