[AMERICAN JOURNAL OF SCIENCE, VOL. 299, SEPT./OCT./NOV., 1999, P. 679–696]

BOND STRENGTH AND THE RELATIVE WEATHERING RATES OF SIMPLE ORTHOSILICATES

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ABSTRACT. Common naturally occurring orthosilicates can be grouped into those in which the major non-tetrahedral cations are (1) Fe^{II} and/or Mg, plus or minus Al (olivine, pyralspite garnets, staurolite); (2) Al (Al_2SiO_5 polymorphs), or (3) Zr. Fe- and Mg-bearing orthosilicates have the weakest bonds between non-tetrahedral cations and structural oxygen (M-O bonds), and zircon the strongest, with Al-O bonds intermediate; thus, the relative vulnerability to weathering of the three groups decreases in the order Fe-Mg(±Al) orthosilicates > Al_2SiO_5 polymorphs > zircon. Among Fe(±Mg±Al)-orthosilicates, Fe-O bond lengths vary with Fe coordination number (CN), and Fe-site energies decrease in the order fayalite olivine > almandine garnet >> staurolite. If other factors did not intervene, almandine ($CN_{Fe} = 8$) could weather approximately as fast as olivine ($CN_{Fe} = 6$). However, reactant-product molar-volume ratios involving almandine and common weathering products of oxidizing environments favor the formation of transport-limiting, rate-limiting protective surface layers on almandine and not on olivine; thus, almandine's weathering rate is commonly suppressed by these protective surface layers to a sufficient extent that almandine weathers more slowly than olivine. Short, strong Fe-O bonds involving tetrahedral Fe render staurolite more resistant to weathering than either common olivines or common pyralspite garnets. Relative weathering rates within the Al_2SiO_5 group vary with the coordination number of Al.

When formation of protective surface layers on garnet is taken into account, relative weathering rates of common orthosilicates decrease in the same order as the M-O bond energies for the dominant non-tetrahedral cations, giving rise to the commonly observed natural orthosilicate weathering series:

Olivine > Garnet > Staurolite > Kyanite > Andalusite > Sillimanite > Zircon.

The lengths and strengths of bonds between major non-tetrahedral cations and structural oxygen are a fundamental control of relative orthosilicate weathering rates in nature as in laboratory experiments.

INTRODUCTION

The purposes of this paper are to summarize recent studies of the weathering of orthosilicate minerals; to expand upon a previous simple crystal-chemical framework for explaining experimentally determined dissolution kinetics of different orthosilicates (Casey and Westrich, 1992; Westrich and others, 1993; Casey and Ludwig, 1995); and to apply the expanded concept to the relative susceptibility to weathering of naturally weathered orthosilicates.

The underlying theme being built upon here is stated by Casey and Ludwig (1995, p. 114) as follows: "The most important determinant of reactivity is the M-O bond strength." Casey and Ludwig (1995, p. 113) observe that their bond-strength/dissolution-rate relationship "works well for simple oxide and orthosilicate minerals that have no extensive covalent polymer in their structure and where dissociation of simple M-O bonds controls the overall reaction rates. Minerals with extensive polymerized fabrics exhibit a more complicated chemistry because the dissociation of individual M-O bonds is difficult to isolate within the overall process of leaching and dissolution." Casey and Ludwig (1995) base their conclusions on detailed experimental kinetic studies of olivine- and willemite-type orthosilicates. They acknowledge, however, that other factors complicate the story even for olivine (Banfield, Veblen, and Jones, 1990), and that some other orthosilicates (garnet; Velbel, 1984) weather by very different mechanisms.

This paper extends the bond-strength argument of Casey and coworkers to common orthosilicates with structures other than the olivine and willemite structures. Orthosilicates with a single non-tetrahedral cation are emphasized; a few common more complex orthosilicates are also discussed, but detailed discussion of complex mixed-cation orthosilicates is beyond the scope of the present contribution. This paper also combines the bond-strength approach of Casey and co-workers with the product-reactant molar-volume criteria for the formation of transport-limiting protective surface layers presented by Velbel (1993a). The extended and combined approach is applied to orthosilicate mineral-persistence series compiled from the literature on natural weathering of heavy minerals.

BACKGROUND

Silicate minerals are classified in part on the basis of how many corners per tetrahedron are shared with neighboring tetrahedra. The vulnerability of common rock-forming silicate minerals to weathering appears at first to be a consequence of the degree of connectedness (corner-sharing, sometimes referred to as polymerization) of their silica tetrahedra (Goldich, 1938). Olivine consists of completely unpolymerized tetrahedra (no corners shared), whereas silica tetrahedra in pyroxenes share two corners (forming chains of silica tetrahedra and Si-O-Si bonds); in amphiboles, 2.5 (forming double chains); in micas, three (forming sheets); and in quartz, four (forming a three-dimensional network of Si-O-Si bonds). The more polymerized the silicate mineral's structure, the more resistant to weathering it appears to be. This is one of the main "textbook" explanations for the relative susceptibilities to weathering of different silicate minerals and in its broad outlines is borne out by laboratory experimental data. Brantley and Chen (1995, fig. 12) show that experimental silicate dissolution rates increase as the minerals' connectedness (number of bridging oxygens per silica tetrahedral unit) decrease; Lasaga (1984, 1998) demonstrated that ranking silicate minerals by their experimental dissolution rates results in a list that parallels the Goldich (1938) weathering series. However, there are many silicate-mineral groups (for example, micas; tectosilicates in general, feldspars in particular) within which individual members all have equal degrees of tetrahedral connectedness, yet whose individual members range widely in their vulnerability to weathering.

Orthosilicates (nesosilicates) are silicate minerals in which there is no corner-sharing of silica tetrahedra. The orthosilicates discussed here, and their formulae, are summarized in table 1. Olivine and zircon are both members of the orthosilicate group and are, respectively, the most easily weathered and the most resistant silicate minerals (Morton, 1984, 1985; Bateman and Catt, 1985). Several other common minerals (garnet, staurolite, the Al_2SiO_5 polymorphs) are also orthosilicates but are of intermediate vulnerability to weathering (Morton, 1984, 1985; Bateman and Catt, 1985; Velbel, 1984, 1987, 1993a; Velbel, Basso, and Zieg, 1996). Additionally, orthosilicates include examples of silicate minerals on which etch pits and interface-limited weathering reactions are ubiquitous (olivine), and the only well-documented natural examples of the formation of diffusion-limiting protective surface layers (almandine and spessartine garnets; Velbel, 1984, 1987, 1993a, and references therein). This observed large range of susceptibilities to weathering and of rate-determining mechanisms cannot be a consequence of different degrees of silica connectedness, as all orthosilicates contain completely unpolymerized silica tetrahedra. Therefore, the different weathering kinetics of different orthosilicates must involve differences in the crystal chemistry of sites other than the silica tetrahedral sites.

