



## **Concentration gradients at the mineral-solution interface: implications for understanding dissolution mechanisms**

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Dissolution is a key process in fluid-rock interactions, such as in chemical weathering, CO<sub>2</sub> carbonation reactions, metasomatism, and metamorphism. Many multicomponent rock-forming minerals are reported to dissolve incongruently, because the elemental molar ratios, measured in the fluid during dissolution experiments, that differ from those in the solid. This frequently results in the formation of chemically and structurally altered zones at the fluid-solid interface of varying thickness that are depleted in some elements relative to the bulk mineral composition. Although the mechanisms of the formation of these altered layers is still a matter of debate (see e.g. Ruiz-Agudo et al. 2012 and Schott et al. 2012), recent AFM studies on the dissolution of two multicomponent minerals, dolomite, Ca<sub>0.5</sub>Mg<sub>0.5</sub>CO<sub>3</sub> (Urosevic et al. 2012), and wollastonite, CaSiO<sub>3</sub> (Ruiz-Agudo et al. 2012), provide experimental evidence showing that these layers are formed in a two-step process: (i) stoichiometric dissolution of the pristine mineral surfaces and (ii) precipitation of a secondary phase. This occurs despite the fact that the bulk solution is undersaturated with respect to such a phase. It has been suggested that after stoichiometric dissolution of the mineral, a boundary layer of fluid in contact with the surface becomes supersaturated with respect to a secondary phase that then precipitates. Here we present in situ observations of the evolution of the fluid composition at the interface during dissolution in acidic solutions (pH 1.5) of dolomite and wollastonite using real-time phase-shift interferometry. We show that immediately when the sparingly soluble dolomite or wollastonite crystals are in contact with the solution, the refractive index of the solution at the crystal surface sharply increases. A steep refractive index gradient (i.e. concentration gradient) develops as a consequence of mineral dissolution producing an interfacial fluid with a different composition to the bulk. Similar observations have been made during the replacement of KBr by KCl (Putnis et al. 2005). Thus, it seems that incongruent dissolution is essentially similar to any other mineral-fluid equilibration process: when a fluid interacts with a mineral with which it is out of equilibrium the mineral will tend to dissolve. Depending on the fluid composition, the interfacial fluid may become supersaturated with respect to a secondary phase that will eventually nucleate on the parent mineral surface.

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