|  |  |  |
| --- | --- | --- |
| Symbol | Definition | Units |
|  | atomic weight of element | g /mol |
|  | gram-based\* mass fraction of the solid in a mixture | g /g total solid |
|  | fraction of mass of element that is retained in solid after dissolution |  |
|  |  |  |
|  | concentration of species in mineral/rock/solid | g /g solid |
|  | mass of solid | g |
|  | molar weight of solid | g /mol |
|  | stoichiometry of species in solid | mol /mol |

\* I am working in grams here, though I prefer to work in moles in general. But, it seems simpler to stay in grams, as we will likely always report concentrations in units of wt. %.

Equations used to generate element concentration-concentration trajectories when considering so-called “enhanced weathering” —

**Consider**: a mixture of solids (e.g., soil and basalt or soil + plagioclase + olivine + clinopyroxene), in which any component can be reactive.

* *Note*: it is obviously simpler to consider only the basalt to be reactive, but it would be useful to build in the capacity for any component to react.

The bulk concentration of element in the solid mixture is:

Eq.

where there are components contributing to the mixture. The endmembers can be described by their bulk chemistry (if it is thought that is how they dissolve) or by their mineralogical composition (again, if that is how they are thought to dissolve). A similar equation holds for the bulk concentration of in a rock, comprised of minerals.

Following reaction, the parameterization of which is up to the user (e.g., do you want it to be a function of time or reaction progress? It doesn’t really matter, just depends on preference), one must determine the concentration of the mixture (i.e., what is being measured and tracked to verify the extent of reaction). This is done by considering the total mass of mineral/rock dissolved and the fraction of element that is immobile. The immobile phase must be accommodated into a secondary phase, the molar mass and stoichiometry of which determines its mass in the mixture and, hence, the concentration of in the bulk solid.

For any step in the reaction, the bulk concentration (Eq. I) is modified by the mass of element lost via dissolution and the amount retained via precipitation:

Eq.

It is up to the user how to track mass loss. The first term here can be the initial (=*step 0*) and one can apply a cumulative mass lost/retained (this is how the equation is presented above; “cum.diss” refers to the cumulative dissolved mass of solid ). Or, one can perform this calculation every step (either in time or reaction progress) and then the first term is the mass of element at the previous step and refers to the mass of solid dissolved in the most recent step.

The term is calculated by assuming a host phase for the immobilized fraction. It is simplest to assign a single phase for each element, as inaccurate as this may be. Otherwise, the calculation gets that much more complicated, as one must decide how then to partition the element between the phases (better off with Crunch in this case, I think, unless you want to deal with a whole bunch of additional rate laws).

Eq.

where

Eq.

The index ‘*primary’* refers to the initial solids in the mixture, while ‘*secondary’* refers to the authigenic precipitates assumed below (for example):

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | sorption | Mg(OH)2 | sorption | CaCO3 | SiO2 | AlOOH | FeOOH | TiO2 |
| *MW immobile phase [g/mol]* | *NA* | *34.0138* | *NA* | *60.008* | *31.998* | *33.0059* | *33.0059* | *79.868* |
| *[mol /mol minl ]* | *1* | *1* | *1* | *1* | *1* | *1* | *1* | *1* |
| *Fraction element retained* | *0* | *0* | *0* | *0* | *0* | *0* | *0* | *0* |

**Assumption**: Element labeled ‘sorption’ are assumed not to form solid precipitates but to sorb to existing solid surfaces. Thus, no secondary mineral mass is generated in these cases.

**Parameterizing mass loss**

There is no need to apply kinetics here; in my calculations, I just have steps (i.e., reaction progress) and assign a cumulative mass loss in each step. I can differentially react minerals by assigning a fraction of initial mineral dissolved, which I use to determine a final mass of mineral. I then assume a linear decrease in mass over time and calculate the cumulative mass loss in each step (other functional relationships can be used).

If one wants to use some kind of rate law, a simple TST-type rate law works:

Eq.

where is the mineral surface area , is the intrinsic rate constant , is the activation energy , the term is the dependence of rate on the aqueous activity of the species, is the reaction quotient, is the equilibrium constant, and , , and describe the dependence on rate on the departure from equilibrium .

The issue with using any rate law is that you must then track the fluid composition. This is, I think, not necessary for the exercise we have in mind.