Electronic Supplementary Information for

A Mechanistic Understanding of Plagioclase Dissolution Based on Al Occupancy and T−O Bond Length: from Geologic Carbon Sequestration to Ambient Conditions

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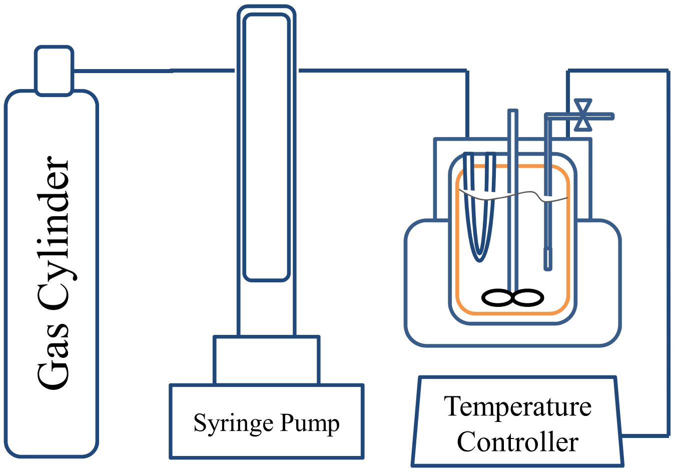

Figure S1. Schematic diagram of experiments setup.

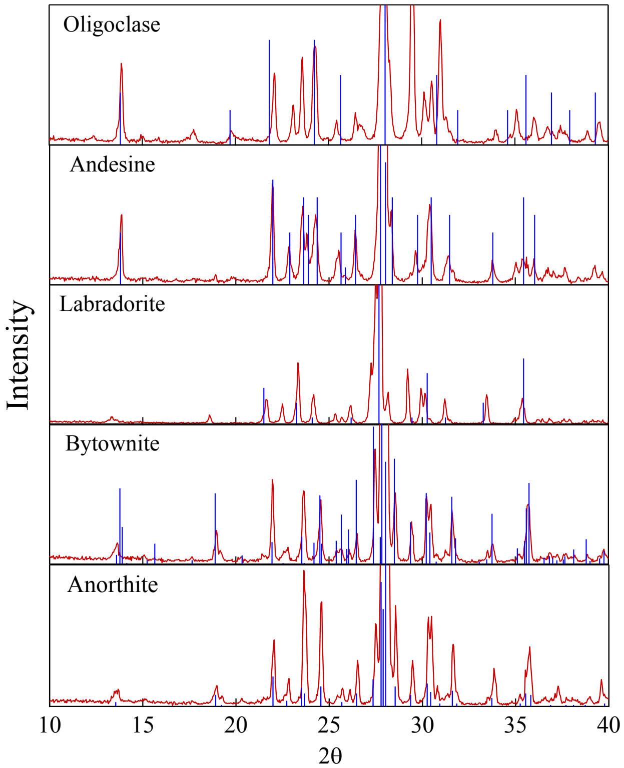

Figure S2. The X-ray diffraction patterns of the plagioclases used in this study. Reference patterns are shown as blue lines.[1]

Table S1. The results of the X-ray florescence analyses of the plagioclases used in this study. Chemical formula calculated based on the table are given in section 2.

	Oligoclase	**Andesine**	**Labradorite**	**Bytownite**	**Anorthite**
K_2O	0.81	0.67	0.35	0.06	0.01
CaO	5.87	6.42	12.30	15.28	19.49
TiO_2	0.00	0.00	0.08	0.04	0.01
MnO	0.00	0.00	0.00	0.01	0.00
Fe_2O_3	0.08	0.04	0.38	0.47	0.61
Na_2O	9.02	7.63	4.11	2.61	0.29
MgO	0.24	0.00	0.01	0.06	0.00
Al_2O_3	21.41	25.80	29.81	31.97	35.51
SiO_2	60.08	59.38	52.99	48.65	44.12
LOI	2.82	0.79	0.06	0.62	0.05

S1. Additional discussion regarding secondary mineral precipitation

The importance of secondary precipitates of feldspar−water interactions under hydrothermal conditions has been discussed in the literature.[2-5] The concern is manifold: first, is the precipitation thermodynamically favorable? Second, if secondary mineral precipitation can occur, will its kinetics be fast enough to appreciably change the water chemistry within the time frame of our dissolution experiments? (In other words, was the concentration evolution we observed actually a net effect of the primary mineral dissolution and the secondary mineral precipitation?) Third, does the formation of precipitate change the reactivity of the substrate (e.g., does an interfacial layer formed by reprecipitation constitute a diffusion barrier for mineral dissolution?[6]). In this study, the third concern is characterized as the change in the solid phase induced by mineral dissolution, and will be discussed in Sections S2 and S3. Regarding the first concern, the thermodynamic calculations described in the Experimental Methods and Materials section showed no supersaturation with respect to any mineral phase at the end of experiments for oligoclase, andesine, labradorite and bytownite. The intensive stirring used during the experiments also ruled out the possiblity of the establishement of concentration gradients within the batch reactor, and hence the possible formation of precipitate due to localized supersaturation.[7-10] For anorthite, the formation of diaspore, boehmite, and gibbsite was suggested by the calculation to be thermodynamically favorable at the end of the experiment. Because the precipitation rates of these Al-containing minerals are largely unknown under the GCS conditions used in this study, we cannot completely rule out the possibility that the Al concentration evolution for anorthite in Figure 4 is a net outcome of anorthite dissolution with secondary mineral precipitation. However, as discussed below, we assumed that the Al concentration profile for anorthite was solely derived from anorthite dissolution, and, based on that we were able to predict the Si release rates for a series of plagioclases with good accuracy. This good fit may suggest that the kinetics of Al-reprecipitation were not fast enough to appreciably change the solution composition within the time frame of our experiments.

