Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: implications for hydrologic control of differences in absolute rates

Michael Anthony Velbel
Department of Geological Sciences, Michigan State University, 206 Natural Science Building, East Lansing, MI 48824-1115, USA
(Received March 1, 1992; revised and accepted August 12, 1992)

ABSTRACT

Inverse models which apportion watershed effluxes (geochemical mass balance) over estimated mineral surface area give weathering rates for individual silicate minerals (e.g., feldspar) 1–3 orders of magnitude slower than laboratory rates. Comparisons of rates calculated from several recent watershed geochemical mass-balance studies with experimentally determined rates reveal that the ratio of mineral weathering rates for a given silicate–mineral pair determined in an internally consistent field study equals the ratio of rates for the same minerals in any internally consistent set of laboratory experimental data. Thus, the coefficient which corrects the weathering rate for any mineral from a laboratory data-set to a field setting is identical to the corresponding coefficient for any other mineral in the same data sets. The “correction factor” linking experimental and natural rates must be independent of composition. Physical (e.g., hydrologic) controls, rather than compositional or chemical controls, cause the difference between weathering rates in nature and the laboratory. Because flow in natural weathering profiles is spatially heterogeneous, not all of the potentially available surface in natural systems actually participates in reactions with pore fluids.

1. Introduction
Predictive modeling of landscape geochemical response to acidification and other environmental stresses is a major focus of current environmental research. There is increasing interest in rates of weathering and their relationship to ion budgets in natural systems (e.g., Sverdrup and Warfvinge, 1988; Bergström and Lindström, 1989), including direct application of experimentally determined rates and rate constants to forward modeling of natural soil–solution compositions (e.g., Furrer et al., 1989, 1990; Madé and Fritz, 1989, 1990). Such modeling requires thorough understanding of the relationship between laboratory data on the rates of silicate–mineral weathering and rates of geochemical reactions in natural systems (Drever and Swoboda-Colberg, 1989, 1991; Drever et al., 1989; Schnoor, 1990).

Rates calculated from geochemical mass-balance studies of elemental fluxes in natural watersheds are up to three orders of magnitude slower than in the laboratory (Pačes, 1983; Velbel, 1985a, 1986a, b; Schnoor and Stumm, 1986; Sverdrup and Warfvinge, 1988; Drever and Swoboda-Colberg, 1989, 1991; Drever et al., 1989; Frogner, 1990; Schnoor, 1990; Sver-
In these calculations the field rate, determined from measured net fluxes out of natural watersheds and the stoichiometry of the weathering reaction, is divided by an estimate of the reactant mineral's surface area in the regolith. Natural solute fluxes or concentrations are also orders of magnitude lower than those predicted by forward models using laboratory rate constants for silicate-mineral weathering and conservative estimates of mineral surface area in soils or aquifers (e.g., Lerman, 1990). These lines of evidence, along with laboratory experiments (Holdren and Speyer, 1985a, b, 1986, 1987), theoretical considerations (Berner, 1978; Helgeson et al., 1984), syntheses (Berner, 1978; Velbel, 1986a) and observations of the etched character of naturally weathered mineral surfaces (e.g., feldspar; Berner and Holdren, 1977, 1979; review by Velbel, 1986a), all suggest that mineral surfaces in nature are either less reactive than their laboratory counterparts (rate constants may actually be lower in the field than in the laboratory), or that rate constants are equal but environmental factors intrinsic to the watershed alter some other term in the rate equation. Previous work on the influence of surface area, chemical affinity, temperature differences between the laboratory and the field, dislocation densities and partial coatings of products on the laboratory–field rate discrepancy is reviewed by S.L. Brantley and M.A. Velbel (in prep.); for the natural watershed systems studied to date, none of these factors alone is sufficient to account for the difference (Velbel, 1985a, 1986a, 1989, 1990).

