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APATITE DISSOLUTION KINETICS AND THE LONG-TERM PHOSPHORUS CYCLE

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ABSTRACT

Apatite is the primary exogenic sink of phosphorus (P). The weathering of apatite contained in continental rocks and sediments compensates for the P loss via sediment subduction over geologic time scales. P availability may control marine net ecosystem production over geologic time scales and thus apatite weathering rates may control long-term marine net ecosystem production.

It is hypothesized that apatite dissolution rates can be quantified and modeled in a manner similar to silicate and carbonate minerals and that they are primarily a function of mineral composition, pH, degree of undersaturation, and temperature. This hypothesis is tested by a series of experiments measuring the steady-state dissolution of five apatite compositions over a range of pHs ($2 < pH < 8.5$) and temperatures ($25 - 55^{o}C$) that are applicable to past earth surface conditions.

The dissolution rate of igneous apatite ($2 < pH < 8.5$) and marine sedimentary apatite ($4 < pH < 7$) decreased with increasing pH over the respective pH ranges studied with igneous apatite dissolving faster at comparable pHs. The effect of pH on igneous apatite dissolution was most pronounced in the acidic pH range ($2 < pH < 5$); after which, the rate was relatively invariant with pH change over $5.5 < pH < 8.5$. The initial stage of the dissolution reaction is incongruent with calcium being released to solution in stoichiometric excess of P and fluoride. The degree of undersaturation has a significant effect on igneous apatite dissolution rates and was taken into account when determining the apparent activation energy of igneous apatite dissolution (8.3 kcal mol^{-1}).

Apatite experimental dissolution rate dependency on solution and temperature variation suggests that the long-term P release from apatite weathering is partly a function of global temperature and apatite surface area. This hypothesis was explored by modeling how Phanerozoic variation in temperature and igneous rock surface area influenced apatite weathering rates. Model results show that elevated global average temperature and igneous rock surface area during the mid- to early-Paleozoic resulted in an increased apatite weathering P flux. These results suggest that temperature and rock surface area variation exert control on the dissolved P flux from apatite weathering over geologic time scales.