GEOCHIMICA et COSMOCHIMICA ACTA

TITLE: Experimental study of epidote dissolution rates from pH 2 to 11 and temperatures from 25 to 200 °C

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KEYWORDS:

Epidote

Experiments

Dissolution rates

Mafic alteration

Aluminosilicate minerals

ABSTRACT

The dissolution rates of Green Monster Mine epidote at temperatures of 25, 100 and 200 °C, and over the pH range 2-11, were determined from far-from equilibrium experiments performed in both batch and mixed-flow reactors. Epidote dissolution rates based on silicon release decrease with increasing pH to pH ~8, then increase in response to further pH increases. The apparent relative metal release rates from epidote at chemical steady-state were found to vary with pH and temperature, in part due to secondary phase formation. At 100 and 200 °C, Al is preferentially released relative to Si at alkaline pH, but preferentially retained by the solid at 2<pH<8. This behaviour is interpreted to stem from the precipitation and re-dissolution of Al oxy-hydroxides such as boehmite, diasporite, and gibbsite, as observed in solids recovered after the experiments. Calcium tends to be preferentially released compared to Si and Al at acidic and near to neutral pH. Iron was found to be retained in the solid phase due to the prompt formation of secondary Fe minerals. Nevertheless, neither the dissolution of 20 wt% of the initial epidote mass nor the formation of secondary phases on the epidote surface substantially changed epidote dissolution rates. As epidote i) is almost three times more Ca-rich than a typical basaltic glass, ii) preferentially releases Ca at pH typical of CO₂-charged water injections, and iii) exhibits increasing dissolution rates as pH increases at alkaline conditions, it seems likely that the presence of epidote in altered basalts may be beneficial for the formation of calcite and other Ca-carbonates during mineral carbonation efforts. In addition, the relatively rapid rates of epidote dissolution at acidic conditions suggest that epidote has a significant role in the weathering of altered mafic rocks.

1. INTRODUCTION

Epidote ($\text{Ca}_2\text{FeAl}_2(\text{SiO}_4)_3(\text{OH})$) is a common secondary alteration mineral often found in veins or replacing plagioclase in hydrothermally altered basic igneous rocks at temperatures of 200 to 400 °C (e.g., Kristmannsdóttir, 1979; Seyfried et al., 1988). Epidote is also a major phase in low to medium grade regional and contact metamorphic rocks (Grapes and Hoskin, 2004). Epidote dissolution plays a role in a number of natural and industrial processes. In nature, it can influence the weathering of volcanic terrains (Sverdrup, 1990; Sverdrup and Warfvinge, 1995) as well as the water chemistry in geothermally active areas at high temperature (Bird and Spieler, 2004). Epidote dissolution can also promote subsurface mineral carbonation efforts by releasing Ca into the fluid (Marieni and Oelkers, 2018; Oelkers et al., 2008a).

Relatively few studies have experimentally measured epidote dissolution rates (Blanchard, 1994; Kalinowski et al., 1998; Nickel, 1973; Rochelle, 1990; Rose, 1991; Sverdrup, 1990), and fewer explored these rates at alkaline conditions (see **Table 1**). Dickson-type autoclave experiments at 250 °C and 500 bars performed by Blanchard (1994) and Rochelle (1990) showed that Ca and Si are the main cations released to the aqueous fluid phase, whereas liberated Al and Fe tend to precipitate as sparingly soluble secondary phases such as Al oxy-hydroxides and hematite, respectively, in oxic and near to neutral pH conditions. These studies also highlighted how fluid composition changes can alter the epidote dissolution mechanism and can accelerate its dissolution. For example, Blanchard (1994) reported that adding fluoride to the aqueous solution increased the Al release rate from epidote due to the formation of strong aqueous AlF complexes. Kinetic studies at lower temperatures (≤ 90 °C) demonstrated that epidote dissolution rates vary with fluid pH, with more rapid rates observed at low and high pH, and the slowest rates were measured at near to neutral conditions (Kalinowski et al., 1998; Nickel, 1973; Rose, 1991; Sverdrup, 1990). Rose (1991) reported that epidote dissolution at 90 °C and $\text{pH} < 7$ is stoichiometric with respect to Si, Al, and Ca. At $\text{pH} > 7$, this author observed an initial preferential release of Al and Si, suggesting the formation of a Ca-enriched surface layer. Contrasting results were reported by Nickel (1973) and Sverdrup (1990), who observed the preferential release of Al and Ca from epidote at acidic conditions. Kalinowski et al. (1998) found that in experiments at 25 °C, some cations are preferentially released in fluids with $\text{pH} < 7$ in the order $\text{Ca} > \text{Si} > \text{Fe} > \text{Al}$. Such observations suggests that i) Ca ions in the interchain position are the most easily released from the epidote structure, ii) Si is released from the framework during a surface protonation reaction, iii) Al ions, having high degrees of polymerisation, are the most firmly bound cations, and iv) the dissolution behaviour of epidote is often incongruent and overall a complex process. Similar conclusions were reached by Barman et al. (1992)

during their study on the effect of selected aqueous organic acids on the weathering of silicate minerals.

This study builds upon these past efforts by systematically measuring the dissolution rates of epidote as a function of temperature from 25 to 200 °C, and pH from 2 to 11. The goals of this work are 1) to complement the existing knowledge on epidote with further experimental data towards developing a predictive equation describing epidote dissolution rates, and 2) to use these results to assess the consequences of epidote dissolution rates on natural geochemical phenomena and industrial processes.

2. MATERIAL and METHODS

2.1. Starting solutions and materials

Experiments in this study were performed in batch and mixed-flow reactors with selected reactive fluids. All initial reactive fluids were prepared from reagent grade chemicals (HCl, NaOH, NaCl, and NaHCO₃) and ultrapure water (18.2 MΩ cm⁻¹ at 25 °C, Millipore), with pH ranging from ~2 to ~11. The compositions of these fluids are reported in **Table 2**. All initial reactive fluids had low ionic strength (<0.1 M) to minimize possible effects of ionic strength on measured dissolution rates.

The epidote used for all the dissolution experiments originated from the Green Monster Mine, Alaska, USA. This mineral sample is relatively free of defects and impurities. Epidote is a monoclinic calcium silicate and a member of the sorosilicate group (**Figure 1**). Its structure is characterized by two linked silicate tetrahedra (Si₂O₇), along another single Si-tetrahedron and continuous chains of Al-octahedra. The chemical composition of this epidote was determined by X-ray fluorescence spectrometry (XRF) using a S2 ranger Bruker spectrometer; this composition is provided in **Table 3** and consistent with Ca_{2.07}Al_{2.00}(Al_{0.08}Fe³⁺_{1.02}Mn_{0.01}K_{0.01}S_{0.01}Ti_{0.01})Si_{3.00}O₁₂OH, which conforms closely with the idealized epidote formula. The epidote sample was manually ground and sieved to obtain the grain size fraction between 20 and 100 μm (**Figure 2**). The 20-100 μm sample was ultrasonically cleaned in alcohol and rinsed repeatedly with deionized water to remove fine particles before being dried at 50 °C. Its specific surface area was measured by multipoint Krypton adsorption BET method using a Quantachrome Autosorb-1MP, and determined to be 863±5% cm²/g (correlation coefficient 0.9997). Its geometric specific surface area was calculated to be 350 cm²/g, assuming that grains are smooth spheres with a 50 μm diameter (Tester et al., 1994).

2.2. Experimental methods

Epidote steady-state far-from equilibrium dissolution rates were determined from Si release rates as function of pH and temperature. At 25 °C, these experiments were performed in batch reactor systems due to the relatively slow reaction rates. At 100 and 200 °C, rates were measured using the mixed-flow reactor system illustrated in **Figure 3**. The initial conditions of all experiments are listed in **Table 2**.

Batch reactor experiments

Batch-reactor experiments were performed in 250 mL Azlon polypropylene reactors, each loaded with ~2 g of 20-100 µm sized epidote, ~150 g of initial aqueous reactive fluid, and a floating polytetrafluoroethylene (PTFE)-coated magnetic stir bar. The reactors were covered with custom-made polyether ether ketone (PEEK) lids with two sampling ports: one for the collection of liquid samples (~1 mL each) for elemental analysis via a 0.2 µm PTFE filter and syringe, and a second for *in situ* pH measurements. All batch reactors were immersed in a water bath, which i) was held at a constant temperature of 25±0.2 °C by a thermostat control system, and ii) was positioned on a magnetic stir plate to keep the epidote powder in suspension by stirring at ~200 rpm.