Most previous work comparing weathering rates in nature and in the laboratory has concentrated on feldspars. Because feldspars are the most abundant mineral in the crust, they have received the most attention, and consequently there are more experimental determinations of weathering rates for feldspar than for any other silicate mineral. However, weathering rates of other silicate minerals have also been determined, both in the laboratory and in the field. The purpose of this paper is to compare field and laboratory weathering rates of multiple silicate minerals, and to examine the implications of the comparison for explaining the disparity in silicate–mineral dissolution rates between laboratory and natural systems.

2. Methods

In this paper, ratios of silicate–mineral weathering rates calculated from several recent watershed geochemical mass balances are compared with experimentally determined rates. To minimize the possibility that methodological inconsistencies among studies affect the ratios, rate ratios were determined only from studies in which weathering rates of multiple minerals were determined simultaneously.

In the case of field studies, mass balances which yielded only weathering rates for single minerals were not used. Only weathering rates determined from watershed-scale geochemical mass balances using solutions of systems of simultaneous linear equations for multiple minerals were used. Thus, ratios used in this study presumably do not contain variability due to differences in specific details of the construction or solution of the mass balance [the kinds of assumptions which might affect weathering rates calculated by watershed mass balance, and comparisons of such rates are discussed by Velbel (1985a, 1986b, 1992) and Taylor and Velbel (1991)]. Ideally, there would be numerous solute mass-balance studies which report weathering rates of multiple silicate minerals, along with data on mineral modal abundance, grain size, grain geometry and regolith thickness, enabling estimation of the reactive mineral surface area contributing to the observed flux (Velbel, 1985a, 1986a, b). However, few mass-balance studies contain sufficient data to estimate mineral surface area (e.g., Pačes, 1983; Velbel, 1985a; April et al., 1986; Sverdrup and Warfvinge, 1988; Frogner, 1990; Kirkwood and Nesbett, 1991), only some of these are both based on measured solute
RATIOS OF WEATHERING RATES IN LABORATORY AND FIELD

fluxes and are unaffected by significant cation depletion in response to environmental acidification (Pačes, 1983; Velbel, 1985a), and only one of these involves multiple minerals, permitting calculation of rate ratios (Velbel, 1985a).

As a consequence of the small number of studies reporting all the required data, it is impossible to renormalize most weathering rates determined by solute mass balance to mineral surface area for direct comparison of absolute rates in the field with rates in the laboratory (e.g., Pačes, 1983; Velbel, 1985a). However, modal abundance data are more commonly available. Therefore, the following calculations are based on rates determined by geochemical mass balance for three watersheds in the eastern and north-central U.S.A. Both ratios of absolute rates (normalized to estimated mineral surface area; Velbel, 1985a) and rate ratios of field rates (normalized to modal abundance) (Siegel, 1984; Siegel and Pfannkuch, 1984a; Velbel, 1992) are used.

Use of modal mineral abundances from parent rocks assumes that relative mineral abundances within the watershed have not been extensively modified by weathering. In the case of glaciated landscapes (e.g., Siegel, 1984; Siegel and Pfannkuch, 1984a), the parent materials of soils are often glacial tills of local derivation, with initial mineral contents essentially identical to the local bedrock. Soils are relatively young, having experienced little differential depletion of primary silicate minerals. Furthermore, where glacial deposits are thin, percolating solutions interact directly with bedrock. Thus, use of parent-rock modal abundances as a first approximation is justified. Similarly, despite the thick saprolites and mature soils in the southern Blue Ridge study areas (Appalachians, Georgia–North Carolina, U.S.A.) of Velbel (1985a, 1992), even the uppermost (oldest) soil horizons on the thickest (oldest) saprolites in the Blue Ridge landscape still contain weatherable primary minerals. Feldspar, almandine garnet, biotite mica and hornblende are common in the upper parts of weathering profiles at Coweeta and elsewhere in the Blue Ridge (Velbel, 1992 and references therein). Furthermore, subsurface flow paths in the southern Blue Ridge study areas are such that essentially all of the water which ultimately appears as streams leaving the study watersheds is apparently brought into contact with unweathered rock at the base of the saprolite (Velbel, 1985b). Use of parent-rock modal abundances as a first approximation is once again reasonable.

