

Natural weathering mechanisms of almandine garnet

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ABSTRACT

The weathering of almandine garnet in the oxidized, vadose zone of saprolite near Otto, North Carolina, begins at grain boundaries and along fractures traversing the garnet grains. Radially oriented fibrous intergrowths of gibbsite and goethite form layers of uniform thickness, which grow by centripetal replacement as weathering proceeds. The contact between the garnet surface and the layer of weathering products is sharp and smooth, and garnet corners are rounded. Large, well-defined etch pits are absent on the underlying garnet surface. These observations suggest that diffusion (transport) of reactants and/or products through the gibbsite-goethite layer is the rate-limiting step in the weathering of almandine garnet in the oxidizing environment of the saprolite.

In soils overlying the saprolite, garnet surfaces are directly exposed to weathering solutions without the intervening surface layer. Such "unprotected" grains in soils (and stream sediments) exhibit numerous large, well-developed etch pits. Surface-reaction control, rather than transport control, prevails during weathering of almandine garnet in the absence of protective surface layers of weathering products. Biochemical or biological processes in the soil apparently prevent the gibbsite-goethite layer from forming or persisting. Soil solutions can therefore react directly with the garnet surface, rather than requiring reactants or products to diffuse through the gibbsite-goethite coating as in the saprolite. The mechanism, and rate-limiting step, of almandine garnet weathering is apparently strongly dependent on the chemical environment in which weathering occurs.

INTRODUCTION

The mechanisms and rate controls of silicate-mineral weathering have been the subject of much interest in recent years (Berner, 1978, 1981). A large body of experiment, interpretation, and theory suggested the once-prevalent notion that diffusion (transport) of reactants and/or products through some kind of "protective surface layer" is the rate-limiting step in silicate-mineral weathering reactions (e.g., Wollast, 1967; Helgeson, 1971, 1972; Luce et al., 1972). More recently, surface-chemistry and micromorphological techniques have been used to seek direct evidence of such protective coatings; these studies found, instead, much evidence (e.g., etch pits and "fresh-mineral" compositions on weathered mineral surfaces) that surface-reaction control, rather than transport-control, is the rate-limiting step in the weathering of feldspars (Wilson, 1975; Berner and Holdren, 1977, 1979; Holdren and Berner,

1979) and iron-free pyroxenes, amphiboles, and olivines (Berner et al., 1980; Grandstaff, 1980; Schott et al., 1981; Berner and Schott, 1982). On the basis of this more recent work, surface-reaction control is increasingly accepted as the rate-controlling mechanism in the weathering of iron-free silicates.

Recent laboratory work on the weathering of iron-bearing silicate minerals has not yet permitted as definitive a resolution of the problem. Siever and Woodford (1979) suggested that iron hydroxide forms a protective surface layer on mafic minerals in oxidizing environments. In contrast, Schott and Berner (1983) suggested that the hydrous ferric oxide layer that commonly forms in oxidizing weathering environments is not "protective towards dissolution" and cite the ubiquitous occurrence of etch pits on soil pyroxenes and amphiboles to support this. Although there is little doubt that hydrous ferric oxide precipitates form during weathering of iron-bearing silicate minerals, their role in controlling the rates of mineral weathering is not well understood.

In this paper I present new micromorphological evidence on the natural weathering of iron-bearing garnet (almandine) from a variety of weathering environments, and I discuss the implications of these findings for rate controls in the weathering of iron-bearing silicate minerals.

Remarkably little is known about the weathering of natural garnet, probably because the chemical complexity of this group of minerals makes it an unattractive candidate for study. What little we do know is due almost entirely to the efforts of sedimentary petrologists; the definitive modern text *Minerals in Soil Environments* (Dixon and Weed, 1977) does not mention garnet, and the fleeting references in two earlier works (Keller, 1957; Loughnan, 1969) are both to Pettijohn's (1941) classic paper on heavy minerals in sedimentary rocks, in which the entire garnet group is ranked between monazite and biotite in a "stability series." Brophy (1959) observed erratic behavior of garnet abundance relative to hornblende and zircon-tourmaline in Sangamon weathering profiles of Illinois. Marshall (1964) believed that "under acidic weathering conditions, garnets disappear at what, in geological terms, would be a rapid rate." Equally little is known about the products of garnet weathering. Grant (1958) reported that garnet (unspecified variety) "[u]sually has [a] thick limonite coat" in Georgia saprolite.

