nonneg suggested comments: P.C. Lichtner, OFM Research June 24, 2015

General comments:

Paper attempts to tackle a difficult problem in modeling geochemical systems when one of the reactants is completely consumed. Most of the comments which follow are minor in nature.

For mineral reactions this does not appear to be an issue since the mineral volume fraction is typically updated explicitly because of slow kinetics and slight negativity can be tolerated (if the mineral volume fraction becomes negative it is simply set to zero). However, this is not generally possible for aqueous reactants. Below are a number of suggested changes.

- Introduction needs rewriting. Background should be moved to introduction and equations moved to next section.
- Why are reactions listed in the appendix not balanced—mass or charge? Is it just because the full reaction is not shown? For example: the "reaction" NH4+ → NO3− when balanced becomes e.g.: 2O2 + NH4+ → NO3− + 2 H+ + H2O, which can be written in terms of any number of different species. One would expect this to be important for calculating the change in pH, for example. Might consider adding + reactants and + products to the left and right hand sides to indicate that the full reaction is not considered.
- L10: The sentence:

  > "As CLM and PFLOTRAN use explicit and implicit time stepping, implementation of CLM biogeochemical reactions in PFLOTRAN can result in negative concentration, which is not physical and can cause numerical instability and errors."

  is not strictly correct and somewhat confusing as written. Suggested rewrite: "Implementation of CLM biogeochemical reactions in PFLOTRAN can result in negative primary species concentrations, which is not physically meaningful."
- Replace throughout: "the nonnegativity challenge" with → "nonphysical solution negativity"

  Change title: 1. Addressing the Challenge of Nonnegativity → 1. Nonphysical Solution Negativity

Minor typos: (comment is near line number)

1. L130: "The reactions and rate formulae are detailed in Appendix ."

   Remove space after Appendix. Should the reactions be balanced on mass and charge?
2. L145: concentration → concentrations
3. L150: using the backward difference → using the backward Euler method

4. L155: use d/dt instead of partial derivative ($\partial/\partial t$) since referring to ordinary differential equation with one independent variable (and throughout text).

   Put periods at end of figure and table captions.

5. L185: "geochemical codes generally prefer analytical Jacobian calculation"

   codes are inanimate objects and can't "prefer" anything: rewrite

6. L195: rewrite the sentence: "Like Eq. (1), one of the basic challenges for using geochemical code for CLM is that Eq. (7) is not guaranteed to be positive."

   Is what is meant the updated solution in eq. 7?

7. L230: "LT is widely used in geochemical codes to enforce positivity ..." This is not the reason LT is used; rather, it is used to be able to describe highly variable primary species such as O2 or Al+++ which can vary over many orders of magnitude as pH or redox state changes without the need to use variable switching. LT can blow up which is the equivalent of negative concentrations in the linear update.

8. L240: by orders of magnitudes → by orders of magnitude

9. L240: comparing to the case without LT → compared to the case without LT

10. L245: no need to indent after eq. 18—this is caused by inserting a blank line in LaTeX (also occurs elsewhere in text).

11. L250: and a $c^{k+1} = 0$ causes → and $c^{k+1} = 0$ causes

12. L610: The following sentence seems to indicate comparison with data: "This introduces a multi-year cycle in addition to the annual cycle (Figs. 10, 11, 12). Overall, CLM-PFLOTRAN roughly reproduces CLM4.5 ..."

    Text needs to be rewritten to clarify.

13. L985: what is the definition of u and d? They appear to be used both as subscripts and as variables.

14. L990: are all the zeros needed in the stoichiometric coefficient for N:

    SOM1 → 0.72SOM2 + 0.28CO2 + 0.020000N,

15. L1055: eq B2: If μ_{ij} is constant it can be brought outside of the partial derivative. In terms of notation, μ is usually reserved for chemical potential. Better might be to use ν_{ij}.

    Change: using geochemical code → using a numerical geochemical formulation

16. Fig. 1 caption: (B) is not mentioned in the caption.

17. Fig. 5 caption: by Eqs. (27 and 28) → by Eqs. (27) and (28)

18. Fig. 10 caption: need to describe figure and meaning of colors