Hydrology and Earth System Sciences Discussions

Interactive comment on "Coupled modeling of hydrologic and geochemical fluxes for prediction of solid phase evolution in the Biosphere 2 hillslope experiment" *by* K. Dontsova et al.

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We are grateful to reviewers for their constructive comments and suggestions. Addressing these comments have led to a significant improvement in the manuscript. Below we have copied the original reviewer comments followed by our italicized response regarding how these comments were addressed in the manuscript.

Anonymous Referee #1

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General Comments

This study presents modeling experiments that attempt to predict the rate and extent of weathering (i.e., the evolution of soils) from an initial granular basalt material for a series of upcoming hillslope-scale experiments taking place in the Biosphere 2 (B2). While the assumptions made in developing these computer models (HYDRUS, CrunchFlow2007, and Rosetta) are limiting in some respects, this study does a good job (along with the companion paper) of covering the first approach towards the goal of a fully-coupled modeling environment capable of adapting and developing in parallel with the actual B2 experiments. While the paper is well written, a few concerns should be addressed by the authors.

Specific Comments

1. The authors could more clearly demonstrate how all the modeling pieces fit together. This could be done by including a simple schematic figure. It is confusing as to how everything fits together.

A new Figure 3, which is a schematic of model integration, was added to address this concern.

2. Additionally, one aspect that was not clear to me (and perhaps needs better justification) is the influence of dimensions and configuration in one-dimension column experiment.

Would the orientation of the column in the one-dimensional modeling influence the transformation? Also, the dimensions of the soil column are selected to simulate the 'longest' flow paths in the hillslope. What about shorter flow paths (i.e., columns of different dimensions)?

The 30 meter column represents the longest flow path possible on the modeled hill-slope. Since this particular configuration permits a continuous distribution of column lengths, including those that are shorter, this allows us to follow changes to the basalt

material occurring close to the surface, as well as further down the flow path (e.g., deeper in the profile and further down gradient). Orientation of the column does not affect results of the simulations as flow direction is defined as parallel to the column length. This is discussed further in the manuscript.

3. In addition, some additional discussion should be included to highlight why each of the models used in this study was selected.

A paragraph was added to discuss advantages of the CrunchFlow program including references where it has been successfully applied to chemical weathering or water-rock interaction in the past. Description of the Rosetta software was also expanded.

4. Another general comment is on the use of laboratory values (as opposed to field values) for the parameters of the basalt material. The authors give sound justification for this; however, since this is a modeling study, some effort should be put into demonstrating the influence of a range of assumed parameterization for the initial basalt material.

Simply put, what would happen if you adopted field values? It makes sense rather than to speculate on the possible outcomes to just run through a few key modeling scenarios to demonstrate the influence. Are the one-dimensional and the two-dimensional experiments influenced in the same way?

In order to address this suggestion, we conducted additional 2-D simulations using dissolution rates that were 10, 100 and 1000 times lower than the ones used before. The rate constant was unchanged, as we consider it an intrinsic property of the mineral, but specific surface areas were changed systematically to test the effects of a change in dissolution rate. We added a summary figure (Figure 9) which shows effect of different SA (hence dissolution rates, as indicated by Eq. 3) on hillslope weathering rate expressed in mol ha^{-1} yr^{-1} for comparison with field results.

5. The title of the manuscript may be considered a bit of an overstatement since the three models feed into each other, but it is debatable to what extent that can be con-

sidered 'coupled'. From the concluding sentences of the manuscript, it sounds as if future models will indeed be fully-coupled and allow for feedbacks and complexities to emerge in the hillslope developments. The current study takes one model result and uses it to drive another model. The authors should consider changing the title to reflect this.

This is a good point, and we have changed title of the manuscript to read: **Solid phase evolution in the Biosphere 2 hillslope experiment as predicted from modeling of hydrologic and geochemical fluxes.**

Technical Corrections

P4450, L22: Clarify if these will be first-order or zero-order watershed.

Zero-order – corrected.

P4454, L8-10: Here and elsewhere, verify that all digits are significant.