In contrast to the limited literature on garnet weathering, alteration of garnet in sedimentary rocks has received much attention; unfortunately, the sedimentary petrologists cannot agree on which morphologic features of garnet surfaces constitute dissolution features and which are due to garnet authigenesis and overgrowth. The details of the controversy are beyond the scope of this report; the reader should refer to Raeside (1959), Rahmani (1973), Nickel (1973), Hemingway and Tamar-Agha (1975), Simpson (1976), Stieglitz and Rothwell (1978), Morton (1979), Gravenor and Gostin (1979), Gravenor (1979, 1980), Howie et al. (1980), and Gravenor and Leavitt (1981). The main reason for this lack of consensus is the complex history of sedimentary garnets. Garnets

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sampled from sedimentary rocks may have experienced multiple episodes of organic and inorganic weathering, erosion, intrastatal dissolution, and authigenesis. Consequently, it is extremely difficult to assign a specific origin to any given feature of the mineral grain surface. This study eliminates most of these uncertainties by concentrating on one process (weathering) of primary metamorphic garnet that has not experienced any prior sedimentary history.

METHODS

Almandine garnet (composition determined by electron microprobe) was sampled from fresh rock, deeply weathered saprolite, soil, and stream sediments, at the Coweeta Hydrologic Laboratory of the U.S. Forest Service near Otto, North Carolina. Saprolite and soil in the study area are usually in the vadose (unsaturated) zone, and pore spaces are consequently partially filled with water in direct contact with an oxygenated atmosphere. Oxidizing conditions therefore prevail throughout the sampled part of the study area. Thin sections were made from fresh rock and saprolite and were examined petrographically. Individual grains from all types of material were mounted directly on SEM stubs, without any sample pretreatment; another collection of grains were selected from saprolite and soils and treated ultrasonically to "clean" their surfaces.

RESULTS

Fresh garnet is often subhedral to euhedral in thin section, and the SEM reveals growth steps on the crystal faces (Fig. 1a). Weathered garnets from saprolite have dark red, almost opaque, very slightly birefringent coatings of uniform thickness at garnet grain boundaries and along intragranular fractures (Fig. 1b). All garnet-limonite boundaries are abrupt and rounded, and regular etch features are not visible in thin section. These coatings appear to thicken with increased weathering. X-ray diffraction of this material shows it to be an intermixture of discrete goethite and gibbsite. Scanning electron microscopy reveals spectacular radial fibrous growths of gibbsite and goethite (Fig. 1c-e).

Ultimately, the enclosed garnet can be either congruently dissolved, leaving voids between septa of limonite that mimic the original grain boundary and fractures of the garnet, or replaced by gibbsite-goethite pseudomorphs (not illustrated here). The former is a natural phenomenon, not the result of plucking during thin sectioning, as evidenced by empty spaces within septa in freshly fractured hand specimens of saprolite. Unusually, however, this ultimate stage is not attained, and intermediate stages of "coated" garnet are preserved. Parisot et al. (1983) observed identical alteration sequences, products, and textures in weathered almandine from Brazilian soils and saprolites.

The ultrasonically cleaned surface of a saprolite garnet (from which the gibbsite-goethite layer was removed by vigorous ultrasonic treatment; Fig. 1f) shows the smooth, unetched appearance of the garnet surface at the contact with the gibbsite-goethite coating. Note that all traces of growth steps on the original bounding surfaces of the garnet have been obliterated.

Some garnets, hand picked from soils, have yellow-orange goethitic coatings and fracture fillings; these products are usually difficult to remove, even with moderate ultrasonic treatment, suggesting that the coatings adhere with moderate tenacity to the underlying mineral surface. Many soil garnets, however, lack such coatings (Fig. 1g), suggesting that the coatings have been removed; alternatively, the coatings may never have formed on these grains in the biologically dominated soil. The "bare," uncoated surfaces of such soil garnets are densely pocked by numerous, well-formed etch pits (Fig. 1g, h).

Garnets picked from sediments of Coweeta Creek downstream of the study area also show regular etch pits (Fig. 1i), which in places coexist with "mammillary surfaces."

