Incongruent dissolution of wollastonite measured with vertical scanning interferometry

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ABSTRACT

In this study, we investigated the dissolution kinetics of wollastonite, a pyroxenoid with composition CaSiO₃, at earth-surface temperatures. We used vertical scanning interferometry (VSI) to quantify the surface normal retreat (or advance) of a crystallographically defined cleavage face on a single wollastonite crystal as a function of time. Nanometer-scale measurements of (100) faces show that the wollastonite surface undergoes a net expansion normal to the surface and relative to the pristine mineral surface. These observations were made during the dissolution process at acidic conditions. The swelling is the result of the formation of a cation-depleted layer at the wollastonite-water interface. We combined VSI measurements with electron microprobe measurements to track the chemical evolution of the leached layer during dissolution, and then used previously reported Ca release rates to calculate the density of the cation-depleted layer. Using an average Ca release of 9.09 × 10⁻⁹ mol/m²·s at pH 3 and 25 °C, the density of the leached layer is 1.2 g/cm³, and grows to a thickness of ~50 nm after 20 hours of reaction. Although our observations do show direct evidence of the formation of a cation-depleted layer during dissolution, they do not favor a particular mechanism of formation of this layer. At this time, our results cannot rule out either cation migration through the depleted crystal structure or re-precipitation at the mineral surface.

Keywords: wollastonite, dissolution kinetics, leached layer, interferometry, mineral dissolution, surface studies

INTRODUCTION

Various minerals, including feldspars (e.g., Casey et al. 1989; Nesbitt et al. 1991), basalt glasses (Berger et al. 1994), and pyroxenoids (Casey et al. 1993; Banfield et al. 1995; Weissbart and Rimstidt 2000) exhibit incongruent dissolution when studied in the laboratory. During dissolution experiments, these minerals release interstitial cations, such as Mg, Ca, or K, more quickly than Si, leaving behind a layer that has been altered both structurally and chemically, commonly referred to as a leached layer.

Various spectroscopic techniques have been used to study depth profiles of these leached layers, showing that for the most part they are enriched in H, O, and Si (e.g., Casey et al. 1993; Kawano and Tomita 2001), while being depleted of interstitial cations (e.g., Farquhar et al. 1999; Muir et al. 1997). Their formation has been attributed by some to the difference in bond strength between the more covalent bonding of silica tetrahedra to the weaker, more ionic bonds holding interstitial cations (Banfield et al. 1995).

The pyroxenoid mineral wollastonite (CaSiO₃) has been shown in many studies to form an extensive leached layer at a rapid rate (Bailey and Reesman 1971; Casey et al. 1993; Rimstidt and Dove 1986; Weissbart and Rimstidt 2000; Xie and Walther 1994). Bailey and Reesman (1971) first reported that the release of Ca exceeds the release of Si during wollastonite dissolution in mildly acidic solutions. However, Rimstidt and Dove (1986), using mixed-flow reactors and SEM imaging, suggested that wollastonite dissolves stoichiometrically for short experiments (<20 h) in solutions of pH varying from 3 to 8. More recent studies have confirmed the initial observations from 1971, including Xie and Walther (1994) at low pH values, as well as Casey et al. (1993) and Banfield et al. (1995). Casey et al. (1993) showed that the wollastonite surface is enriched in hydrogen to depths of up to 1000 Å, whereas Ferruzzi (1994) showed that the surface is depleted in Ca to approximately similar depths as the hydrogen enrichment. Weissbart and Rimstidt (2000) proposed a model for wollastonite dissolution suggesting that large Si polymers are released from time to time, and that the leached surface regenerates to form areas that dissolve more slowly. A recent field study at Hubbard Brook experimental forest also supports the idea of the development of a leached layer during wollastonite dissolution (Peters et al. 2004). However, until the present study, the surface topography of the leached layer itself has never been quantified.

In this study, we use a unique approach to track mineral dissolution, namely using Vertical Scanning Interferometry (VSI) to track nanometer-scale changes in surface height and overall topography as a dissolution reaction proceeds. By tracking the surface-normal retreat of the mineral, it is possible to calculate dissolution rate constants independently of surface area measurements (see discussion in Luttge et al. 1999, 2003). These rate constants then provide a standard to which rates measured via other techniques can be compared. In addition, VSI allows us to track the development of the leached surface layer relative to a non-reacted surface, further clarifying the process of leached layer formation.