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Simulating loss of primary silicate minerals from soil due to long-term weathering using Allogen: Comparison with soil chronosequence, lake sediment and river solute flux data

John F. Boyle

Department of Geography, University of Liverpool, PO Box 147, Liverpool, L69 3ZT, UK

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Abstract

This paper presents ALLOGEN, a process model of soil mineral chemical weathering. Though designed principally to aid interpretation of lake sediment geochemical records by providing mass balance constraints for competing interpretations, the model is also applicable to more general questions about long-term weathering and soil development. The model is constructed around a generalised version of the mineral-weathering submodel of PROFILE, modified to minimise the need for site-specific data and to optimise performance for long-term change. Comparison with observed weathering rate data (river flux studies, chronosequences and lake sediment chemical stratigraphy) suggests that soil mineral depletion can be usefully simulated over timescales applicable to Quaternary and Holocene studies. To illustrate this, the plausibility of a weathering interpretation is demonstrated for sediment records at Lake Hope Simpson and Moraine Lake and the lake chronosequence at Glacier Bay. While long-term soil mineral depletion appears predictable, reliable simulation of past runoff quality is hampered by lack of a suitable long-term model for soil carbon.

Keywords: Geochemistry; Mineral; Model; Palaeolimnology; Sediment; Soil; Weathering

1. Introduction

Soil weathering models, developed to assess anthropogenic acidification, have existed for more than a decade, yet their potential to inform questions about long-term weathering has not been exploited. The purpose of this paper is to describe and test such a model, adapted from the silicate mineral weathering submodel of PROFILE (Sverdrup and Warfvinge, 1988) and optimised to simulate Holocene to Quaternary scale changes in soil mineral concentrations due to chemical weathering. The model, ALLOGEN, is primarily designed to aid interpretation of geochemical palaeolimnological data by providing quantitative mass balance constraints for competing interpretations. However, it is also intended to have application to other questions relating to long-term weathering, such as controls over carbon sequestration by chemical weathering of minerals, and compositional evolution of soils during pedogenesis.

The design specification for a suitable model is constrained by the objective of aiding interpretation of

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E-mail address: jfb@liv.ac.uk.

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lake sediments and soil chronosequence data in terms of changing environment; the model must provide output suitable for comparison with these data types and it must respond realistically to environmental factors. Three characteristics are essential. First, given that sediment and soil analysis typically yields mineral concentration data rather than fluxes, the model must simulate the weathering behaviour of individual minerals, allowing calculation of mineral concentration changes. Second, in order to simulate the impact of environmental forcing realistically, a fundamental process approach to mineral reaction rates must be adopted. Third, to optimise the model for application to long-term palaeoecological problems, it must be as little dependent on site-specific information as possible. These three requirements are not entirely satisfied by any existing soil weathering models, all being designed for quite different purposes. However, the soil acidification model PROFILE (Warfvinge and Sverdrup, 1992) comes very close, two features of its silicate mineral weathering submodel being particularly suitable for long-term modelling. First, it exploits a practical implementation by Sverdrup and Warfvinge (1988) of transition state theory; Lasaga (1995) stresses the importance of using sound chemical theory of this kind even where the macroscale physicochemical framework is poorly understood and must be crudely parameterised. Second, PROFILE has undergone a substantial degree of field testing against measures of current weathering rates (e.g., Sverdrup and Warfvinge, 1995; Duan et al., 2002), even critics finding reasonable agreement with alternative approaches (Langan et al., 2001). Validation against longer term measures has proved less conclusive. Warfvinge et al. (1995) found reasonable agreement between palaeoecological data and SAFE (a dynamic version of PROFILE) simulations of Holocene soil change at Gårdsjön in Sweden, while Hodson and Langan (1999) found poor agreement between PROFILE-derived estimates of base cation release rates and data for two chronosequences. However, in neither case was the mineral depletion rate tested critically, the former investigating runoff pH which is more strongly influenced by dissolved organic carbon and climate than by mineral depletion, and the latter investigating total base release rather than specific minerals. In conclusion, despite the lack of long-term validation, the silicate weathering submodel of PROFILE appears the most appropriately formulated and best tested that is currently available, and has, therefore, been incorporated in a somewhat modified form in ALLOGEN. This paper describes details of model formulation, and validation by comparison with long-term records of mineral weathering.

2. Implementation of the weathering model

2.1. Silicate mineral weathering submodel

The silicate mineral weathering submodel used here is essentially identical to that used in PROFILE. Described in detail elsewhere (Sverdrup and Warfvinge, 1988; Sverdrup and Warfvinge, 1995), the submodel determines the total dissolution rate, R_i, of mineral i from unit area of a particular soil layer using the expression:

$$R_i = r_i A_i \theta \tag{1}$$

where r_i is the area-specific dissolution rate at the mineral surface, A_i is the total surface area of the mineral, and θ is the volumetric soil water concentration (the significance of this is discussed below). The value of r_i is found from the sum of a series of terms representing the different agents contributing to dissolution:

$$r_i = f_i(H^+) + f_i(H_2O) + f_i(pCO_2) + f_i\ (\text{Dissolved organic carbon}) \tag{2}$$

The details of these functions are given in Sverdrup and Warfvinge (1995). In brief they include temperature dependent dissolution constants, reaction orders, and inhibition of reaction by dissolved ions.

The most important underlying characteristics of this mineral dissolution submodel are adherence to mass balance principles, and minimisation of site-specific parameterisation via the use of laboratory-derived rate constants. The mineral reaction rate expression is based on transition state theory, though simplified in regards to its treatment of near-saturation reaction inhibition. The rate coefficients are adjusted for temperature, as are the equilibrium coefficients used for the soil solution calculations. Rate constants were determined for each mineral from laboratory empirical data as described in detail by Sverdrup (1990). Issues relating to contrasts between laboratory and field measurements of dissolution rate constants are addressed below in Section 2.6.

2.2. Calcite weathering rate

PROFILE uses a reaction rate expression for calcite that was designed for silicate weathering. Preliminary investigation showed that this formulation produces results quite different (far slower reaction rates) from those calculated using the expression and coefficients of Wollast (1990). Given that PROFILE has been optimised to work in acidic environments where carbonates are absent, and that the expression of Wollast (1990) is more theoretically reasonable, the latter has been