DISCUSSION

Weathering of garnet begins at grain boundaries, obliterating the primary surface features of the parent garnet. By the criteria of Berner (1978, 1981) the presence of a distinct layer of weathering products that thickens with increased weathering and the paucity of etch pits beneath this layer suggest that the "limonite" coating on weathered garnet in saprolite is a protective surface layer and that diffusion of reactants or dissolved products through this layer is the rate-limiting step in garnet weathering. This is the first report of field evidence for transport control of any silicate-mineral weathering reaction (see Introduction). The coatings originate at the garnet grain boundaries and intragranular fractures and grow inward to the present contact ("centripetal replacement" of Parisot et al., 1983; also called "pellicular alteration" by Stoops et al., 1979), in places completely replacing the garnet, as noted above. The coatings could not have been superposed upon the original garnet surface and grown outward because primary surface features are obliterated, and there is no free space outside a garnet crystal in a rock or saprolite into which crystals may grow. The coatings are much thicker than grain-boundary fractures, and saprolite is the product of isovolumetric weathering (Millot and Bonifas, 1955; Cleaves, 1974; Gardner et al., 1978), allowing for only negligible expansion of grain-boundary fractures to accommodate the coatings. The relatively slow motion of weathering solutions along microfractures in and around altering garnets in the saprolite, the prevalence of oxidizing conditions, and the absence of biological agents in the subsurface permit dissolved Al and Fe to be reprecipitated locally, allowing the protective surface layer to form.

In sharp contrast to the saprolite, conditions in soils and streams of the study area do not favor the formation or preservation of the protective surface layer. Soil is the part of the weathering profile dominated by biological and biochemical processes; that limonite coatings are largely absent on garnet grains from the biologically active part of the weathering profile suggests that the biological activity is in some way responsible for the absence of coatings. Chemical complexing by organic chelating agents in some soils is known to prevent the immediate precipitation of Al and Fe and to cause their removal to, and subsequent precipitation at, loci removed from mineral surfaces (e.g., Graustein, 1976; Holdren et al., 1977). In stream sediments, the rapid motion of the solutions or the chemistry of the solutions passing the garnet surface has the same effect, removing dissolved Al and Fe from the immediate vicinity of the garnet and preventing local reprecipitation. In these weathering environments where the protective surface layer is removed or prevented from forming, selective surface attack takes place, manifesting itself in the form of numerous well-formed etch pits. This strongly suggests that garnet weathering is surface-reaction controlled in the absence of the surface layer and that the surface layer plays an important rate-limiting role in the weathering reaction. Embrechts and Stoops (1982) reported that garnets which were partially weathered in saprolites have thick coatings of "limonite" and persist for long periods of time, whereas garnets that "bypassed" the coating-forming, saprolitic stage of weathering (i.e., were removed to soils directly from fresh outcrops) weather much more quickly. These observations further attest to the protective nature of the coatings.

CONCLUSIONS

Weathered garnet from oxidized vadose saprolite has thick, continuous, tenacious layers of gibbsite-goethite weathering products, which cover unetched garnet surfaces. The absence of etch pits on the garnet suggests uniform attack by weathering of all parts of the garnet surface. Micromorphologic evidence suggests that weathering in the inorganic environment of deep (vadose) saprolites is inhibited by diffusion (transport) through the protective surface layer.

