The mechanism of leached layer formation during mineral dissolution

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Many minerals and glasses dissolve non-stoichiometrically, i.e. the elemental ratios measured in the fluid during dissolution experiments are different to those in the solid. This phenomenon results frequently in the formation of the so-called leached layers, which are chemically and structurally altered zones at the fluid–solid interface depleted in some elements relative to the bulk mineral composition [1,2]. The mechanism of non-stoichiometric dissolution and leached layer formation has been a subject of significant research over the past decades, due to its relevance to a wide range of natural and technological weathering processes, as well as being critical to define kinetic laws for mineral reactions. In this study, *in-situ* nanoscale Atomic Force Microscopy (AFM) observations have been made of reacting surfaces during the dissolution of two minerals: 1) a carbonate (dolomite, $CaMg(CO_3)_2$) and; 2) a silicate (wollastonite, $CaSiO_3$), both of which are known to dissolve non-stoichiometrically under acidic conditions and/or to develop leached layers upon dissolution. Combined with chemical analyses of both the output solutions and the reacting surfaces, AFM observations lead to a clearer understanding of the reaction mechanism.

Our study gives clear evidence that a leached layer is formed via an interface-coupled dissolution-precipitation mechanism [3] in a two step process: stoichiometric dissolution of the pristine mineral surfaces and subsequent precipitation of a secondary phase (a Si-rich and Mg-rich surface precipitate, respectively) from a supersaturated boundary layer of fluid in contact with the mineral surface, and not by preferential leaching of cations as postulated by most currently accepted dissolution models. Furthermore, this study demonstrates that *in situ*, direct observations of the reacting mineral surfaces are important to unambiguously ascertain the kinetics and mechanism of mineral dissolution. The kinetics of the process can be quantified from the measurement of etch pit spreading rates, which are unaffected by the formation of a secondary precipitate, whose existence has been neglected or simply not observed in the past.

References

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An *ab initio* and Raman study of Co(II) complexes in water

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Abstract

The transport of metal ions under hydrothermal conditions such as formation of ore bodies and as corrosion products in nuclear reactors are strongly influenced by temperature, pressure, and the type of complexing ligands. It is difficult to make speciation measurements under extreme conditions, and the interpretation of the measurements is not always unambiguous. *Ab initio* calculations have been shown to be very useful in the interpretation of the spectra of aqueous solutions of metal ions in the presence of complexing ligands, for example Sc^{3+}-Cl^- [1], Zn^{2+}-Cl^- [2] and Zn^{2+}-Br^-[3]. We present here our studies of cobalt(II) in the presence of water, chloride, hydroxide, and ammonia ligands, including predictions of the Raman spectra [4], and compare with recent experimental Raman measurements carried out at the University of Guelph. We will also discuss the stability of mixed OH^-/Cl^- complexes.

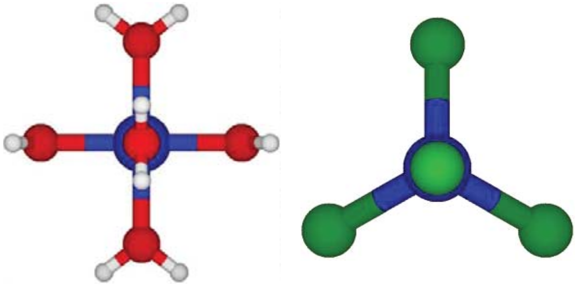

Figure 1: The hexaaquacobalt(II) and tetrachlorocobaltate(II) ions

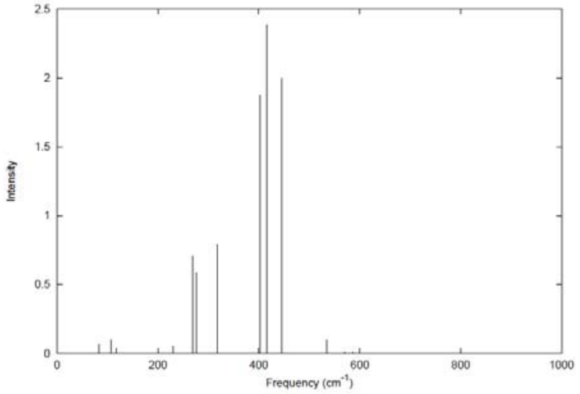

Figure 2: Simulated Raman spectrum of hexaaquacobalt(II) based on a HF/6-31+G* calculation.

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