Previous compilations of experimentally determined feldspar weathering rates consistently show that alkali-feldspar dissolution rates in laboratory systems in the near-neutral to mildly acidic pH range generally vary within and between laboratory investigations by slightly more than one order of magnitude (a factor of 30) (Helgeson et al., 1984; Knauss and Wolery, 1986; Velbel, 1986a). Although some of this variability may be a consequence of using different feldspars (with different composition, i.e. degree of solid solution and/or physical histories and resultant properties, e.g., dislocation densities) in the experiments (e.g., Holdren and Speyer, 1985a, 1987), differences in pre-experimental sample treatment and experimental procedures also likely play a role (Holdren and Berner, 1979; Velbel, 1986a). This large variation in experimentally determined rates extends to other minerals as well (e.g., amphiboles; Velbel, 1992). Choosing weathering rates for different minerals from different experiments thus raises the possibility that the resultant weathering-rate ratios may vary because of differences in experimental conditions, in addition to or instead of intrinsic differences in the reaction rates of the different minerals. Consequently, “mixing and matching” of rates from different experimental studies was avoided, and laboratory rates were selected only from studies in which dissolution rates for the pair of minerals of interest for calculating the ratio were determined by
the same experimentalists, using the same pre-
treatment and experimental conditions, etc.

3. Results

Relative weathering rates (rate ratios) cal-
culated for multiple minerals (e.g., \( r_{\text{garnet}}/r_{\text{alb}} \)) from internally consistent mass-balance studies compare favorably (within a factor of \(~ 4\); Tables 1–3) with similar ratios from laboratory data sets in which all minerals were pretreated, dissolved and analyzed identically. Interlaboratory variabil-

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Dissolution rate*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>2.72 ( \times 10^{-16} )</td>
<td>Velbel (1985a), Taylor and Velbel (1992)*2</td>
</tr>
<tr>
<td>Oligoclase</td>
<td>6.71 ( \times 10^{-17} )</td>
<td>Velbel (1985a), Taylor and Velbel (1992)*2</td>
</tr>
<tr>
<td>Ratio</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

**Laboratory:**

| Garnet | 1.1 \( \times 10^{-15} \) | Nickel (1973) |
| Albite | 3.12 \( \times 10^{-16} \) | Nickel (1973) |
| Ratio | 3.5 |

*In mol cm\(^{-2}\) s\(^{-1}\) .
*2Mineral-area normalized rate of Velbel (1985a), updated using watershed-area normalized rates calculated by Taylor and Velbel (1991) from fluxes representing a longer and more complete period of record.

Olivine weathers 6–25 times faster than calcic plagioclase (Table 1); almandine garnet weathers ~4 times faster than sodic plagioclase (Table 2); and amphiboles and sodic plagioclase weather at approximately equal rates (differing typically by no more than a factor of 2; Table 3). These relationships apply both to rates determined in sets of internally consistent laboratory experiments and to rates deter-
TABLE 3

Amphibole and plagioclase weathering rates, from watershed geochemical mass-balance and laboratory studies

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Dissolution rate*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field (Coweeata Hydrologic Laboratory, watershed 3):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hornblende</td>
<td>115 mol ha⁻¹ yr⁻¹</td>
<td>Velbel (1992)</td>
</tr>
<tr>
<td>Oligoclase</td>
<td>393 mol ha⁻¹ yr⁻¹</td>
<td>Velbel (1992)</td>
</tr>
<tr>
<td>Ratio of rates</td>
<td>0.29:1</td>
<td>Velbel (1992)</td>
</tr>
<tr>
<td>Ratio of modes</td>
<td>19.2:70</td>
<td>Velbel (1992)</td>
</tr>
<tr>
<td>Ratio of field rates corrected for modal abundance = 1.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Laboratory*:

1. Tremolite 1.45·10⁻¹⁵ Schott et al. (1981)
   Albite 4.2·10⁻¹⁶ Holdren and Berner (1979)
   Ratio 3.5 Schott et al. (1981)
2. Tremolite 1.45·10⁻¹⁵ Schott et al. (1981)
   Alkali feldspar 7.33·10⁻¹⁶ Holdren and Speyer (1985)
   Ratio 2.0
3. Tremolite 2.0·10⁻¹⁶ Mast and Drever (1987)
   Oligoclase 1.0·10⁻¹⁶ Mast and Drever (1987)
   Ratio 2.0
4. Hornblende 1.82·10⁻¹⁶ Nickel (1973)
   Albite 3.12·10⁻¹⁶ Nickel (1973)
   Ratio 0.6
5. Hornblende 4.2·10⁻¹⁶ Sverdrup (1990)
   Albite 1.6·10⁻¹⁶ Sverdrup (1990)
   Ratio 2.6·5.2

*In mol cm⁻² s⁻¹, unless otherwise specified (e.g., mol ha⁻¹ yr⁻¹).
*Retrieved from cited references as described in footnotes to Velbel (1992, table 3), except for Nickel (1973) albite, for which two surface areas are reported.

4. Discussion

The rate ratios summarized in Tables 1–3 suggest that the ratio of mineral weathering rates (R) for a given mineral pair (A, B) determined in an internally consistent field study (f) essentially equals the ratio of rates for the same minerals in any individual internally consistent laboratory study (l):

\[
\frac{R_{A,f}}{R_{B,f}} = \frac{R_{A,l}}{R_{B,l}}
\]

Laboratory and field rates for a given mineral are not equal:

\[
R_{A,f} \neq R_{A,l}, \quad R_{B,f} \neq R_{B,l}
\]

but any mineral’s experimentally determined (laboratory) rate can be “adjusted” (reduced) to a field rate for any given natural system:

\[
q_{A,lf} R_{A,f} = R_{A,l}, \quad q_{B,lf} R_{B,f} = R_{B,l}
\]

where 0 ≤ q ≤ 1.

The “lab/field adjustment coefficient” q as used here is a proxy for any combination of chemical and/or physical factors which might account for the difference. For laboratory/field rate disparities of 1–3 orders of magnitude, q takes values of 0.001–0.1.

Substituting the expression for adjusting absolute rates into the ratio equation gives:

\[
\frac{R_{A,l}}{R_{B,l}} = \frac{q_{A,lf}}{q_{B,lf}}
\]

therefore,

\[
1 = \frac{q_{A,lf}}{q_{B,lf}}
\]

implying that \(q_{A,lf} = q_{B,lf}\). Thus, the coefficient which corrects the weathering rate for any mineral from a laboratory data set to a field setting is, within narrow limits, identical to the corresponding coefficient for any other mineral in the same data sets. This is especially significant in light of the broad compositional range and structural variety of silicate–min-
eral groups represented in the comparison: feldspar, olivine, amphibole and garnet. There is no single chemical element or crystal structure common to all minerals which might share a common laboratory/field adjustment coefficient.

The results for the Filson Creek study area (Table 1; Siegel, 1984; Siegel and Pfannkuch, 1984a) illustrate this most clearly. Plagioclase and olivine have no major elements in common except silicon and oxygen, and the extent of tetrahedral polymerization in the two minerals is completely different (unpolymerized tetrahedra linked only by octahedral cations in olivine, in contrast to a three-dimensional network of corner-sharing tetrahedra in plagioclase). This suggests that there is no coordination environment to be modified by weathering or type of bond to be broken by weathering common to all silicates exhibiting this uniform “lab/field adjustment coefficient”. The “correction factor” linking experimental and natural rates is independent of mineral composition. It would require an impressive confluence of coincidences for a number of different, composition-dependent, mineral-specific adjustments to experimental rates all to have essentially exactly the same magnitude. This suggests a physical (e.g., hydrologic), rather than compositional or chemical, basis for the difference between weathering rates in nature and the laboratory.