Each batch reactor was cleaned with ultrapure water and ethanol before each experiment. At the end of batch experiments, the solid reaction products were separated from the liquid by filtration through a 0.45 µm cellulose acetate membrane, rinsed with ultrapure water, and dried at room temperature. All filtered fluid samples were acidified with 0.3% Suprapur HNO₃ prior to storage and elemental analysis.

Mixed-flow reactor experiments

Mixed-flow reactor experiments were performed in 200 mL titanium Parr™ reactors, each loaded with ~1 g of the 20-100 µm sized epidote and ~200 g of ultrapure water. A high pressure liquid chromatography (HPLC) pump injected the inlet fluid into the reactor at a flow rate of ~0.25 g/min (uncertainty ±2%); under these conditions, the time required to completely exchange the fluid in the reactor, known as residence time, was approximately 13 h. The fluid exited the reactor through a 2 µm titanium filter positioned inside the reactor, an external cooling system, and a back pressure regulator. The back pressure regulator was loaded with argon to a pressure of 2 or 22 bar for the 100 or 200 °C experiments, respectively, to avoid water vaporisation inside the reactor. A heater was used to maintain the experimental temperature at 100 or 200 °C, and a thermocouple placed in a thermowell monitored the temperature inside the reactor with an uncertainty of ±1 °C. A mechanical stirring system, consisting of an external stirring motor connected to a titanium magnetic drive and impellor located inside the reactor, kept the epidote grains in suspension at a

149 stirring rate of ~200 rpm. All the other components of the system in contact with the fluid
150 including tubing and valves were made of titanium.

151 Before each individual experiment or experimental series, the reactor was first cleaned
152 with ultrapure water and ethanol, followed by filling it with ultrapure water and heating it up to
153 200 °C for several days. Each experiment was started by placing epidote and ultrapure
154 water into the reactor, closing the reactor, and starting both the stirrer and the HPLC pump.
155 Once the target pressure was reached, the reactor was heated to the desired temperature,
156 which was reached within approximately 1 h in all experiments. The first liquid samples were
157 taken after ~24 h, and the residence time was ~13 h. Further samples were collected over
158 time. Such samples were collected over at least three residence times to assure the reactor
159 fluid was completely mechanically mixed (Oelkers and Gislason, 2001). Once three
160 consecutive samples were found to have identical outlet fluid Si concentrations within
161 analytical uncertainties, Si steady-state release rates were assumed and the experiment
162 stopped. Fluid samples were collected in three separate polypropylene vials. Two non-
163 acidified samples (~1 g each) were taken for pH measurement at room temperature and Si
164 analysis, followed by a ~10 g sample for elemental analysis; this latter sample was acidified
165 with 0.3% Suprapur HNO₃ to avoid precipitation of solid phases due to temperature and
166 pressure changes. After the completion of an individual experiment or an experimental
167 series, the reactor was opened and the solid reaction products were separated from the
168 liquid by vacuum filtration through a 0.45 µm cellulose acetate membrane, rinsed with
169 ultrapure water, and dried at 50 °C.

170 The experiments run at 100 °C were performed in series, a common technique in
171 mineral and rock dissolution studies (e.g., Flaathen et al., 2010; Gudbrandsson et al., 2011;
172 Saldi et al., 2010) that optimizes time and repetition of work. Ten consecutive dissolution
173 experiments were performed on a single epidote powder sample. The series was started by
174 placing the epidote powder into the titanium mixed-flow reactor, and sealing it. The first inlet
175 fluid was passed through the reactor at a constant flow rate until Si steady-state outlet fluid
176 compositions were observed, as described above. After the attainment of steady-state, the
177 inlet fluid composition was changed to a fluid of different composition and a new experiment
178 started. The first inlet solution in the series had a pH of 2, and subsequent inlet solutions had
179 increasingly higher pH, up to pH 11. After the pH 11 experiment, a duplicate run was made
180 with a pH 2 inlet solution to verify that the running of these experiments in series and the
181 potential precipitation of secondary minerals did not affect the measured epidote dissolution
182 rates. Experiments at 200 °C were run individually because at this temperature epidote
183 would dissolve too quickly to be reused in a succeeding experiments. For each of these
184 experiments freshly cleaned epidote powder was reacted with a single inlet fluid until steady-

state Si concentrations were observed in the outlet fluid. After the attainment of steady-state, the reactor was emptied and the solids collected for further analysis. Each experiment was stopped before 10 wt% of the initial epidote was dissolved.

2.3. Analyses

The fluids from the batch reactor experiments, along with inlet and outlet fluids of mixed-flow reactor experiments were analysed for their pH and Si concentrations. Liquid pH was measured using an Orion ROSS Ultra™ pH electrode connected to a Hanna Instruments™ pH meter. The electrode was calibrated using NIST pH 4.01, 7.00 and 10.01 buffer solutions, and replicate analyses of buffers and samples showed analytical accuracy of 0.03 pH units and precision of ± 0.02 pH units at room temperature. For the 25 °C experiments, the fluid pH was measured *in situ*, whereas the *in situ* pH of the fluids from the experiments at 100 and 200 °C was recalculated from the 25 °C pH measurements using PHREEQC v3 (Parkhurst and Appelo, 2013), together with its *carbfix.dat* v1.1 thermodynamic database (Voigt et al., 2018). The same approach was used to calculate the saturation indices of potential secondary phases. Silicon concentrations of the collected fluids in each experiment were measured daily by colorimetry using the molybdate blue method (Strickland, 1952) following the procedure of Tréguer and Le Corre (1975). Measured Si concentrations have an uncertainty (two standard errors) of $\pm 5\%$ for measurements between 0.05 and 10 ppm. Selected output solutions from each experiment were also analysed for Ca, Al, Fe, and Si concentrations using a Horiba Ultima Expert Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), with an analytical accuracy within 3% and precision better than $\pm 3\%$, as determined by replicate analyses of certified solutions and samples, respectively. Detailed information on detection limits and data uncertainties are given in Electronic Supplementary 1 and 2, respectively. Given the lower uncertainty of ICP-OES analyses, they were preferred over colorimetric measurements to calculate elemental release and epidote dissolution rates. For the case of batch reactor experiments at 25 °C, samples for spectrometric analyses were taken only at the end of the experiments as not to significantly alter the water-rock ratio in the reactors by sampling. As such, epidote dissolution rates from these experiments were calculated using Si colorimetric results. Nevertheless, the two methodologies for aqueous Si concentration measurement are in close agreement, with a coefficient of determination R^2 of 0.99 (Electronic Supplementary 3).

Microscopic analyses on the fresh epidote powder and the solid reaction products recovered from the reactors after each experiment were performed with a Jeol JSM7800F

scanning electron microscope (SEM) equipped with an electron dispersive spectroscope (EDS).

2.4. Calculation of steady-state epidote dissolution rates

Epidote dissolution rates (r) from the results of batch reactor experiments were calculated from measured reactive fluid Si concentrations by first calculating the slope a of a least-squares fit of the total mass of Si in the fluid, n_{Si}^{aq} , as a function of elapsed time t . Here, n_{Si}^{aq} was calculated by multiplying the aqueous Si concentration by the mass of the fluid in the reactor at the time of the sampling, which was monitored throughout the entire duration of the experiments. In total, less than 10 wt% of the reactive fluid was removed during sampling from each experiment. Rates were then calculated using

$$r = \frac{a}{3.0 * A * m} \quad (1)$$

where 3.0 corresponds to the stoichiometric number of moles of Si in each mole of epidote, A denotes the specific BET surface area of the epidote in the reactor, and m stands for the initial mass of epidote in the reactor. Rates in this study were normalized to the measured BET specific surface area to allow their direct comparison with literature data.

