A mass balance approach to groundwater evolution in a shallow, clastic, polyphase aquifer, Vilas County, Wisconsin, USA

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Studies on the geochemical controls of surface and groundwater compositions have characteristically dealt with geologic settings that are mineralogically simple and relatively uniform, allowing quantitative estimates of mineral weathering rates in natural environments (Drever, 1997; White and Brantley, 1995). However, clastic sediments comprising multiple mineral (polyphase) assemblages, exhibiting a wide range of chemical compositions, are more typical for many watersheds or aquifers. Laboratory dissolution studies of individual silicate and carbonate phases permit comparison of the relative weathering rates of specific mineral phases (Velbel, 1993), but application to estimating rates for field-based, multiple-phase environments, that are typical of most weathering situations, is difficult and frought with uncertainties. It is generally recognized that mineral weathering rates are determined in no small part by the specific detailed chemical composition of the phases, especially the plagioclase feldspars and the principal mafic silicates, such as biotite, amphibole, and pyroxene. Complex mixtures of these phases in clastic systems reflecting multiple source rocks unevenly distributed over the terrain (e.g. glacial deposits) are common and cannot be ignored in attempting to understand mass transfer in specific watersheds or groundwater aquifers.

Often, significant attention has been paid to the mineralogy and chemical composition of the reactant (source) and product (sink) phases, but to highly varying degrees in different studies. Despite the equal importance of products of silicate weathering processes as the reactants, the sufficient definition of mineralogic character and chemical composition has been commonly lacking, largely due to the difficulty of identifying phases and chemical compositions of specific clay minerals and oxyhydroxide products in surficial enviroments, as well as the problem of distinguishing between autochthanous weathering products and allochthanous clays from sediment source areas.

A shallow, carbonate free, silicate aquifer in glaciofluvial sediments in northern Wisconsin has provided the medium in which field-based, quantitative estimates of highly mixed mineral mass transfers have been attempted. A unique groundwater flowpath has been identified using the boundary between two, isotopically distinct, groundwater masses resulting from recharge of a plume of lake water upgradient from the study site. Several wells positioned along the flowpath allow the definition of the evolutionary sequence of waters passing through medium to coarse-grained clastic silicate (dominantly quartzose) sands and silts. A silt layer with a greater proportion of primary mafic minerals and clays positioned approximately half way along the flow path strongly influences the composition of the water down gradient. Mineralogic analysis (electron probe and X-ray diffraction) has been used to define the phases. Characteristically the plagioclases range in composition from An_5 to An_{55} (modal compositon = An_{20}). A mixture of amphiboles, biotite, and pyroxenes, each varying significantly in chemical complication, are also present (Kim, 1997).

Mass balance approaches have been used to anlyse the evolutionary sequence of waters along the flow path using a spreadsheet model developed by the authors several years ago (Bowser and Jones, 1990). Formal, mass balance models require that the number of mineral phases considered be equal to the number of solute species. The maximum number of solute species available to constrain our analyses is ten, thus limiting the mass balance analysis to no more than ten phases, far less than are present in the aquifer. Other approaches must be used to expand the number of mineral phases considered.

We have used a 'mean reactive' mineral composition for some phases (for example, mean reactive plagioclase would be an intermediate composition that would correspond to a single plagioclase composition yielding a water of the same Na/Ca ratio as the mixture of plagioclases observed in the aquifer). An added approach is to use 'fictive' minerals that represent a fixed ratio of two minerals of known chemical composition (for example a 'phase' composition representing a fixed ratio of biotite to chlorite, each of known composition). The ratio of phases chosen can be in proportion to their respective dissolution rate constants, thus, compensating for fictive phases of differing reaction kinetics.

A characteristic, and puzzling feature of the evolutionary sequence of the water is its constant sodium content after passing through the silt layer, yet its calcium content continues to increase along the flow path (Kim, 1997). Simple mass balance analysis would suggest that plagioclase dissolution had ceased at this point, despite its strong undersaturation at these concentrations, or that some mechanism operates to maintain a fixed sodium in the water despite continued plagioclase dissolution.

A model is proposed that couples plagioclase and ferromagnesian mineral dissolution and kinetic exchange driven processes operating between iron and sodium in intergranular micropores of the silicate phases undergoing weathering. Inasmuch as the proportion of nanoporous mineral matrix is much increased in the silt layer, initial silicate dissolution appears best modeled as a stepwise intergranular diffusive process driven by local concentration gradients, such as proposed by Wood, Kraemer, and Hearn (1990). It is suggested that this process is especially applicable to the alteration of the primary mafic silicates, so that ferrous iron (as well as alkaline-earths) released prior to oxidation and probable incorporation in secondary ultrafine particulate is exchanged for sodium, perhaps obtained in part from weathering of sodic plagioclase.

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