Table 1

Names and formulae of orthosilicates

Phenacite Group	
Phenacite	Be_2SiO_4
Willemite	Zn_2SiO_4
Olivine Group	
Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Tephroite	Mn_2SiO_4
Liebenbergite	Ni_2SiO_4
Ca-olivine	Ca_2SiO_4
Co-olivine	Co_2SiO_4
Garnet Group	
Pyralspite series:	
Pyrope	$Mg_3Al_2(SiO_4)_3$
Almandine	$Fe_3Al_2(SiO_4)_3$
Spessartine	$Mn_3Al_2(SiO_4)_3$
Ugrandite series:	
Uvarovite	$Ca_3Cr_2(SiO_4)_3$
Grossular	$Ca_3Al_2(SiO_4)_3$
Andradite	$Ca_3Fe^{III}{}_2(SiO_4)_3$
Al_2SiO_5 Group	
Andalusite	Al_2SiO_5
Sillimanite	Al_2SiO_5
Kyanite	Al_2SiO_5
Ungrouped	
Zircon	Zr_2SiO_4
Topaz	$Al_2SiO_4(F,OH)_2$
Staurolite	$Fe_4Al_{18}Si_8O_{46}(OH)_2$
Titanite	$CaTiO(SiO_4)$
Chloritoid	$(Fe,Mg)_2Al_4O_2(SiO_4)_2(OH)_4$

Formulae from Klein and Hurlbut (1993), except liebenbergite (Casey and Westrich, 1995) and staurolite (Hawthorne and others, 1993c).

RELATIVE WEATHERING RATES OF DIFFERENT ORTHOSILICATES

Experimental Dissolution Kinetics

There have been a number of experimental studies of orthosilicate dissolution kinetics, mostly of olivines; many are reviewed by Casey and Ludwig (1995).

Between-group variations in experimental orthosilicate weathering rates.–Nickel (1973) included several orthosilicates in his experimental study. At pHs relevant to weathering (pH = 5.6), Nickel determined the following sequence of relative weathering rates (from fastest to slowest):

$$\text{Almandine} > \text{Staurolite} > \text{Kyanite} > \text{Zircon}$$

Within-group variations in experimental weathering rates; solid-solutions.–Wogelius and Walther (1991) reported that Fo_{91} and Fo_{100} olivines dissolved at essentially the same rate under experimental conditions. Casey and Westrich (1992) and Westrich and others (1993) found Wogelius and Walther's (1991) data for forsterite dissolution rates to be indistinguishable from those reported by Blum and Lasaga (1988) and used these rates for forsterite in their compilation (next section).

Wogelius and Walther (1992) reported that Fo_6 olivine weathered about six times faster than Fo_{91} olivine under similar experimental conditions. Grandstaff (1986) reported rates for Fo_{82} olivine that are typically one to two orders of magnitude slower than Wogelius and Walther's (1991) rates at similar pHs. However, this large difference is not a consequence of compositional differences between the different olivines but results from differences in experimental procedures. Grandstaff's (1986) experiments were performed using olivine from Hawaiian beach sands, without any of the conventional sample-preparation steps (for example, crushing, grinding) that commonly increase the dissolution rates of experimentally dissolved silicates (Holdren and Berner, 1979; Berner, 1981; Velbel, 1986). This two-order-of-magnitude variation in forsterite dissolution rates with different sample treatment illustrates some of the challenges and limitations involved in attempting to compare dissolution-kinetics data from multiple published studies that used different experimental protocols (Velbel, 1993b).

Within-group variations in experimental weathering rates; isostructural compounds of different compositions.–The most complete and internally consistent dissolution-kinetics data set for orthosilicate minerals comes from the work of Casey and his coworkers (Casey and Westrich, 1992; Westrich and others, 1993; Casey and Ludwig, 1995). In a carefully designed study, including use of uniformly synthesized starting materials, Casey and Westrich (1992) plotted the logarithm of the dissolution rate against the radius of the divalent cation for eight different orthosilicates. Casey and Westrich (1992) examined only orthosilicates with a single divalent cation. They found that a single regression line linked the three alkaline earths (the two extreme points, for Be, the smallest cation, and Ca, the largest, with the point for Mg also falling on the regression line). Their rate data are reproduced here in figure 1. Deviations of the first-row transition metals from the simple ionic-radius/size relationship were explained in terms of ligand-stabilization energies of the divalent cations.

One additional factor may play a role in explaining the rate of willemite dissolution. Willemite dissolves approximately two orders of magnitude faster than predicted from the regression proposed by Casey and Westrich (1992). Willemite is the only orthosilicate among those studied for which the cation changes coordination in going from the reactant mineral structure (in which Zn is tetrahedrally coordinated) to the hydrated aqueous phase (in which Zn is coordinated to six water molecules; Casey and Ludwig, 1995, table 1). The change in Zn coordination is likely rapid (Casey and Ludwig, 1995), and this may contribute to the rapid dissolution of willemite relative to other orthosilicate with cations of comparable ionic radius.

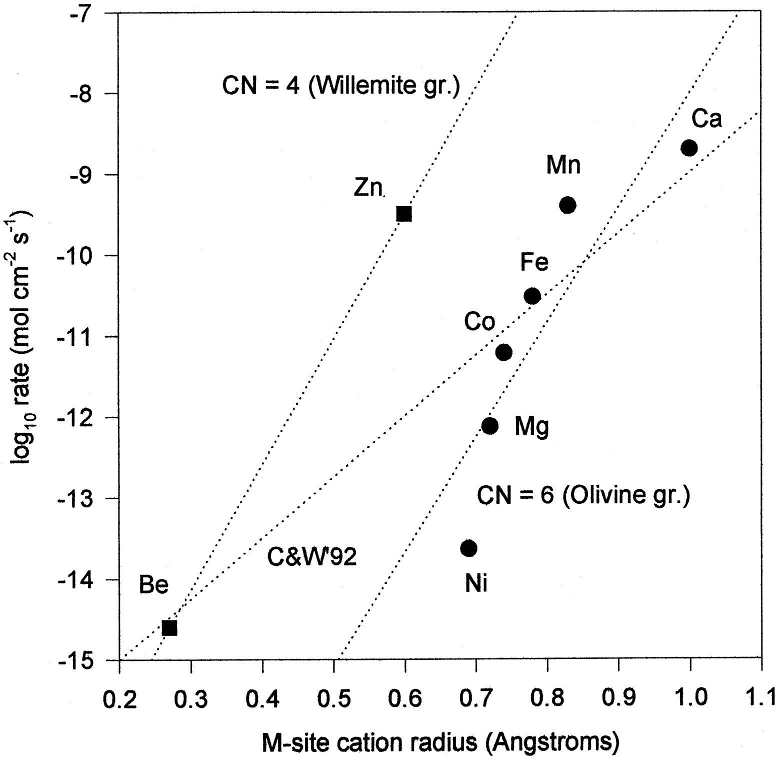

Fig. 1. Dissolution rate (from Casey and Westrich, 1992) versus ionic radius (from Smyth and Bish, 1988) for homoionic M_2SiO_4 orthosilicates with olivine and willemite structures. C&W'92 regression line fits a single regression to data for both structure types, as was done by Casey and Westrich (1992, fig. 1A). Regression lines are also shown for the two different structure types (CN = 4, willemite group; and CN = 6, olivine group) separately. Compare with Casey and Westrich (1992, fig. 1A).