All measured values were checked and number of significant digits corrected, number of significant digits for values derived from the EQ3/EQ6 database were decreased to agree with those from the literature.

Figures: The color scales do not print well in black and white. If possible, consider this

in the selection of color bars.

Authors modified color scheme for the figures to improve presentation when printed in black and white.

Figure 7: Change 'finction' to 'function' and 'a nd' to 'and'.

Corrected.

Anonymous Referee #2

Received and published: 1 August 2009

General comments

This manuscript presents the results of a modeling exercise of coupled geochemical transport simulations at steady state flow taking into account weathering reactions of dissolution and precipitation with potential feedback of secondary minerals changing the soil hydraulic properties. The mathematical assumptions are valid while rather large simplifications have been allowed for.

No biological influence is present, no water uptake by plants is allowed for and steady state flux is assumed throughout the whole modeling period.

The reviewer raises valid questions regarding including effect of plants (both water and lithogenic element uptake and release of organic compounds), temperature effects and temporal change in flow. While we plan to include these factors in future modeling, particularly when the hydrologic and geochemical models are more fully coupled, we feel it is essential to test the model for abiotic steady state conditions as a first step toward testable model validation.

The authors are very sparse with explanations of the mathematical equations that underlie their hydraulic model equations and the chemical reactions. I would request an electronic attachment that displays at least some of the governing equations with regards to hydrology and to geochemical reactions considered.

A CrunchFlow reactive transport governing equation was added to the text. However, as indicated in the manuscript text, extensive model documentation is readily available on line and also in the published literature. Since this publication is intended to describe a hillslope geochemical weathering application of the CrunchFlow code, we do not think it would be an efficient use of space to duplicate extensive narratives that describe the model details when those are available elsewhere. For this reason, the reviewer's suggestion to include an attachment that describes the code details was an excellent one and we have done that.

The authors do not clearly present the concept of reactive surface area and no information is given on the reactive surface area development of the secondary minerals formed.

The following statement was added to the manuscript: "Reactive surface area for primary minerals was calculated from the measured specific surface area for the basalt and mass fraction of the minerals in the basalt. In the model, therefore, bulk surface area decreases linearly with the volume fraction of the dissolving mineral phase. For secondary minerals an initial bulk surface area of 100 m^2 mineral/m^3 porous medium was assumed for lack of any specific data on how nucleation and precipitation in its early stages occurs. Once precipitation occurs, surface area is recalculated so that it increase with a 2/3 dependence on the secondary mineral volume fraction."

Too little information on species distributions considered in the aqueous phase is presented.

While aqueous phase speciation was included in the output from the simulations, a detailed discussion of this is outside the scope of the paper. As discussed, our principal intent was to evaluate solid phase transformations that result from such aqueous phase speciation, because it is the solid phase evolution that gives rise to changes in hydraulic properties of the hillslope. Understanding those solid phase changes and their hydrologic impacts was the primary objective of the work.

Did the authors check for saturation states of other potential forming phases such as imogolite or amorphous silica?

Poorly-crystalline minerals were not included in the simulations due to the inherent difficulty of handling metastable phases at the same time that we are simulating precipitation of minerals with greater thermodynamic stability. However, we did conduct some simulations in response to this suggestion. For example, when we conducted simulations with both ferrihydrite and goethite as potential precipitates, precipitation of only more stable goethite was observed. To model this appropriately, it would be nec-

essary to include an "mineral aging" conceptual model. This was discussed extensively by Steefel and Van Cappellen (1990.)

The calculated weathering rates are very high! There are plenty of field based weathering rates in the literature some of which the authors could cite and compare to their own rate. It has been demonstrated that Al3+ activity has a significant effect on the weathering rate of basaltic glass [Wolff-Boenisch, et al., 2004] and feldspar ([Gautier, et al., 1994]) . Did the authors choose to incorporate this effect according to their equation 3?