One possibility is that not all of the potentially available surface in natural systems actually participates in reactions with pore fluids. The ratio of “effective” (reactive) surface area to total surface area may be lower in natural systems than in laboratory experiments. There are numerous possible mechanisms of reducing the effective-to-total surface area ratio in natural systems relative to their laboratory counterparts. Simple mechanical occlusion of portions of the mineral surfaces would achieve this, if the coatings prevent transport of reactants or products. However, the extensive etching widely observed on naturally weathered silicate-mineral grains (see reviews by Velbel, 1986a, 1987) indicates that reactive solutions have essentially complete access to mineral surfaces, militating against an extensive surface-covering role for coatings (Velbel, 1993).

Hydrologic factors, such as inhomogeneous fluid migration through pore or fracture networks, may limit the amount of water coming into contact with mineral surfaces, so that the amount of mineral surface participating in fluid–rock interactions at any instant is some fraction of the total available surface area of that mineral (e.g., Velbel, 1986a; Walther and Wood, 1986; Sverdrup and Warfvinge, 1988; Drever and Swoboda-Colberg, 1989; Schnoor, 1990). Water and solute movement through soils in the vadose zone is known to be spatially and temporally heterogeneous. Only a fraction of the total available porosity is occupied by fluid at any instant; the fraction is highest after rainfall or snowmelt and lowest during prolonged dry spells. Furthermore, the movement of whatever water is present in the vadose zone is known to be confined to only a portion of the total available porosity. This has been demonstrated: (1) visually by experiments in laboratory soil-column simulants (Hill and Parlange, 1972; Glass et al., 1988, 1989a, b, c, 1990); (2) by employing dyes in natural soils (Ehlers, 1975; Bouma and Dekker, 1978; Starr et al., 1978; Bouma and Wosten, 1979; Bouma et al., 1979; Omoti and Wild, 1979; Glass et al., 1988; Sollins and Radulovich, 1988; Kung, 1990; Booltink and Bouma, 1991; Hornberger et al., 1991); and (3) quantitatively through application of chemical tracers (e.g., Hornberger et al., 1990, 1991). This type of spatially heterogeneous flow is known in various manifestations as “preferential flow”, “short-circuiting”, “bypass flow”, “channelized flow”, “macropore flow” (Bouma and Dekker, 1978; Beven and Germann, 1982; McDonnell, 1990; Booltink and Bouma, 1991) and “fingering” or “unstable” flow (Hill and Parlange, 1972; Starr et al.,
Horizontal slices of soil, taken at various depths, demonstrate "fingering" in the spotty, areally restricted distribution of dye; the "spots" represent the intersections of the (three-dimensional) vertical to subvertical "fingers" with the (two-dimensional) horizontal slice. More complex patterns of spatially restricted flow appear when large vertical exposures are excavated through dye-infilttrated porous media (Kung, 1990). Such regions of preferential flow are sometimes associated with visible macroscopic porosity between soil aggregates (e.g., animal burrows, decayed-root channels, soil cracks; Ehlers, 1975; Bouma and Dekker, 1978; Omoti and Wild, 1979; Beven and Germann, 1982; Sollins and Radulovich, 1988), or with primary (e.g., sedimentological) heterogeneity in the porous medium (e.g., Kung, 1990), but also occur in porous media that are macroscopically homogeneous in their pore structure (e.g., Hornberger et al., 1991), often as a consequence of inherent instability in wetting fronts (e.g., Hill and Parlange, 1972; Starr et al., 1978; Glass et al., 1988, 1989a, b, c, 1990).