In a subsequent extension of the Casey and Westrich (1992) study, Westrich and others (1993) added several mixed-cation orthosilicates and constructed a plot of the logarithm of the dissolution rate against lattice energy (their fig. 10). Their rate data (for the single-cation orthosilicates only; the four mixed-cation orthosilicates studied by Westrich and others, 1993, are omitted here) are plotted here against M-site energies (from Smyth and Bish, 1988) in figure 2; the topology of this diagram is essentially identical with that of figure 10 in Westrich and others (1993). Data for mixed-cation orthosilicates plot between the points for homoionic orthosilicates (for example, the point for monticellite, the Ca-Mg olivine, plots halfway between the points for Ca-olivine and forsterite; Westrich and others, 1993, fig. 10). On the basis of their diagram for their entire data set, Westrich and others (1993, p. 885) suggest: "The poor correlation between lattice energies and dissolution rates indicates that important interactions are missing from the calculation." In the next sentence, they list several specific such interactions.

One factor not suggested by Westrich and others (1993) in explaining their "poor correlation" is that their correlation is based on trying to fit a single regression to data from two structurally distinct orthosilicate groups. The single regression line employed on the dissolution-rate/cation-radius regression by Casey and Westrich (1992) links dissolution-rate data for two structurally distinct orthosilicate groups (structure types), and both groups are plotted on figure 10 of Westrich and others (1993). Phenacite and

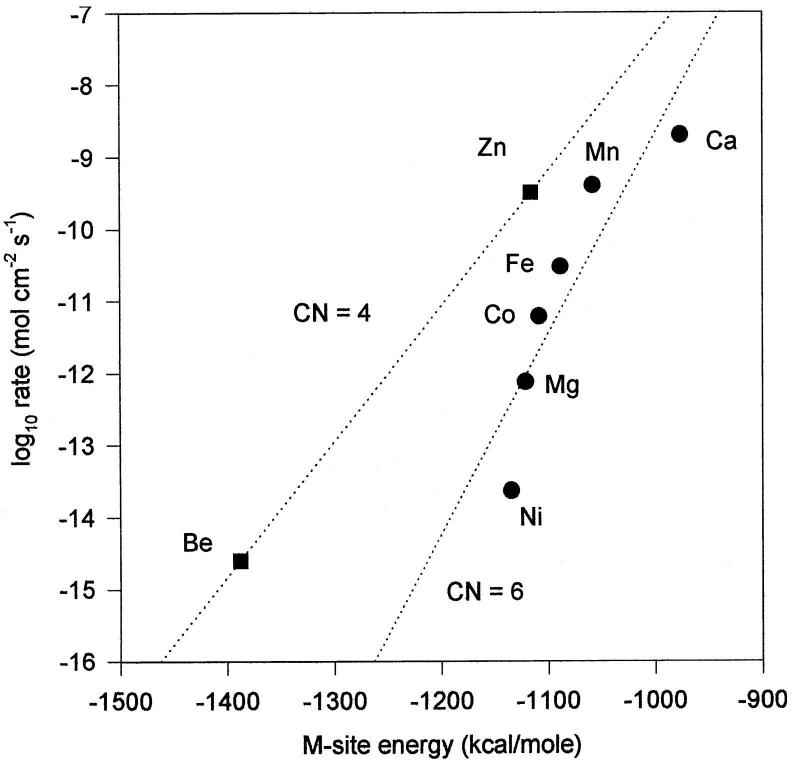

Fig. 2. Dissolution rate (from Westrich and others, 1993) versus M-site energy (from Smyth and Bish, 1988) for homoionic M_2SiO_4 orthosilicates with olivine and willemite structures. Regression lines are shown for the two different structure types (CN = 4, willemite group; and CN = 6, olivine group) separately. Compare with Westrich and others (1993, fig. 10).

willemite both have structures in which the divalent cation is four-coordinated (willemite structure type), whereas the other six orthosilicates investigated (forsterite, fayalite, tephroite, liebenbergite, Co-olivine, and Ca-olivine) all have the olivine structure, in which the divalent cation is six-coordinated (Smyth and Bish, 1988).

If separate regressions are determined for the two different structural groups on dissolution rate versus ionic radius (fig. 1) or dissolution rate versus lattice energy (fig. 2) plots, the picture that emerges differs somewhat from that presented by the original authors. The overall pattern observed by Casey and Westrich (1992) and Westrich and others (1993) is preserved, in which the dissolution rate is proportional to ionic radius or lattice energy, within each structure type; orthosilicates with larger divalent cations and with higher lattice or M-site energies dissolve more rapidly than those with smaller cations. However, this trend is now seen to describe each of the structural groups separately, rather than the data set as a whole. The slopes of the regression lines (that is, the dependence of dissolution rate on ionic radius or lattice energy) for each individual group are higher than for the dataset as a whole (figs. 1 and 2). Correlation coefficients within each individual group are also better than for the dataset as a whole but no significance should be attached to this as the regression for the willemite-structured minerals is based on only two points. However, similarities and differences in the behaviors of the two structural groups are apparent despite the limited usefulness of the regression coefficients.

Regression lines on the dissolution-rate/ionic-radius plot (fig. 1) are parallel for the two structural groups; that is, rate has the same functional variation with ionic radius in the both structural groups. However, the offset between the two regression lines indicates that, for cations of comparable radius (for example, willemite and fayalite), orthosilicates with four-coordinated divalent cations dissolve more rapidly than orthosilicates with six-coordinated divalent cations. This is unexpected and contradicts several lines of evidence from studies of natural weathering of orthosilicates; as discussed in the next section, it is more common for orthosilicates with higher coordination numbers to weather more readily.

