The Microbe-Mineral Interface: Chemical Reaction Kinetics in Real Time

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We have evidence that some microbes can assume control over subaqueous dissolution of carbonates. Microbial surface recognition and attachment is an important prerequisite step to biofilm formation, and biofilms may play an important role in the dissolution and precipitation of minerals. We are studying surface recognition and attachment of microbes to mineral surfaces with a method that exploits the capability of vertical scanning interferometry to visualize and quantify this microbial behaviour. We have demonstrated that the disimilatory metal-reducing bacterium, *Shewanella oneidensis*, (strain MR-1) has the capability to inhibit calcite dissolution in conditions under which the mineral would otherwise dissolve, were the microbes not present. The MR-1 organisms completely take control over dissolution rates by retarding the formation and propagation of etch pits on crystal surfaces.

In addition, we have studied the effects of chemical substitution in carbonate crystals ($MgCO_3$, $MnCO_3$, $CaMg(CO_3)_2$, $FeCO_3$) and also the relative abilities of both anaerobic MR-1 versus aerobically grown MR-1 to produce the same level of dissolution inhibition in the same crystals. Dolomite ($CaMg(CO_3)_2$), for example, is resistant to this effect, with the MR-1 biofilm exhibiting relatively little effect on crystal dissolution.

Here we will present results on our probe of the microbe/mineral interface and the effect of microbes on the stability and dissolution rates of environmentally important minerals. If our results are consistent in the natural environment, the impact on mineral weathering and the global carbon cycle could be profound.

References

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Segregation of Isovalent Impurities to the {00.1} and {01.2} Surfaces of Hematite (α-Fe_2O_3) Using Atomistic Simulations

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We will describe recent work studying the segregation of a number of iso-valent metals from the bulk structure to the two of the most stable surfaces of hematite (α-Fe_2O_3), namely the {01.2} surface and both the Fe and O terminated {0.01} surfaces. Impurities are known to segregate to the surfaces of solids thus effecting their composition and hence their surface properties (Davies et al., 1989).

Our work used atomistic simulation techniques based on the Born Model of Solids (Watson et al., 1996) and the parameters used in the potential models for hematite were those derived by Lewis and Catlow, (1985).

Ten iso-valent cations, namely Al^{3+}, Cr^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, La^{3+}, Lu^{3+}, Nd^{3+}, Tb^{3+} and Y^{3+}, were chosen for study and each was substituted onto each surface, replacing a varying number of surface Fe^{3+}, ions. We found that the calculated segregation energies were negative thus indicating the process is favoured and further that this effect increases as the size of the ion increases. For example at 33.33% coverage the segregation energy to the (01.2) surface was -8.55, -101.16 and -284.17 kJmol[-1] for Al^{3+}, Y^{3+} and La^{3+} respectively.

Since many non-equivalent configurations were considered we are able to study the effect of coverage and estimate the configurational free energy of the system and by using lattice dynamics calculate the vibrational free energy contribution. Our results show that for the {01.2} the most favourable surface concentration of impurity is 33.33%, similar to that found in Garnet ($Fe_5X_3O_{12}$). No such minima are observed when considering the Fe termination of the {00.1} surface but when the effect of temperature on the system is considered an energy minimum also at 33.33% impurity coverage appears at high temperatures. A minimum is observed for the O termination of the {00.1} surface however the concentration at which this occurs varies between 16.67% and 33.33% depending on the cation being considered, possibly suggesting the true minimum lies between these values.

In summary, this work suggests that atomistic simulation represent a useful technique for modelling the surface structure and stability of minerals.

References

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