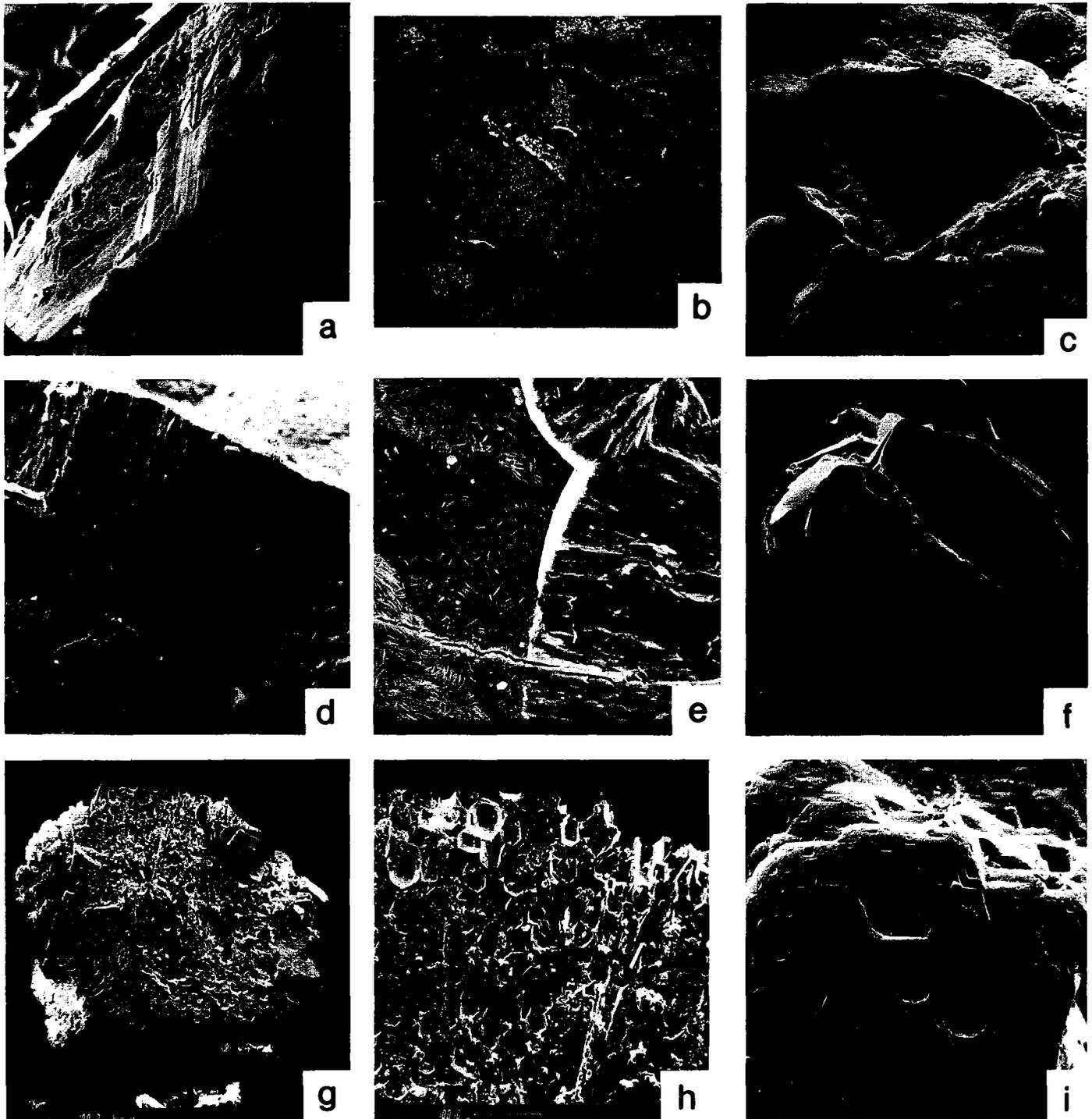


Figure 1. a: Scanning electron photomicrograph (SEM) of garnet from fresh, unweathered metamorphic rock. Note growth steps. b: Thin-section photomicrograph (plane light) of round garnet grain in biotite schist saprolite, with dark, nearly opaque weathering products at grain boundaries and along fractures traversing grain; field of view is 1.5 mm wide. c: SEM of "limonite" coating on weathered garnet grain from saprolite; triangular patch of "limonite" was removed during sample preparation, exposing fresh garnet. d: Close-up of c; note both radial orientation of gibbsite-goethite coating with respect to underlying rounded garnet surface, and absence of etch pits on exposed garnet surface. e: SEM close-up of gibbsite-goethite coating; left half shows outer surface, right half shows cross section of coating, again displaying radial fibrous aspect of products. f: Ultrasonically cleaned garnet grain from saprolite (SEM); this grain, which was covered by gibbsite-goethite coating before ultrasonic treatment, is unetched. g: Soil garnet, untreated, densely pocked with etch pits (SEM). h: Close-up of g, showing numerous well-formed etch pits. i: Garnet grain from stream sediments downstream of studied weathering profile, untreated (SEM); note absence of any coating and presence of crystallographically controlled voids.

In the soil, an environment in which biological processes dominate over inorganic processes, protective surface layers cannot form, and preexisting layers may be removed. The weathering reactions are faster (e.g., Embrechts and Stoops, 1982; discussed above) because they are no longer limited by diffusion through the surface layer, and surface-reaction control prevails.

The ability of a surface layer to form, persist, and exert a rate-controlling influence on the weathering of almandine garnet, and possibly other iron-bearing silicate minerals, is apparently dependent on environmental factors such as oxidizing potential or the relative importance of organic and inorganic influences in the local weathering environment.