The relationship between lattice energy and dissolution rate proposed by Westrich and others (1993) becomes clearer within isostructural groups when the groups are treated separately (fig. 2), but the two different structural groups have different dependencies of dissolution rate on lattice energy. The dissolution-rate/site-energy regressions (fig. 2) from the data of Westrich and others (1993) suggest that within the olivine-structured orthosilicate group, energy-rate correlations are actually better than Westrich and others (1993) concluded on the basis of the entire dataset. M-O bond-strength (and M-O bond length, and cation radius) may be a better predictor of dissolution kinetics within isostructural mineral structural groups than previous conclusions would suggest. However, the many complexities invoked by previous workers still apply to energy-rate relationships involving structurally different mineral groups.

Natural Persistence Series of Orthosilicates

The natural weathering of some common orthosilicates (for example, olivine) is reasonably well studied (see review by Velbel, 1993a). In contrast, garnet is an exceptionally complex group because of the wide range of possible compositions. When measured against the great compositional variability among garnets, the weathering of garnets is not especially well understood; most of what is presently known about garnet weathering is from studies of the two most common garnet varieties, almandine and spessartine (see review by Velbel, 1993a). There are very few studies of staurolite weathering (Velbel, Basso, and Zieg, 1996), and the subject of whether and, if so, how, zircon weathers, is an ongoing and difficult research area, undertaken in part to justify the widespread use of zirconium as a "reference element" in studies of elemental mobility during weathering.

Even less is known about relative weathering behaviors of different orthosilicates than is known about the behavior of individual orthosilicates. Much of what is known about the alteration of orthosilicates in nature is known from studies of heavy-mineral persistence in soils and the sedimentary cycle. Much of this literature is based on studies of relative mineral abundances and how these abundances are modified by weathering (see reviews by Bateman and Catt, 1985; Morton, 1984, 1985) and burial diagenesis (post-depositional heavy-mineral dissolution in clastic sedimentary strata [intrastratal dissolution]; Pettijohn, 1941; Morton, 1984, 1985).

Mineral weathering series are established by comparing relative abundances of heavy minerals in weathered horizons with relative abundances in parent material or less-weathered horizons. In many instances, weathering series are reported from small suites of samples that represent the weathering of the same parent-mineral assemblage over a known period of time. In such instances, the relative depletion of different minerals relative to one another is easily interpreted as a measure of their relative weathering rates (different extents of weathering over the same time interval). In larger literature-survey studies, many different samples with wide ranges of weathering histories and durations may be examined; however, the rankings in such multisite studies are the same as in studies with uniform exposure histories, suggesting that the literature surveys sample enough different cases that the "average" weathering behavior of heavy-mineral assemblages in multiple studies resembles the actual behavior of mineral assemblages in individual weathering profiles. Finally, Lasaga (1984, 1998) showed that a list of silicate minerals ranked in order of experimental silica release rate closely matched Goldich's (1938) weathering series. For the purposes of this paper, the relative persistence of minerals in naturally weathered materials is assumed to reflect their relative rates of weathering, and mineral persistence series in weathering are regarded as consequences of the kinetics of weathering reactions. (The term "stability series" is a misnomer, despite its historical precedence. Such series rank the persistence of different heavy minerals, which is a consequence of the kinetics of the reactions, not the thermodynamic "stability" of the minerals being discussed. Such series could more accurately be termed "mineral persistence series.")

Several orthosilicate persistence series from papers on heavy-mineral weathering are summarized here; others are reviewed by Nickel (1973) and some of the other references discussed here (older papers refer to titanite as sphene). Orthosilicate minerals are arranged in order of decreasing weathering rate (most rapid weathering to most durable in the weathering environment).

Olivine > Titanite > Garnet > Chloritoid > Staurolite > Kyanite > Andalusite > Sillimanite > Zircon

(Morton, 1984);

Olivine > Garnet > Titanite > Topaz > Staurolite > Kyanite > Andalusite > Sillimanite > Zircon

(Bateman and Catt, 1985);

Garnet > Sillimanite > Zircon

(Tejan-Kella, Chittleborough, and Fitzpatrick, 1991);

Garnet > Staurolite > Kyanite > Sillimanite > Zircon

(Dryden and Dryden, 1946).

The relative placement of titanite, topaz, and chloritoid cannot be reliably established. However, there is sufficient agreement among the individual orthosilicate weathering persistence series to suggest that the relative weatherability of the more common orthosilicates is well established:

Olivine > Garnet > Staurolite > Kyanite > Andalusite > Sillimanite > Zircon.

BOND-ENERGY/WEATHERING-RATE RELATIONSHIPS

All minerals listed above share one attribute: there is no corner-sharing between silica tetrahedra (no tetrahedral oxygens are bridging oxygens). They differ in a number of important crystal-chemical characteristics. This section discusses bond-energy/relative-weathering-rate relationships of different orthosilicates, building on the work of Casey and co-workers. Following a statement of how their approach is applied to other orthosilicates, various minerals and mineral groups are discussed. Isochemical minerals that differ in structure and cation coordination (the Al_2SiO_5 polymorphs) are discussed first. Two isostructural mineral groups involving solid-solution (olivine, garnet) are discussed next. Finally, the weathering of these groups relative to one another and relative to staurolite and zircon are discussed.

Formulation and extension of experimentally derived bond-strength/dissolution rate relationships.–To test the bond-energy/weathering-rate relationships proposed by Casey and co-workers (Casey and Westrich, 1992; Westrich and others, 1993; Casey and Ludwig, 1995), important characteristics of M-O bonds in orthosilicates are summarized in table 2. Following Casey and Ludwig (1995), emphasis is on M-O bond lengths and bond strengths. Westrich and others (1993, p. 884) observe that "The largest contribution to the lattice energy of a crystal is the Coulombic (or Madelung) energy." For bonds of predominantly ionic character (recall that the Si-O bond is about 50 percent ionic in character, and most other cation-oxygen bonds have greater ionic character), Coulomb's law states that the attractive force between two oppositely charged ions depends on the product of their respective valences, divided by their equilibrium M-O distance. (By itself, this neglects repulsive forces; Smyth and Bish, 1988, and Westrich and others, 1993). When making comparisons among different minerals with the same anion (for example, oxygen in orthosilicates), the anionic radius can be treated as being approximately constant from one mineral to another, and variation in length and strength of the M-O bond will scale with variation in the M-cation radius. Thus, for the purpose of ranking bond strengths for isoanionic compounds, cation radius can serve as a proxy for the M-O bond length.