Steady-state epidote dissolution rates for mixed-flow reactor experiments were determined using

$$r = \frac{F * c_{Si}}{3.0 * A * m} \quad (2)$$

where F refers to the fluid flow rate, c_{Si} designates the concentration of Si in the outlet fluid, and 3.0 again corresponds to the Si stoichiometric number of moles of Si in one mole of epidote. The fluid flow rate was monitored throughout the experiments, and the mass of epidote dissolved during each experiment was determined from mass balance calculations. Note that for the experimental series at 100 °C, the epidote mass at the beginning of each experiment of the series was calculated, based on the mass of Si released from the reactor during the previous experiments of the series. This calculated mass was used for rate calculations using Equation 2.

3. RESULTS

3.1. Temporal evolution of reactive fluid compositions

The Si composition and pH of the reactive fluids during the 25 °C batch reactor experiments evolved significantly (**Table 4, Figure 4**). Silicon concentrations rapidly

increased at the beginning of each experiment; this increase subsequently slowed from the third day to an approximately linear increase with time. The fastest Si release rate was observed during the experiment with initial fluid pH of 2, where the dissolved Si concentration reached values of up to 0.24 mmol/kg, which is approximately 5 times more than in the experiment with an initial pH of 12. The experiments run at intermediate initial fluid pH values attained lower aqueous Si concentrations ranging from 0.02 to 0.04 mmol/kg. A near constant pH was observed throughout the whole duration of the experiment run with an initial fluid pH of 2. In the experiment with initial fluid pH of 7 and 8, the pH progressively increased from this initial pH, whereas in the experiment with initial fluid pH of 12, the pH progressively decreased, reaching the value of 10.28 after 48 days. Finally, the pH of the reactive fluids of the experiments run with an initial pH of 4 and 10 exhibited a rapidly changing pH in the first 48 h, attaining values of 5.50 and 8.00, respectively, remaining stable afterwards. Cation concentrations measured at the end of each experiment showed that Ca was preferentially released from the solid relative to Al, Fe and Si in the experiments run at initial pH values ranging from 4 to 10. Iron concentrations were observed to be ~0.1 mmol/kg higher than Si in the experiment run with initial fluid pH of 2, but were close or below the detection limit in all the other experiments.

At 100 and 200 °C, the measured pH of outlet fluids was identical to those of inlet fluids within analytical uncertainties due to the experimental design, as the continuous injection of initial fluid buffers potential pH changes induced by fluid-mineral interactions. In contrast, the major element concentrations measured throughout the mixed-flow reactor experiments exhibit distinct behaviours depending on pH, and to a lesser extent as a function of temperature (see **Figure 5** and **Figure 6**) as described in detail below.

Aluminum – At 100 °C, the maximum reactive fluid Al concentrations, ~0.27 mmol/kg, were observed in the most acidic fluids; measured dissolved Al concentrations decreased progressively as the imposed reactive fluid pH is increased towards neutral pH in succeeding experiments, reaching values lower than 0.01 mmol/kg in near to neutral pH conditions, and maintaining similar levels at alkaline conditions (pH>9). A notable decrease of aqueous Al concentrations as function of time was detected in the experiment run at pH 9 (**Figure 5**). At 200 °C, a different Al behaviour was observed: Al concentrations increased with increasing pH from below the detection limit at pH 3 to ~0.08 mmol/kg at pH 10.

Calcium – In contrast to Al, no significant difference was found in the relative Ca release rates as function of temperature. The highest reactive fluid Ca concentrations were observed in the most acidic reactive fluids; 0.27 mmol/kg of Ca was present in 100 °C and pH 2 fluids, and 0.52 mmol/kg in 200 °C and pH 3 fluids. Ca concentrations progressively decreased

with increasing reactive fluid pH up to pH ~8, then remaining close to zero or even below detection limit at more alkaline conditions.

Iron – The Fe concentrations were below the detection limit in most of the sampled reactive fluids. Measurable fluid Fe concentrations with values ≤ 0.03 mmol/kg were found at 100 °C in experiments performed in fluids having a pH of 2, 3, and 4, and at 200 °C only in reactive fluids at pH 10.

Silicon - Dissolved silicon concentrations in the reactive fluids tended to be highest at acidic conditions, at a minimum at near to neutral pH, and then increasing again at alkaline pH. At 100 and 200 °C, the highest reactive fluid Si concentrations were observed at pH 2 and 3, with values up to 0.37 and 0.68 mmol/kg, respectively; the lowest Si concentrations at pH 9 and 8 with values of 0.003 and 0.03 mmol/kg, respectively.

Insight into the epidote dissolution process can be gained by considering the relative cation abundances in the reactive fluids. This is particularly true for the experiments performed at 100 °C, where the experimental design resulted in the precipitation and subsequent re-dissolution of some secondary phases. The relative cation release rates of various elements concentrations are provided in **Table 5**. If the elements were released stoichiometrically, the Ca/Si and Al/Si ratios would be 0.69, and the Fe/Si ratio would be 0.34. As shown in **Table 5**, the Fe/Si ratios were <0.1 in each experiment. For Ca, Al, and Si, the release at 100 and 200 °C was close to stoichiometric at pH 2 and 8, respectively. Preferential release of Ca over Al and slightly over Si was observed in the experiments performed at $3 < \text{pH} < 9$, and up to pH 10 at 100 °C, with Ca release rates at 200 °C and pH 3 fluids up to 147 times greater than of Al. Notably, the low Al/Si ratios suggest that Al was retained in a solid phase at these conditions. In contrast, at pH above pH 8 for both 100 and 200 °C experiments, Al is observed to be preferentially released compared to Si.

3.2. Solid alteration products

The epidote grains recovered at the end of the experiments at 25 °C showed no dissolution features or secondary phases despite up to 48 days of reaction, and thermodynamic calculations indicating that the reactive fluids were supersaturated at alkaline conditions ($\text{pH} \geq 7$) with respect to Fe-oxides, Al oxy-hydroxides, and various Al-silicates including zeolites. In contrast, the reacted solids collected at the end of the experiments performed at 100 and 200 °C were substantially altered compared to the starting material (see **Figure 7**). SEM images showed epidote grain surfaces collected after the 100 °C experiments were severely pitted and covered with extensive Fe-oxide precipitates. These Fe-minerals formed “crusts” that partially covered the dissolved epidote surfaces, especially along the grain edges. Often, the crusts were detached from the underlying grains, which

could be a result from the post-experimental quenching and sample preparation. No sign of the precipitation of other secondary phases was detected even though PHREEQC calculations suggested the supersaturation of the reactive fluids with respect to Al oxyhydroxides such as boehmite, diaspore, and gibbsite in the epidote runs at pH 3, 4, and 5. Moreover the Al/Si ratios of the reactor fluids was less than that of the dissolving epidote, suggesting the removal of Al from the fluid phase at these conditions. At 200 °C, extensive alteration was evident, with numerous epidote grains reduced to dimensions below their original size, the presence of dissolution features on both grain surfaces and edges, and the presence of several secondary minerals. At acidic conditions, crystalline Al oxyhydroxides were detected in the solids collected from the experiment run in pH 3 reactive fluids. These were not observed in the experiments run at pH 4 although the reactive fluid was supersaturated with respect to boehmite, diaspore, and gibbsite, as indicated by thermodynamic calculations. At alkaline conditions, minor fibrous Na-Al-silicates were found in the solids collected at the end of experiments performed in the fluids having an initial pH of 8 and 10, with Na coming from the inlet fluids. Hexagonal Ca-Ti-oxides were observed at pH 10. Fe-oxides were detected in all of the solids collected from the 200 °C experiments. The Fe-phases were present as either single crystals or agglomerates rather than as the “crusts” observed in the solids collected from the 100 °C experiments, and differences in their morphology were observed as a function of pH. Acicular and platy Fe-oxide crystals, morphologies likely associated with hematite and goethite (Davidson et al., 2008), were found at acidic pH ($\text{pH} \leq 4$), whereas an octahedral habit typical of magnetite (Saldi et al., 2015) was found at basic conditions ($\text{pH} \geq 8$).