REFERENCES CITED

- Berner, R.A., 1978, Rate control of mineral dissolution under earth surface conditions: *American Journal of Science*, v. 278, p. 1235-1252.
- 1981, Kinetics of weathering and diagenesis, in Lasaga, A.C., and Kirkpatrick, R.J., eds., *Kinetics of geochemical processes: Mineralogical Society of America Reviews in Mineralogy*, v. 8, p. 111-134.
- Berner, R.A., and Holdren, G.R., Jr., 1977, Mechanism of feldspar weathering: Some observational evidence: *Geology*, v. 5, p. 369-372.
- 1979, Mechanism of feldspar weathering; II. Observations of feldspars from soils: *Geochimica et Cosmochimica Acta*, v. 43, p. 1173-1186.
- Berner, R.A., and Schott, J., 1982, Mechanism of pyroxene and amphibole weathering; II. Observations of soil grains: *American Journal of Science*, v. 282, p. 1214-1231.
- Berner, R.A., Sjöberg, E.L., Velbel, M.A., and Krom, M.D., 1980, Dissolution of pyroxenes and amphiboles during weathering: *Science*, v. 207, p. 1205-1206.
- Brophy, J.A., 1959, Heavy mineral ratios of Sangamon weathering profiles in Illinois: *Illinois State Geological Survey Circular* 273, 22 p.
- Cleaves, E.T., 1974, Petrologic and chemical investigation of chemical weathering in mafic rocks, eastern piedmont of Maryland: *Maryland Geological Survey Report of Investigations* No. 25, 28 p.
- Dixon, J.B., and Weed, S.B., eds., 1977, *Minerals in soil environments*: Madison, Wisconsin, Soil Science Society of America, 948 p.
- Embrechts, J., and Stoops, G., 1982, Microscopical aspects of garnet weathering in a humid tropical environment: *Journal of Soil Science*, v. 33, p. 535-545.
- Gardner, L.R., Kheoruenromne, I., and Chen, H.S., 1978, Isovolumetric geochemical investigation of a buried granite saprolite near Columbia, SC, U.S.A.: *Geochimica et Cosmochimica Acta*, v. 42, p. 417-424.
- Grandstaff, D.E., 1980, The dissolution rate of forsteritic olivine from Hawaiian beach sand; in *Proceedings, 3rd International Symposium on Water-Rock Interaction*: Edmonton, Canada, Alberta Research Council, p. 72-74.
- Grant, W.H., 1958, The geology of Hart County, Georgia; *Georgia Geological Survey Bulletin* 67, 75 p.
- Graustein, W.C., 1976, Organic complexes and the mobility of iron and aluminum in soil profiles: *Geological Society of America Abstracts with Programs*, v. 8, p. 891.
- Gravenor, C.P., 1979, The nature of the Late Paleozoic glaciation in Gondwana as determined from an analysis of garnets and other heavy minerals: *Canadian Journal of Earth Sciences*, v. 16, p. 1137-1153.
- 1980, The nature of the Late Paleozoic glaciation in Gondwana as determined from an analysis of garnets and other heavy minerals: Reply: *Canadian Journal of Earth Sciences*, v. 17, p. 958-959.
- Gravenor, C.P., and Gostin, V.A., 1979, Mechanisms to explain the loss of heavy minerals from upper Paleozoic tillites of South Africa and Australia and the late Precambrian tillites of Australia: *Sedimentology*, v. 26, p. 707-717.
- Gravenor, C.P., and Leavitt, R.K., 1981, Experimental formation and significance of etch patterns on detrital garnets: *Canadian Journal of Earth Sciences*, v. 18, p. 765-775.
- Helgeson, H.C., 1971, Kinetics of mass transfer among silicates and aqueous solutions: *Geochimica et Cosmochimica Acta*, v. 35, p. 421-469.
- 1972, Kinetics of mass transfer among silicates and aqueous solutions: Correction and clarification: *Geochimica et Cosmochimica Acta*, v. 36, p. 1067-1070.
- Hemingway, J.E., and Tamar-Agha, M.Y., 1975, The effects of diagenesis on some heavy minerals from the sandstones of the Middle Limestone Group in Northumberland: *Yorkshire Geological Society Proceedings*, v. 40, p. 39-46.
- Holdren, G.R., Jr., and Berner, R.A., 1979, Mechanism of feldspar weathering—I. Experimental studies: *Geochimica et Cosmochimica Acta*, v. 43, p. 1161-1171.