While CrunchFlow07 is capable of including the Al activity effect on dissolution rates (as indicated in the methods section), this was not done in simulations. This is because Maher et al. (2009) showed that using the nonlinear Parallel Rate Law of Hellmann results in a dissolution behavior that is similar to when the Al activity effect is included. The Parallel Rate Law of Hellmann was used in this study. A statement discussing the Al-inhibition effect on weathering and relevant references suggested by reviewer as well as reasons for selecting a different rate law are now included in the text. (Maher, K., Steefel, C. I., White, A. F., and Stonestrom, D. A.: The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California, Geochim. Cosmochim. Acta, 73, 2804–2831, 2009.)

What about temperature effects? The authors mention some climate scenarios but do not present data on the temperature profile in the soil and its effect on weathering!

For the purposes of the present work, our intent was to compare the impacts of precipitation, rather than temperature, as the prime climatic influence. While the temperature effect can certainly be incorporated, we wanted to develop in this case a set of scenarios that could be validated under laboratory (298 K) conditions. However, we are quite interested in investigating temperature effects in future research.

How are the redox processes controlled?

Redox reactions are treated similarly to other reactions (e.g., pH or H+ concentration). With the formulation used in CrunchFlow (documented in Steefel and Lasaga, 1994, Steefel and MacQuarrie , 1996), redox reactions require no special treatment. The primary redox active species are oxygen present in both the aqueous and gas phase and the Fe(II) bearing silicate minerals (or glass). The oxidative dissolution of Fe(II) minerals, then, is the primary redox couple here. Oxygen partial pressure is controlled by diffusion limitations.

Why did the authors not choose to impose a constant but realistic element or at least water uptake by plants too?

As discussed above, we need to develop an abiotic baseline understanding of geochemical transformation at the hillslope scale before introducing the effects of plants. This is also most relevant to the B2 experiment because the first several years of the hillslope experiment are intended to be free of vascular plants, and therefore the plant-free conditions is directly relevant. We have clarified that point in the manuscript.

Finally for comparison purposes with other weathering rates at other sites a general average weathering rate in terms of keq m-1 year-1 would be very helpful!

We have now added a figure (Figure 9) that gives average weathering rates in mol ha^{-1} yr^{-1} for the scenario discussed in 2D simulations. We also conducted additional simulations to test how using different mineral dissolution rates would affect these average element release rates under modeled conditions. This allowed us to now make comparisons to published chemical denudation values as suggested by this reviewer.

Specific comments:

The authors have a quite complete list of relevant references. To my opinion some

other references that are very relevant are missing. What about adding the following

references too?

a) [Godderis, et al., 2006] (use of a coupled weathering model to estimate weathering rates including the precipitation of secondary minerals) b) [Sverdrup, et al., 1995] (some earlier but comparably complete model to estimate non-steady state weathering rates) c) [Gerard, et al., 1998] (this paper besides others demonstrates the effect of Al3+ activity on the weathering rates in the field).

Suggested references were reviewed for relevancy and then added to the paper.

P 4453 Line 16 The reader is interested in the actual data, what about sulphur content?

Information about sulfur content of the basalt (0.01% by mass) was added.

How good is the fit between the XRD data and that calculated from the software?

"These concentrations were verified by quantitative X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro MPD X-ray Diffractometer (PANalytical B.V., Almelo, the Netherlands) with Cu-K_ radiation that gave bulk values for the composition of the crystalline minerals and by image"

R^2 *was 0.88 for XRD and 0.90 for image analysis. This information was added to the text.*

P 4457 Line 2 As the authors discuss later these assumptions are far from realistic.

"with a steady state water infiltration for that period that gives a total rainfall equivalent to that expected over the course of the 14 to 18 year (depending on selected climate) B2 hillslope experiment."

We agree that steady state flow does not commonly develop under field conditions. However, unless hydrologic and geochemical models are fully coupled to address hydrologic dynamics, it is difficult to exchange information between the models at the

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level of efficiency needed for non-steady state simulations. Conversely, we prefer the steady state approach as a first cut in any case, since it permits evaluation of spatially resolved data without introducing the complexity of non-steady state conditions. One needs a starting point for simulating hillslope geochemical transformations and as the level of complexity is increased, it becomes increasingly difficult to evaluate the output without a high degree of ambiguity. The steady-state assumption allowed providing an input to the CrunchFlow2007 model that was representative of the expected spatial flow patterns on the hillslope, even if temporal dynamics are not as realistically representative.