Dye tracer experiments in natural soils reveal that individual wetting events in some instances saturate as little as 0.2–15% (Ehlers, 1975; Bouma and Dekker, 1978; Starr et al., 1978; Omoti and Wild, 1979; Sollins and Radulovich, 1988) of the total cross-sectional area through which water might flow. The proportion is higher (up to 50% or more) at shallower depths in the soil profiles, but declines rapidly with depth (Starr et al., 1978; Sollins and Radulovich, 1988; Booltink and Bouma, 1991). The depth range over which the proportions decline to values of 0.2–15% varies with soil texture. Finely textured soils achieve these values at depth of several tens of centimeters (Starr et al., 1978; Sollins and Radulovich, 1988), and may even exhibit slight increases with depth (Ehlers, 1975), whereas such values are attained at depths of several meters in well-sorted sandy media. Values as low as 1% are observed at depths of 5–7 m in sandy media (Kung, 1990). These proportions are not necessarily constant from one wetting event to another, as macropore flow will vary with antecedent moisture conditions (Beven and Germann, 1982). Thin sections of dyed soils exhibit similar volumes of regions of preferred flow (Bouma and Wösten, 1979; Bouma et al., 1979). Pore-size distributions for soils indicate that macropores constitute a comparable proportion (1–12%) of the total porosity in some of the same soils (Germann and Beven, 1981; Radulovich et al., 1989); depending on the method used, macropore volume-fractions as low as $2 \cdot 10^{-4}$ have been reported in some soils (Wilson and Luxmoore, 1988). Theoretical models of preferential flow suggest (Germann, 1990):

"that not more than 1/10 of actual soil moisture is directly participating in the flow process"

The ratio of "mobile" (i.e. macropore) water to "stagnant" (i.e. matrix) water is in the range $1.7 \cdot 10^{-4}$ to $2.5 \cdot 10^{-2}$ for a wide range of soil textures (Germann, 1990).

These experimental and theoretical hydrological findings suggest that most of the flow in any individual wetting event is concentrated in as little as a few percent or less of the soil matrix in the vadose zone, bypassing "inactive" pore space (generally itself not fully saturated) in the soil between the fingers or macropores. During such transport, there may be little exchange of solutes from the mobile water flowing through the "fingers" or macropores and the immobile water distributed as, for example, pellicular water in the surrounding unsaturated pores. A large fraction of the mobile fluid (the fluid which contributes to stream export from watersheds; it is this flux from which the field rates are determined) interacts directly with only a small proportion of the potentially available reactive mineral surface.
This suggests in turn that a large fraction of the volume of the soil, and a correspondingly high proportion of the solid surface area in contact with the “inactive” pore space, do not come into contact with significant percolating fluids or their contained reactant solutes during any individual wetting event. This is consistent with the results of this paper, which suggest that 90–99.9% of the potentially available mineral surface area in soils is not participating in reactions and contributing to watershed effluxes during any individual time increment.

5. Conclusions

Comparisons of rates calculated from several recent watershed geochemical mass-balance studies with experimentally determined rates reveal that the ratio of mineral weathering rates for a given mineral pair determined in an internally consistent field study equals the ratio of rates for the same minerals in any individual internally consistent laboratory study. This holds for feldspar, olivine, amphibole and garnet. The difference between laboratory and field rates for a given mineral can be described by a simple “lab/field adjustment coefficient” the value of which ranges from zero to unity. Incorporating this coefficient into the ratio equation suggests that the coefficient which corrects the weathering rate for any mineral from a laboratory data-set to a field setting is identical to the corresponding coefficient for any other mineral in the same data sets. The “correction factor” linking experimental and natural rates is independent of composition. This in turn suggests a physical (e.g., hydrologic), rather than compositional or chemical, basis for the difference between weathering rates in nature and the laboratory. Because flow in natural weathering profiles is spatially heterogeneous, not all of the potentially available surface in natural systems actually participates in reactions with pore fluids.

Acknowledgments

I am especially grateful to P.F. Germann, for enthusiastically introducing me to the recent literature on vadose-zone hydrology, and to J.F. Dowd for years of thought-provoking discussions of hydrologic–chemical interactions in soils. I would also like to thank W.S. Moore, A.E. Blum, L.R. Gardner, J.B. Maynard, A.F. White, J.I. Drever, O.P. Bricker, N.L. Romero, A.B. Taylor, J.V. Walther, W.M. Murphy and D.S. Brandt, and two anonymous reviewers for their helpful comments, criticisms, conversations and correspondence.

References