- Holdren, G.R., Jr., Graustein, W.C., and Berner, R.A., 1977, Chemical weathering in soils: Evidence from surface compositions: *Geological Society of America Abstracts with Programs*, v. 9, p. 1020-1021.
- Howie, R.A., Simpson, I.M., and Simpson, G.S., 1980, The nature of the Late Paleozoic glaciation in Gondwana as determined from an analysis of garnets and other heavy minerals: Discussion: *Canadian Journal of Earth Sciences*, v. 17, p. 957-958.
- Keller, W.D., 1957, *Principles of chemical weathering*: Columbia, Missouri, Lucas Brothers Publishers, 111 p.
- Loughnan, F.C., 1969, *Chemical weathering of silicate minerals*: New York, American Elsevier, 154 p.
- Luce, R.W., Bartlett, R.W., and Parks, G.A., 1972, Dissolution kinetics of magnesium silicates: *Geochimica et Cosmochimica Acta*, v. 36, p. 35-50.
- Marshall, C.E., 1964, *The physical chemistry and mineralogy of soils. Volume I: Soil materials*: New York, John Wiley & Sons, 388 p.
- Millot, G., and Bonifas, M., 1955, Transformations isovolumétriques dans les phénomènes de lateritisation et de bauxitisation: *Service de la Carte Géologique d'Alsace et de Lorraine, Bulletin*, v. 8, p. 3-20.
- Morton, A.C., 1979, Surface features of heavy mineral grains from Palaeocene sands of the central North Sea: *Scottish Journal of Geology*, v. 15, p. 293-300.
- Nickel, E., 1973, Experimental dissolution of light and heavy minerals in comparison with weathering and intrastatal dissolution: *Contributions to Sedimentology*, v. 1, p. 1-68.
- Parisot, J.C., Delvigne, J., and Groke, M.T.C., 1983, Petrographical aspects of the supergene weathering of garnet in the Serra dos Carajas (Para, Brazil), in Nahon, D., and Noack, Y., eds., *International Colloquium CNRS on the Petrology of Weathering and Soils, Abstracts*: Paris, Centre National de la Recherche Scientifique, p. 47.
- Pettijohn, F.J., 1941, Persistence of heavy minerals and geologic age: *Journal of Geology*, v. 49, p. 610-625.
- Raeside, J.D., 1959, Stability of index minerals in soils with particular reference to quartz, zircon, and garnet: *Journal of Sedimentary Petrology*, v. 29, p. 493-502.
- Rahmani, R.A., 1973, Grain surface etching features of some heavy minerals: *Journal of Sedimentary Petrology*, v. 43, p. 882-888.
- Schott, J., and Berner, R.A., 1983, X-ray photoelectron studies of the mechanism of iron silicate dissolution during weathering: *Geochimica et Cosmochimica Acta*, v. 47, p. 2233-2240.
- Schott, J., Berner, R.A., and Sjöberg, E.L., 1981, Mechanism of pyroxene and amphibole weathering—I. Experimental studies of iron-free minerals: *Geochimica et Cosmochimica Acta*, v. 45, p. 2123-2135.
- Siever, R., and Woodford, N., 1979, Dissolution kinetics and the weathering of mafic minerals: *Geochimica et Cosmochimica Acta*, v. 43, p. 717-724.
- Simpson, G.S., 1976, Evidence of overgrowths on, and solution of, detrital garnets: *Journal of Sedimentary Petrology*, v. 46, p. 689-693.
- Stieglitz, R.D., and Rothwell, B., 1978, Surface microtextures of freshwater heavy mineral grains: *Geoscience Wisconsin*, v. 3, p. 21-34.
- Stoops, G., Altemüller, H.-J., Bisdom, E.B.A., Delvigne, J., Dobrovolsky, V.V., Fitzpatrick, E.A., Paneque, G., and Sleeman, J., 1979, Guidelines for the description of mineral alterations in soil micromorphology: *Pedologie*, v. 29, p. 121-135.
- Wilson, M.J., 1975, Chemical weathering of some primary rock-forming minerals: *Soil Science*, v. 119, p. 349-355.
- Wollast, R., 1967, Kinetics of the alteration of K-feldspar in buffered solutions at low temperature: *Geochimica et Cosmochimica Acta*, v. 31, p. 635-648.

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