

Interactive comment on “Improved parameterization of the weathering kinetics module in the PROFILE and ForSAFE models” by Harald Ulrik Sverdrup et al.

Harald Ulrik Sverdrup et al.

hus@hi.is

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This paper is useful in the sense that it provides a compilation of available data on mineral kinetics. Although empirical rather than mechanistical in approach, it still can have its place in applied science, but the suitability for Biogeosciences is in doubt.

We are of the opinion that the approach underlying the PROFILE-ForSAFE model system does have a complete theoretical foundation, which should be apparent from the published documentation of the model. If the reviewer questions the very presence

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comment

of a theoretical basis for this model system, then it will be difficult for us to satisfy the reviewer that there is a case for publishing this paper, despite the fact that it defines the scientific basis for improvements made in a widely using modeling system.,

The manuscript is not properly executed and does not fit the format of a paper in academic journal. I noted 3 scientific problems that have to be resolved by the authors before the paper can be considered for further review.

1 - Database issue. The manuscript aims to provide a kinetic database for executing some weathering models. This task is not fulfilled. A simple compilation of available kinetic data is not the same as critical evaluation of these data and expert recommendation of rate constants (regardless of the type of equation used to model the rates). Consider some analogy with thermodynamics. A database used in any thermodynamic model is a product of EXPERT evaluation of available thermodynamic information data, and recommendation of definite values based on expert judgement of various experimental (or modeling - if needed) works. The same should be clearly done for kinetic database, but this step is missing or not presented in the manuscript.

In our response we intend to point out that an expert evaluation is presented and the methodology is described over several pages. The manuscript describes how the available data was used for the rate coefficients, and then how the gaps in the data table were filled using interpolation methods. For details, there are references to earlier works, going in detail and showing the path back to the primary data. We will recommend in particular Sverdrup (1990) and Sverdrup and Warfvinge (1995) carefully.

The table of recommended kinetic constants should contain at least some pertinent references in the way it is organized for thermodynamic databases. Example is given in L598-605. This is totally unacceptable.

In our reply we will argue that the models referred to as "thermodynamic" based on the use of a saturation factor which assumes an equilibrium that probably does NOT exist in soils for primary minerals. These models are neither "thermodynamic" nor not

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pass any field test. The resulting weathering rates obtained with these models are from 3 to 4 orders off when tested on field, which means they are not useful. Only the use of massive adjustments make the results appear as publishable. The geochemical community sometimes failed to take this fact in, and failed to make necessary innovations. We will argue that the scientific discussion about weathering should have room for alternatives to the thermodynamic approach. But if this is seen as "totally unacceptable", then we believe that the reviewer would not have accepted any of the papers published on the PROFILE-ForSAFE system of models.

Original data and their quality evaluation should be presented. Another example is L 921-923: the use of inter-mineral interpolations and of analogues is totally obscure.

Sverdrup (1990) explains how this was done, and this has been elaborated in later publications.

2 - Natural application issue. The dissolution of aluminosilicates, at far from equilibrium conditions at least, is controlled by activity of free $\text{Al}^{3+}(\text{aq})$ in solution (unequivocally demonstrated by group of Schott, Oelkers). The binding of Al^{3+} to natural organic ligands decreases the activity of main inhibitor of aluminosilicate dissolution and thus increases the rates. This Al complexation is not considered (or not described) in the model because simple organic ligands (carboxylates, aromatic) cannot be used to predict Al^{3+} speciation in the presence of complex fulvic and humic acids, as well as organo-mineral (Al, Fe) colloids.

We agree that the solution activity Al^{3+} is part of the braking mechanism, and there is more than just Al^{3+} being involved. This is all considered in the model (See the references to our work on this), and described in detail the referenced papers published by the authors on the subject.

The authors mention some acids (L306-307) but what are these acids? Some soils contain 5-10 cm of organic layer and then the mineral layer occurs. These minerals will interact with DOM. The equation 13 is not justified.

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For how this was derived, we will back to Sverdrup (1990), Sverdrup and Warfvinge (1995) and further work by Sverdrup and Holmqvist in the years after. The organic acids were assembled into two groups, depending on reactivity with the surfaces (Sverdrup 1990). We disagree with the reviewer and have data to show the expression is valid and justified. That has been published several times, and we will call the reviewer's attention to this. Other researchers also support such a formulation.

Why mineral dissolution should be slowing with increasing organic ligand concentration (L395)? This contradicts to a large body of knowledge on mineral dissolution, notably of aluminosilicate minerals.

We will disagree with this, by taking the reviewer through the relevant equations, and also with references to Sverdrup (1990), Sverdrup and Warfvinge (1995). The rate of dissolution increases with the activity of the organic ligand at the surface. When all adsorption sites at the surface are occupied, then increasing solution concentration will have no further accelerating effect (Sverdrup 1990). This is evident from the rate equation.

How the secondary mineral precipitation was modelled?

This was modelled as kinetic precipitation, and is detailed in the description of the SkogSAFE model version (Rietz 1995). This was tested at the chronosequences and data from the integrated monitoring sites at the Gårdsjøn Research Catchment.

3 - The quality of modeling is not demonstrated. The use of Na (Figs 13, 14, 15) without considering stoichiometry and Si release rate is not suitable.

The stoichiometry is explained in Sverdrup (1990) and Sverdrup and Warfvinge (1995). We will provide precise direction to where that was discussed, so that we can hopefully make clear that there is no need to republish that.

Original data allowing to see the quality to modeling should be presented. The model curves should be given for other plots (Figs 16 -18). Overall, the need of the empir-

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ical adjustments (braking functions) is not clear or not presented. There are robust equations of mineral dissolution rates, cited in L 904-905

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This section was limited because of lack of space (The original contribution was 63 pages), and after discussions with earlier reviewers, a number of graphs and figures were taken away. A part of the reference list was taken away as we were asked to reduce length substantially (From 63 to 49 pages means that stuff has to go. If we are being asked to put this back again, we could do that). The reference list can easily be made 10 pages longer, but that is not the purpose of the article. Thus discussing every reference is just out of the question. More of the model testing is described in the companion paper by Erlandsson-Lampa et al. 2020 in this VSI, which we do refer to already.

Interactive comment

Some technical issues (to be re-evaluated at the 2nd stage): Abstract is simply impossible to read by non-experts. The braking function should be defined. L568-569: quartz does not belong to clay minerals

Quartz can be removed from the text. Abstracts can be rewritten, but it is not meant for the layman. The reader has to have some background about weathering. The braking functions are in the equations; but we can add some more explanation in the text.

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