

Atmospheric weathering and silica-coated feldspar: Analogy with zeolite molecular sieves, granite weathering, soil formation, ornamental slabs, and ceramics

(architecture)

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ABSTRACT Feldspar surfaces respond to chemical, biological, and mechanical weathering. The simplest termination is hydroxyl (OH), which interacts with any adsorption layer. Acid leaching of alkalis and aluminum generated a silica-rich, nanometers-thick skin on certain feldspars. Natural K, Na-feldspars develop fragile surfaces as etch pits expand into micrometer honeycombs, possibly colonized by lichens. Most crystals have various irregular coats. Based on surface-catalytic processes in molecular sieve zeolites, I proposed that some natural feldspars lose weakly bonded Al-OH (aluminol) to yield surfaces terminated by strongly bonded Si-OH (silanol). This might explain why some old feldspar-bearing rocks weather slower than predicted from brief laboratory dissolution. Lack of an Al-OH infrared frequency from a feldspar surface is consistent with such a silanol-dominated surface. Raman spectra of altered patches on acid-leached albite correspond with amorphous silica rather than hydroxylated silica-feldspar, but natural feldspar may respond differently. The crystal structure of H-exchanged feldspar provides atomic positions for computer modeling of complex ideas for silica-terminated feldspar surfaces. Natural weathering also depends on swings of temperature and hydration, plus transport of particles, molecules, and ionic complexes by rain and wind. Soil formation might be enhanced by crushing granitic outcrops to generate new Al-rich surfaces favorable for chemical and biological weathering. Ornamental slabs used by architects and monumental masons might last longer by minimizing mechanical abrasion during sawing and polishing and by silicifying the surface. Silica-terminated feldspar might be a promising ceramic surface.

Chemical and physical changes in minerals underlie many aspects of human welfare. Agriculture depends on the interaction of soils with water, ionic and molecular species, and biological organisms. The weathering of feldspar minerals (1–4) from bedrock into clays is important for the production of food. Many laboratory experiments have measured the dissolution rate of feldspar minerals by water containing a wide range of ionic and molecular species, including organic acids relevant to biological weathering. Data are available for the range of feldspar chemistry from strongly acid to alkaline conditions (2, 3). Electron and chemical microscopy of feldspar surfaces is revealing a wealth of information on chemical and physical changes, including pitting, honeycombing, and selective dissolution (5). Only scattered data are available for the rate of weathering of feldspars in natural watersheds, but they indicate that natural atmospheric weathering of many

rocks is slower than for short term laboratory experiments of crushed samples (2, 3). Casual examination of granite slabs in cemeteries and city buildings indicates that the alkali feldspars are weathering slowly unless mechanical spalling is occurring. Quarry operators deliberately age rock slabs for some months before shipment to construction sites and cemeteries. Hence, it is important to understand the temporal changes in atomic chemistry at feldspar surfaces and to devise key experiments that use the new analytical and topographic microscopies.

This paper expands on the simple idea (6) that atmospheric weathering of many natural feldspars becomes limited by a structurally continuous, silica-rich atomic skin that is similar chemically to that of silica minerals. This skin could not cover the entire surface of a feldspar crystal or aggregate simply because of various structural imperfections, including edges, vertices, twin boundaries, and heterogeneous inclusions. It might involve only the outer nanometer or so. Current experimental techniques have not demonstrated whether such a hypothetical Si-rich skin exists on untreated natural feldspars, but the absence of an infrared Al-OH stretching band (7) is consistent with the idea. Acid-leached feldspars may have an amorphous silica covering (8), in contrast to a crystallographically continuous termination on natural feldspars subjected to prolonged cycling. Such a proposed structurally continuous termination could be modeled by analogy with atomic positions in H-exchanged feldspar (9). Synchrotron x-ray scattering and electron microscopic techniques need further development to characterize the atomic nature of a feldspar surface from a “normal” interior to the “abnormal” outer surface. If successful, experimental data, including two-dimensional diffraction patterns, could be matched against theoretical atomic positions for an atomically continuous, Si-rich surface modeled from crystal structure data for H-exchanged K, Na-feldspar. Natural feldspars from a range of geographic environments should be sampled in sufficient volume—and curated in a museum repository—to permit evaluation of climatic factors by a range of techniques. Polished granite slabs used in monuments and as ornamental facings of buildings could provide atomic level information that extends the macroscopic observations on the geographic and climatic effects of variations of temperature, humidity, and surface chemistry related to solar radiation, precipitation of rain and snow, and human activities (10).

The hundreds of pertinent papers on the alteration of feldspars are accurately represented by the above reviews, and the following ones illustrate some factors particularly relevant here.

Laboratory Experiments. Papers on laboratory experiments include: synthesis of H-exchanged sanidine (11–12); infrared spectroscopy of H-feldspar (13); polarized infrared spectroscopy

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copy of molecular water in Eifel sanidine (14); various dissolution experiments in the laboratory (15–22); adsorption of protons on adularia (23); adsorption of polyacrylamine (24); interaction of aquated Pb, Cd, and Cu cations with perthite (25); stationary and mobile H defects in K feldspar (26); formation of a nanometer-scale, silica-rich amorphous layer on acid-treated feldspars (27–30); demonstration that a plagioclase/K feldspar mineral isolate from a weathered granodiorite loses silica at the same rate as in the arid Southern California climate after 4 years of comparable leaching in the laboratory (31); and description of de Saussure's (1794–1795) demonstration that mineral weathering was faster when heating was combined with periodic wetting, as for rocks in Nature (32).