3.3. Epidote dissolution rates

Epidote dissolution rates in the present study are based on Si release rates. Retrieved rates are referred to as steady-state rates, as although Si steady-state release was observed, Ca, Al, and Fe were not released in stoichiometric quantities in every experiment (**Table 5**). Resulting rates, together with their uncertainty and *in situ* pH for all experiments are listed in **Table 6** and plotted in **Figure 8**. Epidote dissolution rates tend to decrease with increasing pH under acidic conditions, minimize at near to neutral conditions, and then increase with further increases in pH.

Steady-state epidote dissolution rates for the experiments at 25 °C, were obtained by linear regression of the temporal evolution of reactive fluid Si concentrations. Rates are based on this temporal evolution after day 7 of each experiment to avoid any anomalous initial element release rates. The total mass of epidote dissolved during each of these 25 °C experiments was determined to range from 0.2 to 2 wt% of the initial mass, based on the

total reactive fluid Si concentrations and mass balance calculations. The base-10 logarithm (log) of measured rates ranged from a maximum of $-14.98 \text{ mol/cm}^2/\text{s}$ at pH 2 to a minimum of $-16.07 \text{ mol/cm}^2/\text{s}$ at pH 7. The uncertainty on these rates was estimated to be lower than ± 0.11 log units (two standard errors), based on the sum of the uncertainties associated with fluid composition, BET surface area measurements, and uncertainties of the slopes calculated during least squares regression.

At 100 °C, the total epidote mass dissolved throughout the experimental series was ~20 wt%, based on mass balance calculations using aqueous Si concentrations. The minimum epidote logarithmic dissolution rate was determined to be $-14.40 \text{ mol/cm}^2/\text{s}$ at pH 9, which is almost two orders of magnitude higher than that observed at 25 °C and at alkaline conditions. The steady-state logarithmic rates at pH 2, determined from experiments run at the beginning and end of the experimental series, were found to be almost identical with values of -12.30 and $-12.37 \text{ mol/cm}^2/\text{s}$, respectively. The rate difference is within the uncertainty of the rate measurements, which for all these mixed-flow reactor experiments was estimated to be ± 0.04 log unit (two standard errors), based on the sum of the uncertainties associated with fluid flow, fluid composition, and BET surface area measurements. At 200 °C, the epidote dissolution rates were found to be ~1 order of magnitude higher than corresponding rates determined at 100 °C, with a minimum logarithmic value of $-13.18 \text{ mol/cm}^2/\text{s}$ measured around pH 8.

4. DISCUSSION

4.1. Chemical exchange

At 25 °C, despite significant variations in the Si concentrations as function of pH, and supersaturation of the reactive fluids with respect to several secondary minerals at steady-state conditions, no alteration products were observed. Moreover, substantial pH changes were observed in the batch reactor experimental fluids for those experiments having initial reactive fluid pH of 4 and 10. The rapid pH change at acidic conditions suggests a major role of surface protonation in epidote dissolution, with metal-proton exchange reactions increasing the fluid pH to ~5.5 (e.g., Ganor et al., 2003; Guy and Schott, 1989; Oelkers et al., 2009). It is unlikely that the rapid pH increase observed during the pH 4 experiment is due to the presence of fine particles as this behaviour was not observed in the experiments performed at pH 2. In contrast, the pH decreases markedly at pH 10; this potentially occurred due to the equilibration of the reactive fluid with atmospheric carbon dioxide (CO₂). Similarly, the uptake of CO₂ by the fluid may have affected the pH evolution of the reactive fluid of the experiment run at an initial pH of 12, where the slower pH decrease with time

compared to the pH 10 solution can be explained by the presence of a more strongly pH buffered initial solution (**Table 2**). Thermodynamic calculations performed with the initial fluid composition of pH 10 and pH 12 experiments equilibrated with a partial pressure ($p\text{CO}_2$) of 0.0004 atm confirm the possibility that the observed pH decrease was due to CO_2 gas dissolution into the reactive fluid. According to these calculations, if the fluids initially having pH of 10 and 12 were equilibrated with atmospheric CO_2 , their pH would reach values of 7.00 and 9.06, respectively, and contain up to 0.1 mmol/kg and 8 mmol/kg of CO_2 , respectively.

At 100 and 200 °C, the changes in the chemical composition of the reactive fluids are coherent with observations of the altered solids recovered at the end of these experiments. A general preferential release of Ca was observed for reactive fluids with $\text{pH} < 9$, in particular at acidic conditions, and no Ca-phase was detected or calculated to be supersaturated in these reactive fluids. Such observations suggest the exchange of Ca with protons present in the reactive fluids as previously observed for other Ca-bearing silicates such as wollastonite and diopside (Oelkers et al., 2009; Schott et al., 2012). In contrast, the low Al/Si ratios of the reactive fluids at these same conditions, are likely due to the precipitation of secondary Al-hydroxide phases; these fluids were calculated to be supersaturated relative to Al oxyhydroxide phases, such as boehmite, diasporite and gibbsite, at $2 < \text{pH} < 9$. Moreover, the precipitation of such phases was confirmed directly through the analysis of the solids recovered after the experiment run at 200 °C with a pH 3 reactive fluid (**Figure 7**). The lack of Al-rich solid phases observed in the solids recovered from the experimental series run at 100 °C may be related to the experimental design. The running of sequential experiments with increasing pH in series likely caused the dissolution of previously formed Al-rich secondary minerals. This interpretation could explain the initial high Al concentrations in the experiment run at pH 9 (**Figure 5**), as the solubility of Al-containing minerals increases with pH (Bénézech et al., 2001). In contrast, Ca tended to be preferentially retained in the solid phase in experiment run at $\text{pH} > 8$ at 200 °C, where Si and Al were released in a close to stoichiometric ratio (**Table 5**). No secondary phases were calculated to be stable in the reactive fluids used in these alkaline experiments, yet Ca-Ti-oxide crystals were detected at pH 10, and minor Na-Al-silicates at pH 8 and 10 (**Figure 7**). The precipitation of the Na-rich phase seems to not have significantly affected the reaction stoichiometry, with Al/Si release ratios being similar to that of the dissolving epidote. Similarly, due to the small quantity of Ca-Ti-oxide precipitated, it seems likely that this did not affect substantially the Ca/Si and Ca/Al ratios of the fluids (**Table 5**). The retention of Ca by the solid phase may reflect the formation of a Ca-rich surface layer on the dissolving epidote, consistent with the Ca-for-proton exchange reaction at alkaline pH (Oelkers et al., 2009).

The relative apparent release rate of Fe is low in all experiments at both 100 and 200 °C (**Table 5**). The aqueous Fe^{3+} released from epidote is unstable in the fluid phase for $\text{pH} \geq 3$ and $\text{Eh} \geq 0.4$, as Fe-oxides readily form (Pourbaix, 1966). These phases were observed in all the solids recovered after these experiments.

4.2. Effect of temperature on epidote dissolution rates

The dissolution rates of epidote at 100 °C were found to be up to ~2 log unit higher than corresponding rates at 25 °C, but only ~1 log unit lower than at 200 °C (**Figure 8**). The overall fastest cation release rates at 200 °C explains the observed abundant secondary phases in the solid samples recovered after the experiments run at these temperatures. For instance, the fast Al release rate at 200 °C and pH 3 leads to a more substantial supersaturation of Al oxy-hydroxide phases. In turn, supersaturation with various minerals leads to their rapid precipitation leading to the decrease of Al/Si towards zero (**Table 5**).

4.3. Comparison with literature data

All epidote dissolution rates determined in this study are compared with the results of previous experimental studies in **Figure 9**. A good consistency is evident amongst most of the different datasets. For all the studied temperature conditions, the most pH-sensitive rates were found for acidic pH as suggested by Nickel (1973), Sverdrup (1990), and Blanchard (1994), but in contrast to those proposed by Rose (1991). At 25 °C, the rates obtained in this study from batch reactor experiments are closely consistent with corresponding rates reported by Nickel (1973), Rose (1991) and Kalinowski et al. (1998), but are up to ~2 log unit slower than the corresponding rates reported by Sverdrup (1990). Note that the epidote dissolution rates reported by Sverdrup (1990) were obtained on the dissolution of zoisite from the sum of released base cations rather than from Si release (see **Table 1**). This could be the reason of such discrepancies. At 100 °C, rates determined in the present study agree well with those of Rose (1991) at 90 °C up to pH 9. In contrast, there exist significant differences among rates reported at higher temperature (Blanchard, 1994; Rochelle, 1990), perhaps due to the distinct buffer solutions used in the different experiments. The buffers used in the 250 °C experiments of Blanchard (1994) and Rochelle (1990) contained acetate and Na-fluoride. The presence of these aqueous components may affect epidote dissolution rates, as has been seen for other silicate minerals (Golubev et al., 2006; Golubev and Pokrovsky, 2006; Harouiya and Oelkers, 2004; Pokrovsky et al., 2009; Wolff-Boenisch et al., 2004).

