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Quantification of colloidal and aqueous element transfer in soils: The dual-phase mass balance model

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Abstract

Mass balance models have become standard tools for characterizing element gains and losses and volumetric change during weathering and soil development. However, they rely on the assumption of complete immobility for an index element such as Ti or Zr. Here we describe a dual-phase mass balance model that eliminates the need for an assumption of immobility and in the process quantifies the contribution of aqueous versus colloidal element transfer. In the model, the high field strength elements Ti and Zr are assumed to be mobile only as suspended solids (colloids) and can therefore be used to distinguish elemental redistribution via colloids from redistribution via dissolved aqueous solutes. Calculations are based upon element concentrations in soil, parent material, and colloids dispersed from soil in the laboratory. We illustrate the utility of this model using a catena in South Africa. Traditional mass balance models systematically distort elemental gains and losses and changes in soil volume in this catena due to significant redistribution of Zr-bearing colloids. Applying the dual-phase model accounts for this colloidal redistribution and we find that the process accounts for a substantial portion of the major element (e.g., Al, Fe and Si) loss from eluvial soil. In addition, we find that in illuvial soils along this catena, gains of colloidal material significantly offset aqueous elemental loss. In other settings, processes such as accumulation of exogenous dust can mimic the geochemical effects of colloid redistribution and we suggest strategies for distinguishing between the two. The movement of clays and colloidal material is a major process in weathering and pedogenesis; the mass balance model presented here is a tool for quantifying effects of that process over time scales of soil development.
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1. INTRODUCTION

At a fundamental level, the development of soil involves the gain and loss (i.e., mass balance) of chemical elements. Since soils are open systems, neither mass nor volume is constant and thus assessing elemental mass balance over the course of soil development is challenging. One solution to quantifying changes in individual elements has been to reference gains and losses to an index constituent that is assumed stable (immobile) within given bounds. Brimhall et al. developed models describing relationships between mass, volume, and mobile and immobile components (Brimhall et al., 1985, 1988; Brimhall and Dietrich, 1987). That work yielded a concise model that has become a crucial and widely used means for assessing open system mass balance and volumetric change by referencing an index constituent, usually an element presumed to be chemically immobile (Brimhall et al., 1991, 1992; Chadwick et al., 1990). Application of the Brimhall model has allowed Earth scientists to trace mineral weathering and soil development across pedogenic time scales inaccessible through

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contemporary monitoring, thus contributing to understanding how the Critical Zone evolves and the growing effort to predict its response to natural and anthropogenic perturbations (Brantley and Lebedeva, 2011).

The fundamental idea of using an assumed immobile component to quantify changes in mass, volume, and mobility of elements has a long history, but has undergone relatively little evolution in that time. One early example comes from Merrill (1897) who used Fe or Al as a "constant factor" to determine the percentages of mobile constituents retained and lost in weathered material. A rearranged form of Merrill's equation was used by Reiche (1943) to calculate the fraction of a constituent retained (x):

$$x = \frac{(A_w \cdot C_f)}{(A_f \cdot C_w)} \quad (1)$$

Here A and C are the "weight percentages of the variable and the (assumed) non-variant constituents", respectively and the subscripts refer to weathered (w) and fresh (f) rock (Reiche, 1943). The hazard of assuming constancy was apparent to Reiche, but the technique became a useful tool for indexing weathering losses in rock and soil (e.g., Goldich, 1938; Morgan and Obenshain, 1942; Nesbitt, 1979). Muir and Logan (1982) presented a metric called the eluvial/illuvial coefficient (EIC) to determine chemical change and mass fluxes from soil horizons resulting from pedogenesis. That paper cites Rode (1935) and Barshad (1964) as the source of the method, but in the style of Merrill (1897) includes a separate "parent material quotient" to account for the change in mass relative to the index constituent (Muir and Logan, 1982).

