

## The control of calcium silicate weathering and climate evolution by dissolution-precipitation processes at the mineral-water interface

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The kinetics of mineral weathering on the Earth's surface and the feedback through atmospheric and ocean chemistry controls climate evolution. The formation of surface coatings during early low-temperature silicate weathering may significantly affect the rate of silicate dissolution over geological timescales, and thus influence predictions made by climate models. The mechanism of formation of these layers is critical for understanding and evaluating dissolution kinetics of major rock-forming minerals, and is a matter of vigorous debate and controversy. Here we present *in situ*, high spatial resolution data on the evolution of mineral surface topography and interfacial fluid composition during dissolution of wollastonite (CaSiO<sub>3</sub>). Our study provides clear, direct experimental evidence that leached layers are formed in a two-step process: stoichiometric dissolution of the pristine mineral surfaces and subsequent precipitation of amorphous silica from a supersaturated layer of fluid in contact with the mineral surface. This occurs despite the fact that the bulk solution is undersaturated with respect to the secondary phase. The thickness of the supersaturated zone depends on fluid flow rate and suggests an origin for the well-known discrepancy, of up to four orders of magnitude, between dissolution rates measured in the field and in the laboratory. Our model suggests that transport-controlled dissolution kinetics due to the formation of surface altered layers leads to higher  $p\text{CO}_2$  and  $T$  (up to 2 °C) estimates over the last 90 Myr if compared with scenarios where these layers do not develop.