The preferential initial release of Ca at acidic pH was reported by Nickel (1973), Sverdrup (1990), and Kalinowski et al. (1998). Such release was also observed in this study indirectly at 25 °C from surface protonation, and directly at 100 and 200 °C through aqueous

Ca measurements. As Ca ions are not part of the epidote framework, it is generally agreed that the first step of its dissolution is the relatively fast removal of alkaline earth metals at acidic conditions through proton exchange reactions (e.g., Guy and Schott, 1989; Oelkers, 2001). In contrast, no conclusions can be made for exchange reactions of other metals because of the formation of secondary minerals.

4.4 Epidote dissolution mechanisms

The far from equilibrium dissolution rate is controlled by the fastest pathway available for breaking the slowest bond structurally crucial for the mineral. As shown for many Al-silicates, such as albite, kaolinite, and basaltic glass (Oelkers and Gislason, 2001; Oelkers et al., 1994), the epidote dissolution mechanism is most probably associated with the breaking of the Al-O structure through Al-proton exchange reactions, after the partial liberation of the adjoining Si tetrahedra. However, given the precipitation and re-dissolution of Al-hydroxide phases in several experiments in this study, this mechanism cannot be explored in detail with the obtained dataset. Following the approach of Palandri and Kharaka (2004), a more pragmatic rate model based only on protons activity was adopted for fitting epidote rate data. In this model, the epidote dissolution rate is expressed as the sum of terms for the dissolution mechanisms driven by H^+ , OH^- , and independent of pH as Arrhenius-type equations:

$$r = \left[A_A * e^{-\frac{E_a^A}{RT}} * a(H^+)^{n_A} \right] + \left[A_N * e^{-\frac{E_a^N}{RT}} \right] + \left[A_B * e^{-\frac{E_a^B}{RT}} * a(H^+)^{n_B} \right] \quad (3)$$

where r indicates the BET surface area normalized steady-state epidote dissolution rate at far-from equilibrium conditions, A_i refer to pre-exponential factors, E_a^i designate the activation energies, R stands for the gas constant, T signifies temperature in K, $a(H^+)$ denotes the hydrogen ion activity, and n represents the reaction orders with respect to H^+ . The values for A , E_a , and n were calculated for acidic (A), neutral (N), and basic (B) conditions by non-linear least squares regression of all the experimental rate data of this study simultaneously. The Levenberg-Marquardt algorithm was used for optimization, and the fitting was carried out on the log-transformed data and rate equation so that residuals of each experimental data point are effectively weighted according to a constant relative uncertainty of each rate. Only results from this study were used to calibrate the equation i) to maintain consistency with respect to experimental and analytical procedures and the epidote sample, and ii) because it is the only dataset providing epidote dissolution rates throughout most of the pH scale and at several temperatures. Data from Sverdrup (1990) were not considered because rates were measured on zoisite, a Fe-depleted epidote subgroup.

The modelled epidote dissolution rates resulting from the best-fit calculations are shown in **Figure 10**, and the best-fit parameter values listed in **Table 7** along with the parameters proposed by Palandri and Kharaka (2004). Lower activation energies, and different reaction orders n were determined for epidote dissolution in comparison to those reported in the literature by Palandri and Kharaka (2004). Overall, the uncertainty in the fitted parameters is much lower in the acidic and neutral regions due to the greater availability of measured rates. The scatter in rates obtained at basic conditions may suggest the presence of additional mechanisms, but some of these rates could be considered as outliers based on their reported uncertainties. The rates proposed by Rose (1991) at 90 °C for pH ~8 and ~11 have reported uncertainty of ± 0.2 log units, which exceeds the average relative error in the Rose study based on the uncertainty in temperature, pH, and regression of element release data. This uncertainty estimate does not account for the uncertainty on surface area measurements. In turn, the rate measured at 25 °C in this study for the reactive fluid with initial pH of 12 has the highest uncertainty associated with the rate measurement, and may have been affected by the effect of fluid equilibration with atmospheric CO₂ that at these conditions could have led to supersaturation with respect to calcite.

4.5. Implications for natural processes

The calculated epidote dissolution rates show that this mineral, as many other aluminosilicate solid phases (e.g., Casey et al., 1991; Gudbrandsson et al., 2011; Oelkers and Gislason, 2001), is relatively rapid at acid weathering conditions. This means that the presence of epidote is most likely to have a significant impact on the weathering of soils, as suggested by Sverdrup and Warfvinge (1993), in particular of epidote-bearing rocks, such as mafic reservoirs. Moreover, it appears that aqueous Al concentration is a major rate inhibitor of the dissolution of many aluminosilicate minerals, such as feldspars, muscovite, and kaolinite (e.g., Oelkers et al., 1994; Oelkers et al., 2008b). As such, the rapid dissolution of epidote, with its high relative aluminium content (**Table 8**), could lead to the increase of aqueous fluid Al activity during its dissolution. This aluminium could slow the weathering rates of other minerals. Such effect needs to be taken into account during the evaluation of mineral dissolution in weathering profiles.

4.6. Implications for carbon storage

Mineral storage in mafic and ultramafic rocks through mineral carbonation has been considered by a plethora of studies. To date there is only one on-going industrial scale mineral carbonation, the CarbFix project in Iceland. This project is successfully mineralizing water-dissolved CO₂ through its reactions with fresh and altered basalt in the subsurface. The carbon storage potential of fresh mafic rocks, such as basalt has been quantified by

numerous experimental, modelling, and field studies (e.g., Clark et al., 2019; Dessert et al., 2003; Galeczka et al., 2014; Gislason and Oelkers, 2014; Godard et al., 2011; Goldberg et al., 2008; Gunnarsson et al., 2018; Gysi and Stefánsson, 2008; Gysi and Stefánsson, 2012; Kelemen and Matter, 2008; Marieni et al., 2020; Matter et al., 2016; Paukert et al., 2012; Rosenbauer et al., 2012; Schaef et al., 2010; Snæbjörnsdóttir et al., 2018; Snæbjörnsdóttir et al., 2020; Wolff-Boenisch et al., 2011). These studies generally highlight the advantage of basalt for this purpose due to the fast release rates of cations such as Ca, which are crucial for mineral carbonation. However, many potential basaltic reservoirs for CO₂ mineral storage contain altered mafic rocks, particularly in geothermal systems (e.g., Browne, 1978) and ophiolites (e.g., Gillis and Robinson, 1990). These rocks contain abundant secondary Ca-bearing silicates, such as epidote and amphiboles, which have also the potential to provide the cations necessary for mineral carbonation. Epidote is one of the main high temperature (>200 °C) alteration products of Ca-rich plagioclase; it can constitute up to 50 vol% of a crystalline basalt (Marieni and Oelkers, 2018). Its Ca/Si ratio is higher than that of basalt, Ca-amphiboles such as actinolite, Ca-pyroxene such as diopside, and the common Ca-plagioclases, labradorite and anorthite (see **Table 8**). As such, it only takes ~20 tons of epidote to mineralize 1 ton of CO₂ as calcite compared to ~40 tons required by the Stapafell basaltic glass (Oelkers and Gislason, 2001). Furthermore, the absence of Mg in epidote may limit the precipitation of some pore filling clays and chlorite, which compete with carbonate minerals for pore space. Note that results from the experiments performed in this study at 100 °C confirmed that Fe-oxide precipitates do not slow the epidote dissolution at pH 2 even after the dissolution of ~20 wt% of this mineral. As such, it seems unlikely that these precipitates will slow epidote dissolution in natural systems. In contrast, the Al/Si ratio of epidote is almost twice that of crystalline and glassy basalts (see **Table 8**), but is similar or lower than that of the Ca-pyroxene and the Ca-plagioclases. The high Al content of epidote could be a disadvantage for carbon storage because of the inhibitory effect of aqueous Al concentrations on dissolution rates of many aluminosilicate minerals, as discussed above.