The discussion that follows also employs the concept of the ionic potential, defined as z/r, the ion's valence (z) divided by its radius (r). This can be thought of as the "charge density" of the cation, the "amount" of positive charge per volume. Among alkalis and alkaline earths, for example, smaller cations of a given valence have the same "amount" of charge packed into a smaller volume than do larger cations with the same valence. For ions of comparable size but different valence, those with higher valence have "more" positive charge in the same volume. Because the anion with which cations are bonded in orthosilicates is always oxygen, the ionic potential can serve as a simple mnemonic proxy for the cation's valence and ionic radius; the higher the ionic potential of a cation (that is, the higher the cation's valence and smaller its radius), the greater its Coulombic attractive force with a given anion (for example, oxygen in silicates). Other measures of bond strength could be employed and should be for a more rigorous treatment, but, as will be shown, existing data for naturally weathered orthosilicates can be adequately explained in terms of ionic potential and M-O bond length. At present, data for naturally weathered orthosilicates are not sufficiently abundant or quantitative to require greater rigor.

Within-group Variations in Bond-strength and Weathering Rate

Polymorphs.–The Al_2SiO_5 polymorphs provide an opportunity to investigate crystal-chemical influences on weathering kinetics that has not been exploited sufficiently, especially in studies of naturally weathered materials. All weathering series concur that kyanite weathers more readily than sillimanite, and most concur that the ease of andalusite weathering is intermediate.

The basis for the different relative persistence of different Al_2SiO_5 polymorphs to weathering almost certainly rests on the coordination of Al. In all Al_2SiO_5 polymorphs, half the aluminum is in six-coordinated (octahedral) sites; they differ in the nature of the sites occupied by the other half of the Al. In kyanite, all Als are in octahedral sites; in andalusite, half the Als are in five-coordinated (Al2) sites; and in sillimanite, half are in tetrahedral (4-coordinated; Al2) sites.

It is evident that the higher the "average" coordination number of Al in the Al_2SiO_5 polymorph (and the lower the "average" ionic potential of Al in the structure), the more readily it weathers. For bonds of predominantly ionic character (most cation-oxygen bonds in silicates), coordination number (CN) is related to cation radius (and, consequently, bond length). Smaller cations have smaller coordination numbers and shorter bond lengths with coordinating anions. Simple Coulombic attraction suggests that, for three different compounds differing in Al coordination (and Al-O bond length), bonds become stronger as CN_{Al} and bond length decrease and weaker as CN_{Al} and bond length increase. From CN/bond-length/bond-strength considerations alone, we would expect that, other factors (crystal size, defect density, et cetera) being held constant, kyanite would weather the most readily, followed by andalusite, with sillimanite being the most

TABLE 2

Ionic radii, coordination numbers, ionic potentials, bond lengths (M-O distances), and site energies in orthosilicates (in order of decreasing ionic potential)

Ion	radius (Å)	CN	Ionic potential	Mean M-O bond distance	Site energy	Mineral
Divalent						
Ca^{2+}	1.12	8	1.79	2.429	-1010	Uvarovite
Ca^{2+}	1.12	8	1.79	2.433	-1015	Andradite
Ca^{2+}	1.12	8	1.79	2.405	-1022	Grossular
Ca^{2+}	1.06(est)	7	1.89	2.458	- 999	Titanite
Ca^{2+}	1.00	6	2.00	2.352	- 945	Ca-olivine M1
Ca^{2+}	1.00	6	2.00	2.392	-1008	Ca-olivine M2
Mn^{2+}	0.96	8	2.08	2.326	-1080	Spessartine
Fe^{2+}	0.92	8	2.17	2.299	-1101	Almandine
Mg^{2+}	0.89	8	2.25	2.270	-1126	Pyrope
Mn^{2+}	0.83	6	2.41	2.206	-1015	Tephroite M1
Mn^{2+}	0.83	6	2.41	2.227	-1102	Tephroite M2
Fe^{2+}	0.78	6	2.56	2.161	-1041	Fayalite M1
Fe^{2+}	0.78	6	2.56	2.177	-1136	Fayalite M2
Co^{2+}	0.74	6	2.70	2.119	-1090	Co-olivine M1
Co^{2+}	0.74	6	2.70	2.142	-1153	Co-olivine M2
Mg^{2+}	0.72	6	2.78	2.094	-1082	Forsterite M1
Mg^{2+}	0.72	6	2.78	2.129	-1160	Forsterite M2
Ni^{2+}	0.69	6	2.90	2.078	-1090	Liebenbergite M1
Ni^{2+}	0.69	6	2.90	2.100	-1179	Liebenbergite M2
Fe^{2+}	0.63	4	3.17	2.008	-1395	Staurolite
Zn^{2+}	0.60	4	3.33	1.976	-1109	Willemite M2
Zn^{2+}	0.60	4	3.33	1.958	-1123	Willemite M1
Be^{2+}	0.27	4	7.41	1.645	-1379	Phenacite M1
Be^{2+}	0.27	4	7.41	1.646	-1397	Phenacite M2

TABLE 2

(continued)

Ion	radius (Å)	CN	Ionic potential	Mean M-O bond distance	Site energy	Mineral
Trivalent						
Fe^{3+}	0.65	6	4.62	2.024	-2455	Andradite
Cr^{3+}	0.62	6	4.84	1.985	-2527	Uvarovite
Al^{3+}	0.54	6	5.55	1.911	-2365	Staurolite Al1A
Al^{3+}	0.54	6	5.55	1.914	-2365	Staurolite Al1B
Al^{3+}	0.54	6	5.55	1.935	-2490	Andalusite Al1
Al^{3+}	0.54	6	5.55	1.896	-2531	Kyanite Al4
Al^{3+}	0.54	6	5.55	1.902	-2532	Kyanite Al1
Al^{3+}	0.54	6	5.55	1.918	-2543	Kyanite Al3
Al^{3+}	0.54	6	5.55	1.913	-2563	Kyanite Al2
Al^{3+}	0.54	6	5.55	1.912	-2573	Sillimanite Al1
Al^{3+}	0.54	6	5.55	1.905	-2619	Staurolite Al2
Al^{3+}	0.54	6	5.55	1.924	-2640	Grossular
Al^{3+}	0.54	6	5.55	1.896	-2655	Almandine
Al^{3+}	0.54	6	5.55	1.901	-2658	Spessartine
Al^{3+}	0.54	6	5.55	1.887	-2666	Pyrope
Al^{3+}	0.48	5	6.25	1.836	-2569	Andalusite Al2
Al^{3+}	0.39	4	7.69	1.764	-2526	Sillimanite Al2
Tetravalent						
Zr^{4+}	0.84	8	4.76	2.198	-3884	Zircon
Ti^{4+}	0.61	6	6.56	1.959	-4160	Titanite

Ionic radii from Klein and Hurlbut (1993, table 4.8).
Ionic potential is z/r, where z is the valence and r is the ionic radius.
Mean M-O bond distances and site energies from Smyth and Bish (1988).

resistant of the Al_2SiO_5 polymorphs to weathering. This is precisely what is observed. Average Al-O CNs and bond lengths decrease, and relative weathering rates decrease in the sequence kyanite > andalusite > sillimanite.

