

Using molecular dynamics to understand the early stages of calcium carbonate formation

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The precipitation of calcium carbonate plays an important role in nature and in the household. In nature calcium carbonate is one of the most prevalent biominerals and the major component of limestone. Meanwhile, in industry and the household calcium carbonate, in the form of limescale, is a menace that decreases the lifetimes of many components.

In contrast to many other crystals the rate of formation of calcium carbonate in solution is fast and increases with temperature. In addition experiments [1] have shown that crystalline calcium carbonate forms via an amorphous precursor.

Recently, we have used molecular dynamics simulations of concentrated CaCO_3 solutions to examine the formation of this amorphous pre-cursor [2]. We find that the formation of amorphous calcium carbonate clusters is initially driven by electrostatic forces between the highly charged calcium and carbonate ions. Subsequent growth is then limited only by the rate of diffusion.

We have also investigated the mechanism through which polyacrylates act to slow the rate of formation of calcium carbonate from solution [3]. These investigations have demonstrated that polyacrylate-calcium-carbonate complexes are very stable. In addition in simulations of calcium carbonate precipitation in the presence of polyacrylates we observe that clusters of amorphous calcium carbonate are formed in the vicinity of the polyacrylate. This suggests that the rigid polyacrylate molecules prevent calcium carbonate precipitation by strongly binding calcium and carbonate ions to their carboxylate functional groups. Further growth of the CaCO_3 clusters is prevented because of the rigidity of the polyacrylate and the strong binding of the calcium carbonate to the polymer both of which prevent the free diffusion of calcium carbonate through the solution.

[1] J. Rieger, T. Frechen, G. Cox, W. Heckmann, C. Schmidt & J. Theime (2007) *Faraday Discuss* **136** 265 [2] G.A. Tribello, F. Bruneval, C. C. Liew & M. Parrinello (2009) *J. Phys. Chem. B*, **113**, 11680 [3] Tribello, Liew & M. Parrinello (2009) *J. Phys. Chem. B* **113** 7081

Carbon and nutrient export dynamics in small mountainous watersheds prone to landsliding in Guatemala

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Small mountainous rivers (SMRs) are recognized as an important component in the global carbon cycle as they transport a disproportionately large fraction of sediment and organic carbon to the world ocean fluvially compared to their small size. Tectonic and precipitation-triggered landsliding, one mechanism that is important to carbon delivery in many SMRs, has attracted attention because of its potential to mobilize multiple pools of carbon (biomass, soil carbon, and lithosphere). This study examines the impact of landsliding on carbon and nutrient export dynamics in mountainous watersheds altered by human activities.

The Sierra de las Minas, located at the North American-Caribbean plate boundary in central Guatemala, provides an ideal site for landslide research. In June–July 2009, water, sediment and bedrock samples were collected from 34 sites in three adjacent watersheds with varying degrees of landsliding within and among the watersheds. Water samples were analyzed for dissolved organic carbon (DOC) using a Shimadzu TOC 5050A Analyzer; for major anions and cations using a Dionex DX-120 ion chromatograph; and for Si using a Skalar flow-injection nutrient analyzer. Watershed response to landslides appears to vary across scales but water analyses were restricted to major sub-basins. Watersheds with higher density of landsliding (landsliding area/catchment area) are positively correlated (Pearson correlation, $p < 0.05$) with higher yields of most major cations (K, Ca, Mg), Si, SO_4 , and DOC. Marginal significance was found for Na ($p = 0.07$). Chemical weathering and CO_2 consumption from silicate weathering also had a significant positive correlation with landslide density ($p = 0.004$ and 0.05 , respectively).

Sediments and bedrock samples were analyzed for $\delta^{13}\text{C}$, $\%C_{\text{org}}$, and C/N ratios. While these results lack strong trends for source mixing models, there is evidence that exported carbon comes from multiple pools and that other factors such as landslide depth strongly influence carbon characteristics.