A comparison of epidote dissolution rates with corresponding basaltic glass dissolution rates is presented in **Figure 9**. Epidote dissolution rates calculated from Si release rates at 25 °C are from one to three orders of magnitude lower than those of basaltic glass (Gislason and Oelkers, 2003). The difference in these rates at 100 °C is somewhat lower at acidic pH, which represent the conditions of CO₂-charged aqueous fluid injections in the current CarbFix project (e.g., Snæbjörnsdóttir et al., 2018), but increases again at 200 °C. However, the availability of divalent cations, such as Ca²⁺, Fe²⁺, and Mg²⁺, required for the mineralization of CO₂ must be considered to constrain carbon mineral storage efficiency. The comparison of Ca release rates from epidote as well as from the other Ca-bearing

silicates provide a more accurate comparison in this context (**Figure 11**). The higher Ca content in the epidote brings its predicted release rates closer to those of the other Ca-silicates. Ca release rates from epidote at 25 °C match, within one log unit of uncertainty, the Ca release rates from numerous other common silicate phases up to pH 8, and at 100 °C are as fast as basaltic glass rates up to pH 5. The observation that epidote can release Ca as fast as a fresh plagioclase suggests that alteration minerals can play a significant role in the carbon mineralization process, and that the absence or limited availability of the fresh basaltic glass in some systems can be overcome by the abundance of divalent metal rich secondary phases. Furthermore, the preferential release of Ca at pH<9 discussed above and the relatively fast pH increase from acidic towards alkaline conditions even at low temperature due to metal-proton exchange reactions, such as in the 25 °C experiments with initial reactive fluid pH of 4 (**Figure 4**), could further promote the precipitation of calcium carbonate (e.g., Snæbjörnsdóttir et al., 2018).

5. CONCLUSIONS

Epidote dissolution rates have been measured as a function of pH at temperatures from 25 to 200 °C. The major results include:

a) The epidote dissolution rates vary with pH in a manner similar to many other aluminosilicate minerals, where rates decrease with increasing pH at acidic conditions, minimize at near to neutral pH, and then increase with increasing pH at alkaline conditions (e.g., Hellman, 1994; Lammers et al., 2017).

b) The results on epidote dissolution rates from this study agree with those previously reported by Nickel (1973) and Kalinowski et al. (1998).

c) Scanning electron microscope images of precipitated secondary minerals were provided as a function of pH and temperature, highlighting the predominance of Fe-oxides at every pH condition along with the supersaturation of Al oxy-hydroxide phases at acidic pH.

d) Alteration products precipitated on epidote grains do not appear to alter epidote dissolution rates even after the removal of ~20 wt% of the initial sample mass in ~80 days of sequential experiments at different pH.

e) Epidote, as well as many other aluminosilicate minerals, dissolves rapidly at acidic conditions so that its presence may have a major impact on weathering rates of mafic rocks.

f) Divalent metal-rich secondary phases such as epidote can play a significant role in the carbon mineralization process due to the abundance of Ca in its structure, and Ca

595 preferential release at acidic pH typical of CO₂-charged fluid injections. Such observations
596 extend the applicability of this storage approach to additional geologic systems.

597

598 **Acknowledgements**

599 We would like to thank Dr. Giuseppe Saldi, Alain Castillo, Carole Causserand, and Stephane
600 Le Blond du Plouy for experimental, technical, and analytical assistance. Helpful reviews
601 from the Executive Editor Dr. Catalano, the Associate Editor Dr. Anovitz, and two
602 anonymous reviewers are very much appreciated. This research has been carried out within
603 the CarbFix2 project that has received funding from the European Union's Horizon 2020
604 research and innovation program under grant agreement No 764760.

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783 **FIGURES**

784 **Figure 1:** Epidote crystal structure a) in 3D, and b) down the *b* axis of the monoclinic unit
 785 cell. Data from Gabe et al. (1973).

788 **Figure 2:** Scanning electron micrographs of the initial epidote used for the dissolution
789 experiments performed in this study. The grain size fraction of this epidote is between 20
790 and 100 μm .

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Figure 3: Experimental systems used for A) batch reactor experiments at 25 °C, and B) mixed-flow reactor experiments at 100 and 200 °C. A water bath with thermostat control and the couple magnetic plate-stir bar were used during the batch reactor experiments to maintain the set temperature and the grains in suspension, respectively, within the polypropylene reactors. In the mixed-flow experiments, a high pressure liquid chromatography (HPLC) pump was employed to deliver the inlet fluid to the heated titanium reactor, where the solution was mechanically stirred, while the outlet fluid exited through a back pressure regulator, placed after the cooling system.

Figure 4: Temporal evolution for all the batch reactor experiments run at 25 °C of (a) reactive fluid pH, (b) Si concentrations determined from both colorimetric analyses (circles) and ICP-OES analyses (diamonds), and (c) cation concentrations determined from ICP-OES analyses (diamonds) of the final fluid sample as a function of reactive fluid pH. The uncertainty in measured values, which in this study represent the 95% confidence interval (or two standard errors), is approximated by the symbol size.

Figure 5: Temporal evolution of reactive fluid concentrations for the experiments performed at 100 °C. Ca, Al and Fe concentrations were measured using ICP-OES analyses, whereas Si concentrations were measured using both colorimetric and ICP-OES analyses. Fe concentrations were below the detection limit of 0.1 $\mu\text{mol/kg}$ in the experiments run at pH 6, 9, 10 and 11. The uncertainty in measured values, which in this study represent the 95% confidence interval (or two standard errors), is approximated by the symbol size. Note the different concentration scales on the y-axis of experiments run at pH 2 and 3.

Figure 6: Temporal evolution of reactive fluids concentrations for the experiments performed at 200 °C. Ca, Al and Fe concentrations were measured using ICP-OES analyses, whereas Si concentrations were measured using both colorimetric and ICP-OES analyses. Fe concentrations were below the detection limit of 0.1 $\mu\text{mol/kg}$ in the experiments run at pH 3, 4, and 8. The uncertainty in measured values, which in this study represent the 95% confidence interval (or two standard errors), is approximated by the symbol size. Note the different concentration scale on the y-axis of the experiment run at pH 3.

Figure 7: Scanning electron micrographs of the solids recovered after various experiments performed in this study. At 100 °C, dissolution features on epidote grain (a), and Fe-oxide “crusts” covering partially or entirely the epidote surface (b and c), particularly along the grain edges. At 200 °C and acidic pH, highly altered epidote grains (d) often covered by Fe-oxide agglomerates and Al-hydroxide crystals (e and f). At 200 °C and basic pH, Fe oxide crystals with the octahedral habit typical of magnetite (g, h, and i), fibrous Na-rich silicates (h and i), and hexagonal Ca-Ti-oxides (i). The scale is provided below every image.

839 **Figure 8:** Steady-state epidote dissolution rates based on the Si release rates determined in
840 the present study as a function of pH, for batch reactor experiments at 25 °C, and mixed-
841 flow reactor experiments at 100 and 200 °C. The rate uncertainty of measured rates, which
842 in this study represent the 95% confidence interval (or two standard errors), is approximated
843 by the symbol size.

844

Figure 9: Epidote (Ep) dissolution rates from this study compared to previously reported epidote dissolution rates and with basaltic glass dissolution rates as a function of pH at 25 (a), 90-100 (b), and 200-250 °C (c) as a function of pH. Note, data from Gislason and Oelkers (2003) refers to basaltic glass (BG) dissolution rates.

851 **Figure 10:** Best-fit epidote dissolution rates as a function of pH and temperature, along with
852 this study and literature data (Kalinowski et al., 1998; Nickel, 1973; Rose, 1991).

Figure 11: Ca release rates from Ep-epidote, BG-basaltic glass (Gislason and Oelkers, 2003), CB-crystalline basalt (Gudbrandsson et al., 2011), Amp-actinolitic amphibole (Critelli et al., 2014), Px-diopside pyroxene (Brantley and Chen, 1995; Golubev et al., 2005), and Plg-labradoritic plagioclase (modified by Gudbrandsson et al., 2011 from Chou and Wollast 1985) at 25 (a), 100 (b) and 200 °C (c), as a function of pH. The release rates were determined by combining the dissolution rates with the stoichiometric concentrations of Ca in each phase.