Although the consistancy between bond-length and relative persistence of these minerals is reassuring, it should be noted that the various Al-site energies in Al_2SiO_5 polymorphs are sufficiently similar to one another that neither average nor individual site-energies scale directly with bond length, ionic potential, or relative weathering rate. The observed relationship between CN_{Al} and weathering rate in Al_2SiO_5 polymorphs is also the opposite of the behavior of willemite- and olivine-structure types observed by Casey and Westrich (1992) and Westrich and others (1993) (figs. 1 and 2), in which the group with the lower CN weathers more readily. Furthermore four- and five-coordinated Al in sillimanite and andalusite, respectively, change coordination number upon dissolution and hydration; Al is coordinated to six water molecules in aqueous solutions (Casey and Ludwig, 1995, table 1). Change of Zn coordination during dissolution of willemite appears to be associated with higher-than-expected willemite dissolution rates (above), whereas those Al_2SiO_5 polymorphs that require change of Al coordination during dissolution (andalusite and sillimanite) weather less readily than kyanite, the dissolution of which requires no change in Al coordination. Changes in non-tetrahedral cation coordination during dissolution and weathering evidently introduce added complexity into bond-strength/weathering-rate relationships for those minerals and mineral groups in which weathering of some members requires change in cation coordination. The role of Al bonding and coordination in the weathering of Al_2SiO_5 polymorphs needs to be further investigated, both experimentally and by weathering studies of coexisting Al_2SiO_5 polymorphs in the same naturally weathered materials; concurrent studies of multiple polymorphs would be especially illuminating.

Isostructural mineral groups, each mineral with homogenous divalent cations; olivine structure type.–For orthosilicates with the olivine structure type, the "weathering sequence" can be predicted from ionic potentials; the higher the ionic potential of the divalent cation, the shorter the M-O bond length, the stronger the M-O bond, and the slower the dissolution rate of the mineral. The weathering sequence predicted from the ionic potentials of the octahedral cations in table 2 (Ca > Mn > Fe > Co > Mg > Ni) is identical to the observed sequence from the experiments of Casey and Westrich (1992):

Ca-olivine > Mn-olivine (Tephroite) > Fe-olivine (Fayalite) > Co-olivine
> Mg-Olivine (Foresterite) > Ni-olivine (Liebenbergite)

Data from naturally weathered olivine-structured compounds are not sufficient to allow a similar ranking to be constructed for naturally weathered materials.

Solid-solutions; olivine group.–Some of the minerals listed are actually entire groups of minerals, with complex solid-solutions (for example, olivine, garnet). Experimental work indicates that fayalitic (Fo_6) olivine dissolves six times faster than forsteritic ($Fo_{91\text{-}100}$) olivine, under similar experimental conditions (Wogelius and Walther, 1992). This is consistent with bond-length/bond-strength considerations; Fe^{II} has a larger ionic radius than Mg and therefore forms longer, weaker bonds with olivine's structural oxygen. Additionally, Fe^{II} is subject to oxidation. Unfortunately, data from naturally weathered olivines are not presently available to test this. It is uncommon for olivines of significantly different compositions to coexist in parent rocks, which would allow comparison of the natural weathering of compositionally different olivines under otherwise-identical weathering conditions.

Solid-solutions; garnet group.–Garnets exhibit even more complex solid-solution behavior than olivines and reveal some limitations of listings of mineral weathering series. Workers in weathering rank garnet as fairly weatherable, but this may reflect the rapid weathering of the two most common varieties, almandine and spessartine. Little is known specifically about the weathering of other garnet varieties. One might infer that at least some compositional varieties are very durable in the entire sedimentary cycle from the persistence of (at least some varieties of) garnet in ancient sedimentary rocks. This is well-illustrated by the persistence series (the reverse of a weathering series; the least persistent are the most weatherable) for heavy-minerals in sedimentary rocks of various ages by Pettijohn (1941):

$$\text{Olivine} < \text{Sillimanite} < \text{Titanite} < \text{Topaz} < \text{Andalusite} < \text{Kyanite} < \text{Staurolite} < \text{Garnet} < \text{Zircon.}$$

One possibility is that some varieties of garnet are easily weathered and cause the entire group to rank near the top of "weatherability" lists; other varieties are almost as durable as zircon, survive multiple episodes of sedimentary recycling, weathering, and diagenesis, and cause garnet to be ranked near zircon in persistence series based on evidence from ancient sedimentary rocks. However, detailed studies of detrital garnet compositions in sandstone provenance studies reveal that, as with garnets in parent materials of weathering, the predominant garnets in ancient sedimentary rocks are also pyralspite (pyrope-almandine-spessartine; $(Mg,Fe^{2+},Mn^{2+})_3Al_2(SiO_4)_3$) garnets. Differences in garnet's place in mineral persistence series for weathering and diagenesis therefore probably reflect the different susceptibility of the common pyralspite garnets to differences in the geochemical characteristics of weathering environments and diagenetic environments (Nickel, 1973; Morton, 1985). This suggests that studies of garnet survival in ancient sediments are not useful tests of compositional influences on garnet weathering rates.

There have been no studies to date comparing the relative extent of natural weathering of different garnets, although one such study is presently underway. However, considerations of bond-strength and ionic potential apparently successfully explain the sequence of dissolution rates observed in experimental dissolution of olivine-structured orthosilicates, and the observed relative persistence in nature of the Al_2SiO_5 polymorphs is apparently related to bond lengths, coordination numbers, and ionic potentials. This suggests that predictions for the relative weathering behavior of different garnets may be worth making. The ugrandite (uvarovite-grossular-andradite; $Ca_3(Cr,Al,Fe^{3+})_2(SiO_4)_3$) garnets all have Ca^{2+} as a dominant cation; its large ionic radius and low ionic potential suggest it is the most weakly bonded major ion in the garnet structure, and thus that the ugrandites as a group should weather more readily than the pyralspite garnets. Differences among the ugrandites are in octahedral sites. Based on the ionic potentials of Fe^{3+}, Cr^{3+}, and Al^{3+}, andradite might be expected to be the most weatherable of the ugrandites, followed by uvarovite and grossular. Among the pyralspite garnets, differences are in the 8-fold (distorted cubic) sites, and it might be expected that spessartine would weather most readily, followed by almandine and pyrope. Based strictly on considerations of M-O bonding, a predicted weathering series for garnets might be:

$$\text{Andradite} > \text{Uvarovite} > \text{Grossular} > \text{Spressartine} > \text{Almandine} > \text{Pyrope}$$

Factors that complicate this predicted ranking include:

1. The iron in andradite is ferric iron. This will almost certainly render andradite less vulnerable to weathering in oxidizing environments than other garnets with ions vulnerable to oxidation (for example, ferrous iron in almandine; Mn in spessartine).

