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The solubility and dissolution rates of natural apatite

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The dissolution of apatite in natural systems is of increasing interest due its role in supplying phosphorous to micro organisms and its potential use in soil remediation. One of the major difficulties in predicting the role apatite in near surface processes is the poor understanding of its thermodynamic and kinetic properties. For example, values of the logarithm of the 25° C equilibrium constant of the apatite dissolution reaction given by

$$Ca_{10}(PO_4)_6F_2 + 6H^+ = 10Ca^{2+} + 6HPO_4^{2-} + 2F^- \qquad (1)$$

reported in the literature range from -28.4 [1] to -68.38 [2]. To overcome these limitations apatite solubilities and dissolution rates have been measured in open and closed system reactors.

Closed system experiments at 25° C, run in excess of five months were used to obtain a preliminary value of the log (K) of reaction 1. The resulting value, -62, is in the process of being refined using the results of open system experiments designed to measure dissolution rates.

Apatite dissolution rates have been measured as a function of aqueous Ca, PO_4 and F concentration, pH from 2 to 11.8 and temperature from 25 to 200° C. Stoichiometric release rates of Ca, P, and F are observed in most experiments. Measured 25° C dissolution rates decrease monotonically with increasing pH; logarithms of measured 25° C rates decrease from -7 to -11.5 mol/m²/s with increasing pH from 2 to 11.8. Rates at acidic pH are in close agreement with those previously reported in the literature [3,4]. Rates measured at elevated temperatures are used to determine the pH variation of apparent activation energies. Measured dissolution rates are used to generate Transition State Theory based equation describing these dissolution rates as a function of solution composition and chemical affinity.

References

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How do microorganisms enhance mineral dissolution rates?

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Microorganisms play a critical role in many geologic and environmental phenomena but their precise functions are unknown. For example, although compelling evidence indicates that microorganisms enhance mineral dissolution rates, particularly those which involve oxidation-reduction and/or essential nutrient release to the environment, it is unclear if this enhancement requires the physical attachment of the microorganism to the mineral surface. In an attempt to illuminate the mechanism of mineral microbial dissolution rate enhancement a number of related studies have been preformed:

1) Both apatite and phosphorous-free feldspar were buried in a peat-rich soil supporting moorland vegetation in Shap, N. England for over 1 year. These samples were recovered and analyzed for microbe attachment on these mineral surfaces. Although this soil is believed to be phosphate limited, no preferential attachment of microbes to the apatite surfaces was observed.
2) Apatite dissolution rates were measured at 25° C in mixed flow reactors as a function of aqueous solution composition. Constant pH, far-from-equilibrium apatite dissolution rates were found to be strongly enhanced by increasing aqueous organic acid concentration, and decreasing aqueous P concentration.
3) Further apatite dissolution experiments were preformed in the (a) absence of *Bacillus megaterium*, (b) with this bacteria in physical contact with apatite, and (c) in the presence of this bacteria but physically separated using dialysis bags. Apatite dissolution was found to be enhanced by the presence of physically separated Bacillus megaterium, but ***inhibited*** by its direct contact with the mineral.

Taken together these observations indicate that microbial enhancement of apatite dissolution occurs indirectly via changing the composition of the aqueous solution (e.g. increasing organic acid or decreasing aqueous phosphate concentration) rather than the direct interaction of microbes with mineral surfaces. The direct attachment of microbes apparently inhibits dissolution; this effect is attributed to the blocking by microbes of reactive sites on the mineral surface.