863 **Table 1:** Summary of epidote dissolution rates reported in the literature. Batch reactor
864 experiments are indicated with “B”, dialysis with “D”, mixed-flow with “MF”, and flow-through
865 with “FT”. Epidote dissolution rates are expressed as logarithm of rates in mol/cm²/s.

Reference	Type	T (°C)	pH	Ionic strength (mol/kg)	log r ^[1] (mol/cm ² /s)	log r ^[2] (mol/cm ² /s)
Nickel (1973) *	MF	25	0.2	0.78	-14.23	-
			3.6	0.0003	-15.17	-
			5.6	deionized water	-15.80	-
			10.6	0.0004	-15.44	-
Sverdrup (1990) **	MF	25	3.0	-	-	-13.6
			3.0	-	-	-13.9
			3.5	-	-	-14.5
			4.5	-	-	-14.9
			5.2	-	-	-16.2
			5.5	-	-	-15.9
			6.2	-	-	-16.1
			10.5	-	-	-16.3
Rose (1991)	B	25	1.29	0.12	-15.31	-
			1.39	0.10	-15.53	-
			2.52	0.07	-15.80	-
			3.51	0.06	-16.02	-
			4.10	0.04	-16.17	-
			5.05	0.06	-16.15	-
Kalinowski et al. (1998)	D ^a	25	1.99	0.01	-15.19	-
			2.99	0.001	-15.63	-
			3.00	0.0005	-15.64	-
			4.05	0.0001	-15.72	-
			4.12	0.0001	-15.65	-
			6.50	deionized water	-15.93	-
	FT	25	1.08	0.1	-14.49	-
			2.01	0.01	-14.73	-
			2.98	0.001	-15.36	-
			3.03	0.001	-15.42	-
			4.02	0.0001	-16.19	-
			4.05	0.0001	-16.00	-
			6.48	deionized water	-16.29	-
Rose (1991)	B	90	1.29	0.12	-12.72	-
			1.40	0.10	-12.90	-
			2.50	0.07	-13.20	-
			2.50	0.07	-13.27	-
			3.47	0.06	-13.42	-
			3.47	0.06	-13.42	-
			3.47	0.06	-13.53	-
			4.38	0.04	-13.58	-
			5.50	0.06	-13.55	-
			6.62	0.08	-13.80	-
			7.75	0.09	-13.89	-
			8.64	0.07	-14.05	-
			10.82	0.12	-12.83	-
Rochelle (1990)	B	250	6.0	deionized water	-13.28	-
			6.3	0.2	-11.94	-
			7.3	0.2	-12.83	-
Blanchard (1994)	B	250	4.5	0.20	-12.70	-
			3.4	0.20	-12.59	-
			5.2	0.20	-13.13	-
			12.27	0.07	-13.22	-
			10	0.09	-13.38	-

* Ionic strength calculated from inlet solutions with PHREEQC v3 (*carbfix* database)

** Values graphically determined from figures as reported by Kalinowski et al. (1998)

^a The eluent solution is pumped to a chamber with the mineral sample in suspension, and the dissolved reaction products diffuse from the mineral chamber across dialysis membranes to the outer eluent flow

^[1] Based on Si release

^[2] Based on sum of released base cations

Table 2: List of initial conditions for each experiment performed in this study. The pH reported in the table for experiments at 25 °C are from in situ pH measurements. The pH for experiments at 100 and 200 °C, and all the ionic strengths (IS) were recalculated with PHREEQC for in situ conditions, from the pH measurements at room temperature and the initial solution compositions.

Exp. ID	Elapsed time (h)	Initial mass (g)	Initial pH	Inlet fluid composition	IS (mol/kg)
<i>Batch reactor experiments at 25 °C</i>					
Ep25_2	1176	2.03	2.19	10 mmol/kg HCl	0.0100
Ep25_4	1176	2.05	4.20	0.1 mmol/kg HCl	0.0001
Ep25_7	1146	2.01	6.99	0.1 mmol/kg HCl, 0.3 mmol/kg NaHCO ₃	0.0003
Ep25_8	1146	2.02	8.15	0.001 mmol/kg NaOH, 1.1 mmol/kg NaHCO ₃	0.0011
Ep25_10	1146	2.00	9.78	0.1 mmol/kg NaOH	0.0001
Ep25_12	1146	2.02	11.89	11 mmol/kg NaOH	0.0112
<i>Mixed-flow reactor experiments at 100 °C</i>					
Ep100_2	137	1.01	2.05	10 mmol/kg HCl	0.0100
Ep100_3	210	0.92	3.05	1 mmol/kg HCl, 8.6 NaCl	0.0095
Ep100_4	191	0.88	4.05	0.01 mmol/kg HCl, 9.4 NaCl	0.0095
Ep100_5	175	0.87	5.05	0.01 mmol/kg HCl, 9.5 NaCl	0.0095
Ep100_6	183	0.87	6.32	0.1 mmol/kg HCl, 0.2 mmol/kg NaHCO ₃ , 9.2 NaCl	0.0094
Ep100_8	214	0.87	7.71	0.001 mmol/kg NaOH, 1.1 mmol/kg NaHCO ₃ , 8.6 NaCl	0.0096
Ep100_9	190	0.87	9.19	1 mmol/kg NaOH, 8.6 NaCl	0.0095
Ep100_10	167	0.87	10.19	10 mmol/kg NaOH	0.0100
Ep100_11	191	0.86	11.02	80 mmol/kg NaOH	0.0793
Ep100_2B	167	0.86	2.05	10 mmol/kg HCl	0.0100
<i>Mixed-flow reactor experiments at 200 °C</i>					
Ep200_3	66	1.03	3.06	1 mmol/kg HCl, 9.4 mmol/kg NaCl	0.0103
Ep200_4	69	1.07	4.06	0.1 mmol/kg HCl, 9.9 mmol/kg NaCl	0.0100
Ep200_8	88	1.03	7.61	0.001 mmol/kg NaOH, 1.1 mmol/kg NaHCO ₃ , 9.1 NaCl	0.0101
Ep200_9	74	1.05	9.21	10.1 mmol/kg NaOH	0.0100
Ep200_10	121	1.06	9.75	50 mmol/kg NaOH	0.0443

872 **Table 3:** Chemical composition of the investigated epidote in the present study obtained by
873 XRF.

wt%		moles	
SiO ₂	37.32	Si	3.00
TiO ₂	0.19	Ti	0.01
Al ₂ O ₃	21.94	Al	2.08
Fe ₂ O ₃	16.78	Fe	1.02
Mn ₂ O ₃	0.16	Mn	0.01
MgO	0.01	Mg	<0.001
CaO	23.99	Ca	2.07
K ₂ O	0.06	K	0.01
SO ₃	0.14	S	0.01
LOI	1.82	O	13.41

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Table 4: Summary of chemical compositions of the reactor fluid samples taken during the batch reactor experiments at 25 °C and used to calculate the epidote dissolution rates with linear regression (the full data is provided in Electronic Supplementary Table 2). The reported pH are from in situ measurements. The Si concentrations below the detection limit (0.02 $\mu\text{mol/kg}$) are indicated as “<LOD”. The uncertainties on Si measurements are listed and represent the 95% confidence interval (or two standard errors).

