

Photophysical studies of biologically produced macromolecules

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The attachment of microbes to solid surfaces is controlled by the macromolecular structure of the cell wall as much as driven by functional genes that are induced to produce cell wall macromolecules. We present here a quantification of the molecular conformation and sorption forces involved in the attachment of cell wall macromolecules such as lipopolysaccharides (LPS), alginates and extracellular polymeric compounds (EPS) extracted from bacteria. Our hypothesis is that the molecule-surface interfacial forces mediate the physicochemical interactions of bacteria cell wall, and its adaptation to the host environment. Photophysics techniques were used to investigate adsorption of biopolymer onto mineral surfaces which should act as model systems for bacterial growth. Adsorption of dilute aqueous solution of macromolecules was studied as a function of pH in the presence of alumina and silica using Time resolved anisotropy studies (TRAMS), fluorescence and ICP-MS. The alumina and silica particles were used to mimic active sites existing on the surface of kaolin-like particles. It was found that LPS for example, had a high adsorption affinity for Al₂O₃ and in contrast adsorbs weakly to SiO₂ surface. Strong adsorption was observed at low pH for both minerals. The dependence of adsorption on the mineral concentration was also examined at different pH conditions: the adsorption amount was observed to increase by increasing the mineral concentration. Macromolecular folding and conformation of the LPS, alginate and EPS at the solid-solution interface was also quantified using TRAMS. The results showed a high pH and ionic strength dependence demonstrating that macromolecule adhesion is favoured and mediated by ions such as H⁺ and Ca²⁺ in solution. These findings indicate that proton bridges and van der Waal forces are responsible for interactions at the interface. A model for macromolecule adhesion at the interface including the role of ions in solution and folding was proposed. This model is representative of the behaviour of biological macromolecules at the aqueous-surface interface in natural environments. The processes described here have a direct implication on bacteria mediated mineralisation via concentration of ions from solution.

Magma, solutions and metals

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Holland^[1] demonstrated experimentally that Cl-bearing magmatic-hydrothermal aqueous fluids can scavenge metals from silicate melt and transport the metals into the surrounding crustal environment where fluid-rock reactions and decompression may cause metal precipitation and form ore deposits. Specifically, the abundance of Cl in the fluid phase was demonstrated to be a master variable that controls the total mobilized quantity of metal. Holland^[1] stated: "It remains to be seen just how useful these criteria will turn out to be; the results of preliminary tests are encouraging". This was a prescient statement indeed. Over the ensuing four decades, scientists have constructed a wonderful house of experimental knowledge on the scaffolding that Holland built, and these data guide our understanding of the incredible role of aqueous fluids in magmatic-hydrothermal systems.

Our research group continues to investigate experimentally the mobility of transition row metals, high field strength, and rare earth elements in aqueous fluids ranging from those exsolved from silicate melt in shallow-level magma chambers to fluids evolved during the blueschist to eclogite transition in subduction zones. Specifically, we are investigating how the complexity of aqueous fluid, i.e., dissolved chloride salts, fluorine, albite, etc., affects element mobility.

Data for the mobility of iron in a silicate melt – aqueous fluid – magnetite – sulfide assemblage indicate that the mass transfer of iron can moderate oxygen fugacity, sulfide stability, the composition of ferromagnesian silicates, and the fractionation of stable iron isotopes. These data have important implications for using iron as a geochemical fingerprint for processes that form porphyry, high-sulfidation, iron-oxide-copper-gold (IOCG), and iron-oxide-apatite (IOA) deposits. New data for the mobility of Y (a proxy for the heavy-REE) and Nb (a proxy for all HFSE) in xenotime- and rutile-saturated aqueous fluids, respectively, indicate that these elements are orders of magnitude more soluble at the moderate temperature and high pressure conditions where fluids evolve in subduction zone environments. These new data have significant implications for element recycling during the high-pressure metamorphism that accompanies subduction, and ultimately for evolution of continental crust.

[1] Holland, H.D. (1972) *J. Economic Geology*, **67**, 281-301.