2. Almandine and spessartine garnets contain sufficient Fe (or Mn) and Al to form transport-limiting protective surface layers in well-leached, oxidizing weathering environments where organic complexing agents are absent (Velbel, 1984, 1993a). Almandine and spessartine weathered in such oxidized saprolitic environments weather more slowly than they would in the absence of such protective surface layers (Embrechts and

Stoops, 1982; Velbel, 1984). Organic complexing agents have been implicated in the removal of Al and Fe from almandine surface in soils and the resulting absence of protective surface layers (Velbel, 1984). The ranking of almandine and spessartine relative to one another and relative to other garnets in garnet weathering series will depend on redox conditions [in the weathering environment] and the role of complexing agents in the weathering environment.

3. Real garnets are complex solid solutions, which seldom approach ideal endmember compositions. Any real garnet will actually contain many or all of the bond types discussed here, in different proportions. Furthermore, this complexity will often be spatially heterogeneous within single crystals as well, in the case of compositionally zoned garnets. This complexity will almost certainly obscure any simple trends predicted here.

In summary, consideration of bond strength suggests that Ca-rich garnets might weather readily, and that Mg-rich garnets might be the most resistant of all garnets to weathering. Further studies of naturally weathered garnets are required.

Between-group Variations in Bond-strength and Weathering Rate

Recent work on the natural weathering of staurolite (Velbel, Basso, and Zieg, 1996) adds to the complexity of weathering phenomena observed among the orthosilicates. Staurolite weathering rates are trivially slow compared with all other major rock-forming silicate minerals (including almandine garnet) except quartz, at all six localities sampled by Velbel, Basso, and Zieg (1996). This is consistent with the results of previous studies of heavy-mineral weathering (van Kersen, 1955; Morton, 1984, 1985; Bateman and Catt, 1985; Edou-Minko, 1988), in which zircon, tourmaline, and minerals of the Al_2SiO_5 group are the only heavy silicate minerals (and quartz the only light mineral) more resistant to weathering than staurolite. Slow weathering of staurolite relative to other silicate minerals is also broadly consistent with the experimental dissolution rates determined by Nickel (1973).

Weathering of staurolite is trivially slow relative to other silicate minerals in natural and experimental oxidizing environments despite the fact that most Fe in staurolite is ferrous and therefore vulnerable to oxidation. Slow weathering of staurolite relative to other silicate minerals may be related to stability of kyanite-like "ribbons" parallel to (010) (which is also the elongation direction of the etch pits) in the staurolite structure (Velbel, Basso, and Zieg, 1996). Kyanite and staurolite have essentially identical persistence in the weathering environment, according to empirical mineral weathering series (Morton, 1984, 1985; Bateman and Catt, 1985).

Another factor that may contribute to the difficulty of staurolite weathering relative to other Fe-bearing orthosilicates (garnet, olivine) involves the coordination of Fe in the structure. As noted above, weathering rates of structurally related alkaline-earth orthosilicates are proportional to the radius of the cation (Casey and Westrich, 1992; Westrich and others, 1993; Casey and Ludwig, 1995). Coordination number is related to cation radius (and, consequently, bond length); smaller cations have shorter bond lengths, and often smaller coordination numbers, with coordinating anions. Iron occurs in tetrahedral sites in staurolite (an uncommon configuration for Fe in silicate minerals), octahedral sites in olivine, and distorted cubic sites in garnet; as coordination number increases, so does the bond length (Smyth and Bish, 1988). Shorter bonds between the same two ions are usually stronger than longer bonds; the site energy for the Fe site in staurolite is lower than the site-energies for Fe sites in garnet and olivine (which are comparable to one another; Smyth and Bish, 1988). In general, silicate dissolution rates vary with site energy (Brady and Walther, 1992); thus, disruption of individual Fe-O bonds may be easier for garnet and olivine than for staurolite. This could explain why staurolite weathers so much more slowly than other silicates under similar conditions.

However, differences in Fe coordination alone do not explain the relative susceptibility to weathering of olivine and garnet. If Fe coordination were the main controlling factor determining weathering rates of these two minerals, garnet ($CN_{Fe} = 8$) would weather more rapidly than olivine ($CN_{Fe} = 6$). This is not what heavy-mineral-persistence series indicate; in natural weathering, olivine weathers more readily than garnet.

Unlike Fe coordination numbers, Fe-site energies decrease in the order olivine > almandine > staurolite. Furthermore, other factors may influence the weathering behavior of almandine garnet relative to fayalite olivine. Under common ferrallitic (lateritic; well-leached, oxidizing) weathering conditions, rate-limiting protective surface layers do not form on olivine, but diffusion-inhibiting layers do form on almandine and spessartine (Velbel, 1984, 1993a). (The different abilities of olivine and Fe-Mn garnets to form protective surface layers during weathering are a consequence of molar-volume relationships between reactant silicates and weathering products; Velbel, 1993a). Soil-mineralogical studies report that both "coated" and "uncoated" almandine garnet grains can occur in the same soil (Graham and others, 1989a,b); garnets which were partially weathered in saprolites have thick coatings of "limonite" and persist in soils, whereas garnets that "bypassed" the coating-forming, saprolitic stage of weathering (that is, were removed to soils directly from fresh outcrops) are much less persistant in soils, and evidently weather much more quickly (Embrechts and Stoops, 1982). These observations attest to the protective, dissolution-inhibiting nature of the coatings. Perhaps the Fe-O bonds in almandine are approximately as weak and favorable for rapid weathering as in olivine in the absence of protective coatings, but the ability of almandine and spessartine to form diffusion-inhibiting protective surface layers (Velbel, 1993a) in common weathering environments usually results in suppression of their weathering rates to the extent that almandine and spessartine weather more slowly than olivine. This would combine several known, simple characteristics of the minerals (bond-length/bond-strength differences, differences in reactant/product molar-volume relations) into a coherent explanation of the relative-persistence relations reviewed above.

For the trio of common Fe-bearing orthosilicates, olivine-garnet-staurolite, their relative rankings in weathering series could be explained as follows:

– Staurolite weathers most slowly because, among other things, Fe is tetrahedrally coordinated, resulting in shorter and stronger Fe-O bonds.