Exp. ID	Sample	Duration (h)	pH	Fluid mass (g)	Si (mmol/kg)	Uncertainty (mmol/kg)
Ep25_2	Ep25C_2_0	0	2.19		<LOD	
	Ep25C_2_10	168	2.09	144.5	0.092	0.002
	Ep25C_2_11	192	2.09	143.8	0.086	<0.001
	Ep25C_2_12	240	2.09	143.1	0.095	<0.001
	Ep25C_2_13	336	2.08	142.3	0.112	<0.001
	Ep25C_2_14	504	2.09	141.5	0.144	0.001
	Ep25C_2_15	672	2.10	140.6	0.169	0.001
	Ep25C_2_16	840	2.04	139.6	0.193	0.003
	Ep25C_2_17	1008	2.13	138.9	0.214	0.003
	Ep25C_2_18	1176	2.01	138.1	0.239	0.001
Ep25_4	Ep25C_4_0	0	4.20		<LOD	
	Ep25C_4_11	192	5.47	144.6	0.017	<0.001
	Ep25C_4_12	240	5.33	144.1	0.018	<0.001
	Ep25C_4_13	336	5.47	143.2	0.021	<0.001
	Ep25C_4_14	504	5.52	141.9	0.024	0.001
	Ep25C_4_15	672	5.60	141.0	0.028	0.001
	Ep25C_4_18	1176	5.64	138.7	0.038	<0.001
Ep25_7	Ep25C_7_0	0	6.99		<LOD	
	Ep25C_7_6	162	7.14	146.2	0.012	<0.001
	Ep25C_7_7	210	7.26	145.5	0.013	<0.001
	Ep25C_7_8	306	7.08	144.7	0.015	<0.001
	Ep25C_7_9	474	7.46	143.9	0.017	0.001
	Ep25C_7_10	642	7.24	143.1	0.019	0.001
	Ep25C_7_13	1146	7.55	140.5	0.024	<0.001
Ep25_8	Ep25C_8_0	0	8.15		<LOD	
	Ep25C_8_6	162	8.22	146.2	0.017	<0.001
	Ep25C_8_7	210	8.14	145.4	0.018	<0.001
	Ep25C_8_8	306	8.14	144.8	0.020	<0.001
	Ep25C_8_9	474	8.25	144.0	0.027	0.001
	Ep25C_8_10	642	8.15	143.1	0.031	0.001
	Ep25C_8_13	1146	8.24	140.8	0.039	<0.001
Ep25_10	Ep25C_10_0	0	9.78	150.8	<LOD	
	Ep25C_10_6	162	7.97	148.1	0.014	<0.001
	Ep25C_10_7	210	7.91	147.6	0.015	<0.001
	Ep25C_10_8	306	7.65	146.9	0.017	<0.001
	Ep25C_10_9	474	7.85	146.2	0.019	0.001
	Ep25C_10_10	642	7.76	145.2	0.023	0.001
	Ep25C_10_13	1146	7.35	143.1	0.033	<0.001
Ep25_12	Ep25C_12_0	0	11.89	150.1	<LOD	
	Ep25C_12_6	162	11.80	146.2	0.043	<0.001
	Ep25C_12_7	210	11.70	145.5	0.047	<0.001
	Ep25C_12_8	306	11.55	144.7	0.046	<0.001
	Ep25C_12_9	474	11.48	144.6	0.048	0.001
	Ep25C_12_10	642	11.37	143.7	0.051	0.001
	Ep25C_12_11	810	11.03	142.9	0.053	0.003
	Ep25C_12_12	978	10.88	141.9	0.051	0.003
	Ep25C_12_13	1146	10.28	140.9	0.058	<0.001

Table 5: Summary of averaged pH, Si concentrations, and cation release ratios in the outlet aqueous solutions at steady-state for each mixed-flow reactor experimental run. The pH reported in the table were recalculated with PHREEQC for in situ conditions, from the pH measurements at room temperature and the outlet solution compositions at steady-state. Often the Fe/Si stoichiometric ratio is not available because values of Fe concentrations are below the detection limit (0.1 $\mu\text{mol/kg}$). The uncertainties on Si measurements are listed and represent the 95% confidence interval (or two standard errors). The full data is provided in Electronic Supplementary Table 2.

Exp. ID	pH	Si (mmol/kg)	Uncertainty (mmol/kg)	Ca/Si	Al/Si	Fe/Si	Ca/Al
<i>Stoichiometric ratios of the epidote used in this study</i>				0.69	0.69	0.34	0.99
<i>Mixed-flow reactor experiments at 100 °C</i>							
Ep100_2	2.11	0.370	0.007	0.71	0.72	0.06	0.99
Ep100_3	3.12	0.047	0.001	0.91	0.53	0.10	1.73
Ep100_4	4.32	0.020	<0.001	1.14	0.01	0.01	79.83
Ep100_5	5.64	0.011	<0.001	1.32	0.05	-	31.98
Ep100_6	6.54	0.007	<0.001	1.40	0.12	-	12.16
Ep100_8	7.61	0.004	<0.001	1.39	1.55	-	0.89
Ep100_9	9.19	0.003	<0.001	1.53	1.61	-	1.08
Ep100_10	10.19	0.05	<0.001	0.92	0.34	-	2.69
Ep100_11	11.02	0.007	<0.001	0.03	0.14	0.01	0.22
Ep100_2B	2.09	0.242	0.003	0.71	0.72	0.08	0.99
<i>Mixed-flow reactor experiments at 200 °C</i>							
Ep200_3	4.37	0.656	0.009	0.76	0.01	-	147.14
Ep200_4	5.47	0.105	0.002	0.67	0.06	-	11.47
Ep200_8	7.58	0.042	0.001	0.79	0.72	-	1.12
Ep200_9	9.03	0.052	<0.001	0.14	0.73	0.001	0.19
Ep200_10	9.75	0.087	0.001	0.01	0.90	0.004	0.02

891 **Table 6:** Steady-state far from equilibrium epidote dissolution rates based on the Si release
892 all the experiments performed in this study. The pH provided for batch-reactor experiments
893 represents the pH average from the fluid samples used to calculate the epidote dissolution
894 rates with linear regression (see Table 4). The two standard error uncertainties are ± 0.11
895 and ± 0.04 log unit for rates obtained from the batch and mixed-flow reactor experiments,
896 respectively.

Exp. ID	pH	log r_{BET} (mol/cm ² /s)
<i>Batch reactor experiments at 25 °C</i>		
Ep25_2	2.09	-14.98
Ep25_4	5.52	-15.82
Ep25_7	7.29	-16.07
Ep25_8	8.19	-15.78
Ep25_10	7.75	-15.85
Ep25_12	11.26	-16.11
<i>Mixed-flow reactor experiments at 100 °C</i>		
Ep100_2	2.11	-12.30
Ep100_3	3.12	-13.13
Ep100_4	4.32	-13.47
Ep100_5	5.64	-13.71
Ep100_6	6.54	-13.89
Ep100_8	7.61	-14.22
Ep100_9	9.19	-14.40
Ep100_10	10.19	-14.09
Ep100_11	11.02	-14.06
Ep100_2B	2.09	-12.37
<i>Mixed-flow reactor experiments at 200 °C</i>		
Ep200_3	4.37	-12.03
Ep200_4	5.47	-12.84
Ep200_8	7.58	-13.18
Ep200_9	9.03	-13.10
Ep200_10	9.75	-12.88

897

898 **Table 7:** Epidote dissolution rate parameters used in Equation 3 in this study, compared to
 899 those proposed by Palandri and Kharaka (2004).

			Acidic	Neutral	Basic
This study	E_a	kJ/mol	60.0	43.2	42.3
This study	A	mol/cm ² /s	1.14E-03	5.13E-09	1.40E-13
This study	n		0.56		-0.40
P&K (2004)	E_a	kJ/mol	71.1	70.7	79.1
P&K (2004)	A	mol/cm ² /s	7.24E-03	2.51E-04	3.39E-08
P&K (2004)	n		0.338		-0.556

900

901 **Table 8:** Atomic Ca/Si, Al/Si, and Ca/Al ratios of epidote, basaltic phases, Ca-amphibole
 902 actinolite, Ca-pyroxene diopside, and Ca-bearing plagioclases (here indicated as "Plg").

	Reference	Ca/Si	Al/Si	Ca/Al
Epidote	This study	0.69	0.69	0.99
Basaltic glass	Oelkers and Gislason (2001)	0.26	0.36	0.72
Crystalline basalt	Gudbrandsson et al. (2011)	0.27	0.33	0.83
Actinolite	Critelli et al. (2014)	0.37	0.12	3.18
Px-Diopside	Brantley and Chen (1995); Golubev et al. (2005)	0.50	-	-
Plg-Labradorite	Deer et al. (1963)	0.25	0.67	0.38
Plg-Anorthite	Deer et al. (1963)	0.50	1.00	0.50

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