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Effects of Al/Si ordering on feldspar dissolution: Part I. Crystallographic control on the stoichiometry of dissolution reaction

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Abstract

The incongruent dissolution of feldspar is associated with the formation and evolution of Si-rich amorphous interfacial structures during its chemical weathering. The stoichiometry of dissolution is compositionally dependent, and this dependence reflects the nature of dissolution reaction as a combination of surface renewal and heterogeneous chemical reaction. We hypothesize that during continuous surface renewal, reactive sites on a feldspar's surface will inherit characteristics from the bulk structure of the primary mineral. Hence, the dissolution rate of feldspar depends not only on water chemistry but also on its crystallographic properties. We propose a new formalism to quantify the dependence of the dissolution rates of feldspars on their crystallographic properties. A correlation between the degree of Al/Si ordering and the stoichiometry of feldspar dissolution is predicted based on this formalism. This correlation is verified by a combination of water chemistry analysis, synchrotron X-ray diffraction with structure refinement (HR-XRD), and Fourier transform infrared spectroscopy (FTIR). We find that the rates of dissolution and the degree to which dissolution is incongruent depend on the frequency of SiOSi and SiOAl linkages (chemistry) and the crystallographic characteristics of these linkages (bond lengths, bond angles, and ordering) in the dissolving mineral. The knowledge of Al/Si ordering provides a means to quantify the relative abundances of Si atoms with different reactivities. Using a $C\bar{1}$-based structure model, we show that the distribution of Al within the Al-rich (T1) type of tetrahedral sites has only a minor effect on dissolution stoichiometry, whereas the distribution of Al between the T1-type and the Si-rich (T2)-type of sites affects dissolution incongruence predominantly. A greater extent of disorder results in higher dissolution incongruence. As an implication, our results suggest that the formation of interfacial structures during silicate dissolution should at least be partially affected by reactivity differences among the framework atoms of a silicate.

1. INTRODUCTION

Feldspars are the most abundant rock-forming minerals in the earth's crust. All feldspars are tectosilicates and share similar "mirrored crankshaft-chain" frameworks of polymerized Al/Si tetrahedra (Ribbe, 1993). Feldspars may differ in composition (interstitial cations and Al content, n_{Al}), average distance between tetrahedral sites and oxygen atoms (mean T–O bond length, $<T\text{–}O>$), and/or the degree of Al/Si ordering (distribution of Al and Si among tetrahedral sites). The geochemical properties of feldspars have been the subject of numerous studies, and a formidable number of publications have accumulated in the literature documenting the dissolution kinetics of feldspars under a wide range of reaction conditions, both natural and experimental (Busenberg and Clemency, 1976; Petrovic et al., 1976; Berner and Holdren, 1979; Gardner, 1983; Holdren

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Glossary of Symbols

$\ll$T–O$\gg$	grand mean T–O bond length (Å)
<Ti–O>	mean T–O bond length for the tetrahedron containing Ti (Å)
C_T	total availability of tetrahedral sites at the solid–liquid interface (mol m^{-2})
I	dissolution incongruence (Eq. (10))
n_{Al}	aluminum content (summed fraction of Al in all tetrahedral sites)
n_{An}	anorthite content (mole fraction of anorthite in feldspar)
$AnXX$	anorthite content (XX mole percentage of anorthite in feldspar)
Q_{OD}	degree of Al/Si substitutional ordering within T1-type of tetrahedral sites
Q_T	degree of Al/Si substitutional ordering between T1 and T2 sites
r	rate of element release (mol m^{-2} s^{-1})
R^2	coefficients of determination
R_{wp}	weighted R-factor of Rietveld refinements
T	tetrahedral site or its occupant (Al or Si)
t	elemental occupancy for the designated tetrahedral site (see subscripts below)
v	normalized availability for the type of the designated tetrahedral site
χ^2	goodness of fit
$\delta\omega$	wavenumber displacement of the peak near 650 cm^{-1} from a reference state
τ_{AlOSi}	characteristic time for the breakdown of intra-crankshaft-chain AlOSi linkages (s)
τ_M	characteristic time for the breakdown of inter-crankshaft-chain linkages (s)
τ_{SiOSi}	characteristic time for the breakdown of intra-crankshaft-chain SiOSi linkages (s)