P 4457 Line 8 Interesting for the reader is which species were chosen !

"of total concentrations was obtained by "sweeping" the EQ3 database for all relevant

species"

Authors added an attachment with a list of secondary aqueous species.

P 4459 Line 14 why not check geometric surface area too? There are a number of papers that demonstrate that geometric surface area is a fair estimate for reactive surface area for a number of minerals. "but several additional lower values (10, 100 and 1000-fold lower than the measured N2 BET) were also used"

Given that our simulations involve the use of surface areas that are variable across several orders of magnitude, it is unlikely that the use of geometric surface area would lead to new insights. Our modeling was conducted for a material that was not homogeneous in size and for which many of the particles are less than 1 μm in equivalent diameter. Such small particles typically contribute the majority of the surface area, which would complicate our ability to provide precise measures of geometric surface area for simulation.

P 4461 Line 5 As mentioned earlier the effect of Al3+ activity on weathering reactions

has probably been incorporated, but the reader does not know when and how?

The fact that the Hellman formulation addresses the Al inhibition of dissolution rates is addressed earlier in this reply.

P 4461 Line 10 This software may only be known to some of the readers. I would propose that the authors give at least some two to three sentences in describing how the software transforms texture to hydraulic conductivity as there are quite a number of ways how to perform this task.

"To assess the feedback effects of mineral transformation on hillslope hydrology, we estimated hydraulic parameters from soil texture evolution using Rosetta software (2001). Rosetta is a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions."

We added additional information in response to this comment. Specifically, the sentence "Rosetta is a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions." was replaced with following description of Rosetta model: "Rosetta is a collection of artificial neural network models that estimate saturated hydraulic conductivity and parameters in the van Genuchten equation from easily obtained soil properties such as soil texture and bulk density. Rosetta was calibrated on a database of 2134 samples containing texture, bulk density, water retention and saturated conductivity data. Correlations and their performance metrics can be found in Schaap (2001).

Table 1

Why should the solubility constants be displayed with 4 digits ? The precision and

uncertainty is probably much higher !

This is a valid point and we have decreased number of digits displayed for the values derived from the EQ3/EQ6 database to agree with the precision associated with solubility constant values that were collected from the literature. For literature values, the number of significant digits was used as reported in the papers.

All Fe is displayed as Fe(II) except when mentioned otherwise as in goethite. I would propose to follow the same nomenclature also for Mn and display Mn as Mn(II) and then for pyrolusite as Mn(IV)O2

The oxidation state of Mn was specified in the revised version of the manuscript.

REFERENCES:

Gautier, J.-M., et al. (1994), Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150_ C and pH 9, Geochimica et Cosmochimica Acta, 58, 4549-4560. Gerard, F., et al. (1998), General implications of aluminium speciation dependent kinetic dissolution rate law in water-rock modelling, Chemical Geology, 151, 247-258.

Godderis, Y., et al. (2006), Modelling weathering processes at the catchment scale: The WITCH numerical model, Geochimica Et Cosmochimica Acta, 70, 1128-1147.

Sverdrup, H., et al. (1995), Modeling Recent and Historic Soil Data from the Rothamsted-Experimental-Station, Uk Using Safe, Agriculture Ecosystems & Environment, 53, 161-177.

Wolff-Boenisch, D., et al. (2004), The effect of fluoride on the dissolution rates of natural glasses at pH 4 and 25[degree sign]C, Geochimica et Cosmochimica Acta, 68, 4571-4582.

We are grateful for the recommended references and after reviewing their relevancy to the manuscript, we have now included them in the paper.

Technical comments:

Fig. 7. Typographical error in figure caption was corrected.

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 6, 4449, 2009.