The element immobility problem spurred an interest in using heavy and weathering-resistant mineral phases as an index (Marshall, 1940). Minerals including tourmaline, anatase and rutile were isolated from soil size fractions to serve as indices. Zircon became a favorite because chemical analysis could be substituted for mineralogical analyses by assuming that all Zr occurred in zircon (Marshall, 1940; Marshall and Haseman, 1942). In addition to elemental redistribution, the index mineral concept had potential to account for the translocation of clay, as described by Barshad (1955). One limitation on the adoption of Barshad's models was that they were described only through text, without accompanying equations. Additional limitations were the assumptions of a uniform transformation of nonclay to clay across the soil profile; the absence of clay weathering; and that no clay migrates out of the soil profile (Brewer, 1964).

A complete mass balance model that quantified changes in soil mass, volume, and gains or losses of constituent elements relative to an assumed immobile constituent was presented by Brewer (1964). This model was a synthesis of existing models (Marshall and Haseman, 1942; Nikiforoff and Drosdoff, 1943), and also utilized the "parent material quotient" concept. Brimhall developed a similar model to better understand the enrichment of ores by metasomatism (Brimhall et al., 1985; Brimhall and Dietrich, 1987) and enrichment of bauxite deposits by dust (Brimhall et al., 1988). The applicability of these ideas to other open-chemical systems was apparent, and so they were rapidly adapted to the study of soils and weathering (Brimhall et al., 1991, 1992; Chadwick et al., 1990). A comparison of the Brewer and Brimhall models shows equations that were formulated in different manners, but that obtain the same results. The Brimhall model has now become the standard tool for assessing and interpreting volumetric change and elemental mass balance during soil formation and weathering (Amundson, 2010; Brantley and Lebedeva, 2011).

Derivations of the three major metrics of Brimhall's model can be found in several papers (Brimhall and Dietrich, 1987; Brimhall et al., 1988, 1991; Chadwick et al., 1990). Each of the metrics references an index constituent (i) for which immobility is assumed. Strain ($\varepsilon_{i,s}$) measures changes in volume as the porosity of soil and density of its particulate components change:

$$\varepsilon_{i,s} = \frac{V_s - V_p}{V_p} = \frac{\rho_p C_{i,p}}{\rho_s C_{i,s}} - 1 \quad (2)$$

Here V_p and V_s are volumes of parent material and soil, respectively, and the bulk density (ρ) and concentration of an index component (C_i) are measured for the parent material (p) and soil (s). If, for example, the volume has doubled in the weathered material then $\varepsilon_{i,s}$ is 1.0, and if volume is halved $\varepsilon_{i,s}$ is −0.5.

The open-chemical-system transport function, $\tau_{j,s}$, is the mass fraction of element j added or lost relative to the mass originally present in parent material:

$$\tau_{j,s} = \frac{\rho_s C_{j,s}}{\rho_p C_{j,p}} (\varepsilon_{i,s} + 1) - 1 \quad (3)$$

Thus strain accounts for changes in mass and volume that would otherwise distort element gain or loss. Where 100% of element j has been lost, $\tau_{j,s}$ equals −1.0; where the mass of element j has doubled in the volume considered, $\tau_{j,s}$ equals 1.0.

The mass of element j gained or lost from a given volume of weathered material (m_j), can then be determined by using $\tau_{j,s}$:

$$m_j = \left(\rho_p V_p \frac{C_{j,p}}{100}\right) \tau_{j,s} \quad (4)$$

When using this equation to determine gains or losses from soil profiles, strain must be calculated in order to correctly define the original volume of parent material from which the gain or loss occurred, rather than using the measured volume of the soil horizon (Egli and Fitze, 2000). Brantley and Lebedeva (2011) have formulated another equation incorporating a strain correction based on the measured volume of weathered material rather than the original volume of parent material.

Two minor modifications have been made in the use of $\tau_{j,s}$. First, the equation can be reduced to a simpler form that eliminates the need for bulk density data or a determination of strain:

$$\tau_{j,s} = \left(\frac{C_{j,s}}{C_{j,p}} \times \frac{C_{i,p}}{C_{i,s}}\right) - 1 \quad (5)$$

(Vidic, 1994; Egli and Fitze, 2000; Kurtz et al., 2000). Such a formulation is comparable to Eq. (1) and earlier models for assessing open system mass balance (Reiche, 1943;