S2. Additional discussion regarding the effects of interfacial area

Mineral dissolution can also induce several property changes in the solid phase, which may in turn affect the reactivity of the primary mineral. Surface area (solid−liquid interfacial area) is one of the core parameters used to quantify heterogeneous chemical reaction rates. When mineral dissolution is concerned, the reactive surface area is usually taken to be correlated with the surface ratio measured using the B.E.T. method, although in many cases they do not equal each other.[11] The essence of the concept of reactive surface area is the quantification of the number of atoms in the solid matrix that have access to the species from another phase, and hence can participate in a heterogeneous chemical reaction. For a given solid, the quantity of this type of atoms can be safely assumed to be proportional to the interfacial area. However, for different elements in one mineral, the proportionalities are also different in general. Throughout this article, we use another concept, C_T, the density of (tetrahedral-site-occupying) atoms at the solid–liquid interface that has access to aqueous species, as a supplement to the concept of surface area, to quantify mineral dissolution rate. Although the utilization of C_T in practice does not differ much from using solely the surface area (see equation (17)), it provides two conceptual conveniences. First, C_T can have different values for different elements. Second, although surface area is strictly a two-dimensional concept, C_T is not. The units of C_T can be either mol/m^2 or mol/m^3. The flexibility in the choice of units is important when it comes to a discussion regarding the effect(s) of the interfacial/altered/leached layer on mineral dissolution.

S3. Additional discussion regarding the dissolution congruency and interfacial layer formation

Although the nature of the interfacial layer formed during feldspar−water interactions is still under debate, the observation of a Si-enriched layer that is structurally different from the bulk feldspar crystal has been confirmed repeatedly.[12-19] An *in situ* characterization of the interfacial structure under the GCS conditions used in this study is very difficult, while with an *ex situ* solid characterization technique it is challenging to distinguish between the interfacial structural alterations induced by water−rock interaction and by the sampling process. Here we assume the formation of an interfacial layer for the plagioclases with Al/Si ratios other than unity,[19, 20] and we discuss whether mechanistic information could be masked due to the development of this layer.

From the mass-balance point of view, the presence of an interfacial layer differing from the primary mineral in composition is inherently related to dissolution incongruence. Similarly, if a steady state of the apparent dissolution rate, measured according to the evolution of the aqueous composition, can be ultimately achieved, the dissolution stoichiometry will be dictated by the bulk chemistry of the mineral. Several questions arise here.

One question is, if the development of the interfacial layer stems from the different reactivities of the elements in the solid matrix, will certain mechanistic information be lost during the transition from a non-steady-state, incongruent dissolution to a steady-state, congruent dissolution? For example, for plagioclase dissolution under acidic conditions, the Al-depletion in the interfacial layer[18] suggests that, when protonated, the Al−O−Si linkages are more reactive than the Si−O−Si linkages.[21] As the interfacial layer develops due to the preferential release of Al, two potential mechanisms may result in a subsequent transition to a steady state congruent Al/Si release. The first mechanism is that the presence of the interfacial layer creates transport resistance, which slows the Al release from the inner part of the solid. A second possibility, rarely mentioned in the literature, is that the existence of the interfacial layer effectively increases $C_{T,Si}$, the density of Si sites at the solid−liquid interface which have access to aqueous species, and hence practically increases the reactive surface "area" for Si (the quotation indicates that the Si-release is a three-dimensional process in this mechanism). It is now generally discredited that the decomposition of the feldspar framework will be limited by a diffusion barrier at the solid–liquid interface,[18, 22] and hence the latter mechanism may be given more credits. An implication of the second mechanism is that, the Al release rate is very important in describing alumosilicate dissolution. The release of Al involves only one type of linkage, while the release of Si involves various linkage combinations (listed in Table 1). Also, the apparent Si-release rate at steady-state may be a net outcome of two causes: a lower Si−O−Si reactivity and a higher $C_{T,Si}$. In the main text of this manuscript, we analyze both Al and Si release rates for our plagioclase dissolution experiments under GCS conditions, as well as for published feldspar dissolution data under ambient conditions.

A second question related to the transient variation of mineral dissolution rate is, if Al-release is not affected by appreciable $C_{T,Al}$ change during the course of alumosilicate dissolution, will the Al release rate remain constant throughout the experiment (while the Si release rate increases gradually to match the Al release). This is not true in Figure 5. Both Al and Si showed faster initial dissolution rates, which has been a prevailing observation in many laboratory measurements of mineral dissolution rates. The rapid initial dissolution, sometimes termed a "start-up artifact", has been attributed to many factors, such as elevated interfacial strain, surface fines, or defects induced by grinding, etc.[23] If the release of a tetrahedral site occupant can be viewed as the consequence of its *connectedness* (*Q*) being reduced from 4 to 0, then an apparent cause of this "artifact" is that many of the linkages, either Al−O−Si or Si−O−Si, have been broken mechanically (during the grinding process), leaving fewer linkages to break chemically (by hydrolysis) for each T-atom. Whether this kind of artifact can be quantified statistically needs further investigation (quantification is not impossible because given the bulk chemistry, the total number of different linkage types are known). If this is the main cause of start-up artifacts in mineral dissolution experiments, then the initial dissolution rates of minerals may contain mechanistic information that is at least equally important as steady state dissolution rates. The initial rates may also effectively distinguish the reactivities of different elements in the solid matrix, and they are not affected by parameter variations (e.g., C_T evolution) during the course of steady state establishment.

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