Subscripts

1o	property of T1o sites in the $C\bar{1}$ space group
1m	property of T1m sites in the $C\bar{1}$ space group
2o	property of T2o sites in the $C\bar{1}$ space group
2m	property of T2m sites in the $C\bar{1}$ space group
Al	aluminum
Si	silicon

and Speyer, 1987; Murphy and Helgeson, 1989; Blum and Lasaga, 1991; Anbeek, 1992; Amrhein and Suarez, 1992; Manning et al., 1992; Welch and Ullman, 1993, 2000; Burch et al., 1993; Gautier et al., 1994; Knauss and Copenhaver, 1995; Oelkers and Schott, 1995; Blake and Walter, 1996; Stillings et al., 1996; Alekseyev et al., 1997; Murakami et al., 1998; Dobrowolski et al., 1999; Luttge et al., 1999; Taylor et al., 2000; Lasaga and Luttge, 2001, 2004; Arvidson et al., 2004; Zhu, 2005; Carroll and Knauss, 2005; Beig and Lüttge, 2006; Hellmann and Tisserand, 2006; Satoh et al., 2007; Sorai et al., 2007; Li and Luttge, 2009; Zhu and Lu, 2009; Fu et al., 2009; Sorai and Sasaki, 2010; Williams et al., 2010). An important yet elusive observation during feldspar dissolution is that the stoichiometries of dissolution products (interstitial cations, Al, and Si) are usually inconsistent with the bulk chemistry of the mineral, i.e., the dissolution is incongruent. Incongruent dissolution is in general considered a transient phenomenon and is typically observed during the initial stage of feldspar dissolution (Nash and Marshall, 1956; Garrels and Howard, 1957; Wollast, 1967; Luce et al., 1972; Paces, 1973; Chou and Wollast, 1985; Rimstidt and Dove, 1986; Muir et al., 1989; Casey and Bunker, 1990; Muir et al., 1990; Inskeep et al., 1991; Casey and Cheney, 1993; Hellmann, 1994; Xie and Walther, 1994; Hellmann, 1995; Brantley and Chen, 1995; Hochella and Banfield, 1995; Schweda et al., 1997; Pokrovsky and Schott, 2000; Weissbart and Rimstidt, 2000; Hamilton et al., 2001; Green and Luttge, 2006; Lee et al., 2008; Daval et al., 2009a,b, 2011; Kameda et al., 2009). The incongruence of dissolution may evolve as reaction progresses. Given enough time, incongruent dissolution may eventually be replaced by a steady-state congruent dissolution. From the mass-balancing point of view, the stoichiometry of steady-state dissolution is dictated by the bulk chemistry of the mineral. Conventionally, it is only this steady-state rate which is considered of geochemical importance in long term water–rock interactions (White and Brantley, 1995). However, it has been pointed out recently that the transient evolution of dissolution stoichiometry contains critical information regarding the regeneration of surface reactive sites during mineral dissolution (Samson and Eggleston, 1998, 2000; Samson et al., 2000), the formation and evolution of structurally and chemically distinct interfacial layers (Criscenti et al., 2005; Kendall and Martin, 2006; Houston et al., 2008; Lee et al., 2008; Gorrepati et al., 2010; Mason et al., 2011; Ruiz-Agudo et al., 2012), and hence potentially the origin of the discrepancies between mineral dissolution rates measured in laboratories and in natural environments (Brantley and Chen, 1995; Zhu et al., 2010; Hellmann et al., 2012). Recently, newly available advanced surface-characterization techniques have reinvigorated the mechanistic studies of this transient phenomenon during the dissolution of silicate minerals (Teng et al., 2001; Hellmann et al., 2003; Fenter and Sturchio, 2004; Fenter et al., 2010; Hellmann et al., 2012; Ruiz-Agudo et al., 2012).

Incongruent dissolution is inherently related to the formation of a new solid structure that is compositionally different from the dissolving (primary) mineral. When reviewing the historical perspectives regarding dissolution incongruence, it is hard to avoid the heated debate concerning the origin of these structures. The observations of interfacial structures, usually amorphous and enriched in Si, have been documented by numerous studies of the dissolution kinetics of mixed-oxides under acidic and neutral conditions (Casey et al., 1989; Banfield and Eggleton, 1990; Casey and Bunker, 1990; Arnold et al., 1992; Casey and Cheney, 1993; Brantley and Chen, 1995; Brantley et al.,