– Olivine weathers faster, because its Fe is octahedrally coordinated, resulting in longer and weaker Fe-O bonds than in staurolite.

– Almandine garnet could potentially weather approximately as fast as olivine, because of its cubic Fe coordination (resulting in Fe-O bonds even longer than, but slightly stronger than, Fe-O bonds than in olivine). Almandine may actually weather faster than olivine in certain environments (those in which protective surface layers do not form), but it is prevented from doing so in other environments because its molar volume and high content of product-forming elements (Al, Fe) allow buildup of a protective surface layer, which slows down the almandine weathering reaction by inhibiting transport of reactants to and/or products from the replacement front.

This hypothesis could be tested if a single rock or a suite of rocks with comparable weathering histories containing both olivine and almandine (so that both weathered simultaneously for the same amount of time and under the same conditions) could be examined for their weathering textures in both soil and saprolite. From the suggestions presented here, I would predict that in oxidized saprolite (where protective surface layers form on almandine), olivine would appear more weathered and/or be more depleted than almandine. I would also predict that, in overlying soils (where protective surface layers do not form on almandine), neither mineral would exhibit protective surface layers, and almandine would be more extensively etched and/or be more depleted than olivine. In other words, almandine would give evidence of weathering faster than coexisting olivine in the absence of protective surface layers. This would confirm that Fe coordination in garnet renders it more weatherable than olivine, and that protective surface layers suppress the almandine weathering rate sufficiently to place almandine below olivine in mineral-weathering series. Existing data for naturally weathered olivine and garnet do not presently permit assessment of this proposal.

Ionic-radius/bond-length/bond-strength considerations also explain the relative positions in weathering series of Fe-, Al-, and Zr-bearing orthosilicates. The site energy for Zr^{4+} in zircon is lower than the site energy for any other common orthosilicate cation except Ti^{4+} in titanite (Smyth and Bish, 1988); the Zr-O bond is thus the strongest of all bonds considered here. (Removal of Ca may be the complicating factor in the weathering of titanite; the Ca-O bond is the weakest in the titanite structure, so titanite may weather easily despite the strength of the Ti-O bonds. Variations in Ca mobility in different weathering environments may therefore indirectly influence the relative stability of titanite; this may be why titanite appears in different positions on different natural weathering series.) Breaking Zr-O bonds is more difficult than for almost any other cation, and zircon is the most resistant orthosilicate to weathering.

The relative weathering rates of seven orthosilicates (of the 10 on the lists) can be explained simply in terms of the relative strengths of Fe-O, Al-O, and Zr-O bonds (ranking three groups based on the main non-Si cation present), and variations in these bond strengths associated with coordination numbers (creating the rankings within these three compositional groups). The only special consideration required is to account for the formation of protective surface layers, a phenomenon unique to Fe- (and Mn-) garnets.

CONCLUSIONS

Weathering of orthosilicates requires breaking bonds between non-tetrahedral cations and oxygen (M-O bonds). Common naturally occurring orthosilicates can be grouped into those in which the major non-tetrahedral cations are (1) Fe^{II} and/or Mg, plus or minus Al (olivine, pyralspite garnets, staurolite), (2) Al (Al_2SiO_5 polymorphs), or (3) Zr. Simple Coulombic attraction suggests that Fe- and Mg-bearing orthosilicates have the weakest bonds, and zircon the strongest, with Al-O bonds intermediate; thus, the relative vulnerability to weathering of the three groups decreases in the order

$$\text{Fe-Mg}(\pm\text{Al})\text{ orthosilicates} > Al_2SiO_5\text{ polymorphs} > \text{zircon}.$$

Among Fe(±Mg)-orthosilicates, Fe-O bond length and bond strength vary with Fe coordination number. Almandine's Fe-O bonds are longer than and similar in strength to olivine's, suggesting that almandine could weather approximately as fast as olivine, but reactant-product molar-volume ratios involving almandine and common weathering products favor the formation of transport-limiting, rate-limiting protective surface layers on almandine and not on olivine; suppression of almandine's weathering rate by these protective surface layers is apparently sufficient to leave olivine at the top of weathering series. Short, strong Fe-O bonds involving tetrahedral Fe render staurolite more resistant to weathering than either common olivines or common pyralspite garnets. Thus, bond-strength and molar-volume considerations indicate that the relative vulnerability to weathering of Fe(±Mg±Al)-orthosilicates decreases in the order

$$\text{Olivine} > \text{Pyralspite Garnets} > \text{Staurolite}.$$

Within the olivine group, weathering rate scales with the radius of the divalent cation; olivines with larger divalent cations (example, fayalite), with their longer and weaker M-O bonds, weather more rapidly than those with smaller cations and shorter stronger M-O bonds (example, forsterite).

Relative weathering rates within the Al_2SiO_5 group vary with the coordination number of Al, with persistence decreasing in order

Kyanite > Andalusite > Sillimanite.

The strength of the M-O bond in orthosilicates explains intragroup variations in the relative weathering rates of olivine-structured compounds, willemite-structured minerals, and the Al_2SiO_5 polymorphs. M-O bond strength also explains intergroup variations in the relative weathering rates of iron-bearing orthosilicates (olivine, almandine garnet, staurolite), relative to one another (if almandine garnet's almost-unique ability to form protective surface layers is accounted for), and relative to Al_2SiO_5 polymorphs and zircon. Relative weathering rates of common orthosilicates decrease in the same order as the M-O bond energies for the dominant non-tetrahedral cations, giving rise to the commonly observed natural orthosilicate weathering series:

Olivine > Garnet > Staurolite > Kyanite > Andalusite > Sillimanite > Zircon.

ACKNOWLEDGMENTS

This project has been supported under the Australian Government's Cooperative Research Centres Program. The manuscript was prepared during a sabbatical leave at the Australian National University, supported by the Cooperative Research Centre for Landscape Evolution and Mineral Exploration (CRC-LEME). I thank Tony Eggleton for sponsoring my sabbatical visit to ANU and CRC-LEME; Graham Taylor and Steve Hill for helping organize a CRC-LEME short course on mineral-water interactions during which this presentation was developed; and Watcharaporn Keankeo, Steve Hill, David Tilley, Tony Eggleton, and Ian Robertson, for stimulating discussions about garnet, staurolite, and Al_2SiO_5 weathering. A grant from the Special Foreign Travel Fund of MSU's Office of International Studies and Programs allowed me to present an earlier version of this work at the Fourth International Symposium on the Geochemistry of the Earth's Surface (GES-IV) in Ilkley (1996). I am most grateful to Jean Delvigne, Jeff Wilson, and Bill Casey for their helpful and detailed reviews.

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