Natural Feldspars. Papers on natural feldspars include: crystallographic control on alteration of microcline perthite (33); formation of pits aligned along microcracks and twin planes, enlargement into honeycombs, and major increase in surface area per volume (34–38; forthcoming papers by M. Lee and I. Parsons); slower dissolution of natural than artificially weathered feldspars at comparable pH, etc., and absence of a protective surface layer of common weathering products (35, 39–43); interaction of feldspar minerals in soils with organic species and microbes (44–45); and various geological factors for feldspars in sedimentary rocks (46–48).

The topology of the atomic bonding in the crystal structure of the feldspar family of minerals allows a fascinating range of choices of silanol/aluminol species at the surface, which has been indicated only briefly (6). First, even for a perfect crystal, a mathematical distinction must be made between a flat surface parallel to a crystallographic plane, an edge between two planar faces, and a vertex at the meeting of three or more edges. Second, a face need not be planar, and there can be a mathematical transition to a curved surface, which might be part of an infinite minimal surface. Third, a flat surface can be chosen at any distance from the reference origin of the unit cell. Fourth, there is an infinity of types of dislocations and arrays, which generally become associated with chemical as well as physical perturbations. A reconnaissance has identified likely positions of surfaces that are terminated by silanols and aluminols (6). Very important is the mathematical demonstration that an Si/Al-ordered (Na/K)AlSi₃O₈ feldspar (low albite/microcline) permits choice of a (010) surface that is terminated only by silanols (figure 2 in ref. 6). A large (010) surface of an alkali feldspar with disordered Si/Al must have some aluminol terminations, but small random areas need not. All plagioclase feldspars (NaAlSi₃O₈-CaAl₂Si₂O₈), whether ordered or disordered, must have some aluminols at a large flat surface simply because the Al/Si ratio is greater than one-third, but small areas need not; for higher Al/Si, these silanol-only areas must decrease. The mathematical constraints on the possible Al/Si distribution over a curved surface should be determined. Feldspars with twin boundaries and feldspars with lamellar intergrowths (perthites and antiperthites; peristerite, Bøggild and Huttenlocher intergrowths) and feldspars with inclusions of Fe/Ti oxides (aventurine, etc.) also cannot develop simple boundaries containing only silanols. The actual choice of surface during dissolution will tend to be governed by minimization of the surface energy, which will be related to both the feldspar crystal structure itself and the nature of adsorbed species, including water molecules and ionic and organic species. Continuity of atomic linkages can be maintained in a chemically zoned crystal by perturbations of bond length and angle (1). Current models of silica surfaces are given in reviews (49–52) and recent papers (53–54).

Atomic modeling of feldspar/silica surfaces is needed not only to provide atomic coordinates for the present challenge but also to provide a basis for understanding the apparent crystallographic epitaxy in feldspar-quartz intergrowths (refs. 1, chapter 20, and 55). Does structural atomic continuity across

some feldspar-quartz boundaries control the toughness of granite as a building material, or is it merely a mechanical interlocking of interfingering crystal boundaries? Particularly intriguing is the possibility that a feldspar-quartz interface may be related to the structure of coesite, which has a 4,8-connected net common with feldspar (56). The strong tendency for silica to precipitate as cryptocrystalline aggregates (57–58) and polytypic structures, for it to be strictly amorphous in biological skeletons (59) and for silica to replace feldspar in chert (60–61), provides many challenges to chemical microscopists and atomic modelers.

The ion exchange and catalytic properties of zeolites (62–70) used in industry, as well as those occurring in Nature (71–74), have been investigated thoroughly and are relevant to alkali/hydrogen exchange and alkali/aluminum removal during feldspar weathering. First, all synthetic zeolites display an Si-OH stretching frequency for silanols projecting outwards from the outer surface, whose properties have been characterized experimentally and by energy calculations (75–81). Many synthetic zeolites upon various laboratory treatments including ion exchange and dehydration can end up with Si-OH vibrations corresponding to silanols projecting into small and large cages and channels. Second, Al can be removed or added to the aluminosilicate framework of many zeolites, which recrystallize (epitactically?) into a new continuous framework with the same structural connectivity (82–93). Processes for extraction of Al include: (i) ion exchange with ammonium, heating to expel ammonia, autocatalytic removal of Al, and epitactic reorganization into a more silicic crystal; (ii) chelation with EDTA; (iii) ionic exchange replacement of Na by ions of higher potential and autocatalytic Al removal/epitaxial recrystallization (e.g., the as-synthesized Na-Type Linde Type A zeolite framework loses Al at room temperature upon ion exchange with a 1 M CaCl₂ solution). Third, repeated cycling in industrial reactors of faujasite-bearing catalysts results ultimately in a mixture of almost-pure Si zeolite and degradation products. Natural feldspar surfaces exposed to repeated hot/cold/wet/dry cycles might undergo similar chemical changes to industrial zeolites but with modifications dependent on slower ionic diffusion in the denser feldspar and complications from different chemistry of incoming chemical species.

Fluorine is important for the catalytic weathering of feldspars because it can substitute for hydroxyl (94). Fluorine speeded up alkali diffusion 10,000-fold across a planar interface between albite and adularia at 873–1,073 K and 200 MPa (95). Silica-rich volcanic rhyolites contain F, especially the variant ongonite, which contains the F-bearing mineral topaz (96). Addition of F to starting mixes for synthesis of molecular sieves has yielded new materials, including the silica polymorph silicalite (trade name), which is hydrophobic/organophilic (97). The chemical nature of bonding of F to the feldspar framework needs further study, especially for possible implications for the stability of the outer surface.

Turning to aspects of feldspar weathering that are relevant for human welfare, the physical and chemical properties of feldspar surfaces partly determine the long term stability of granite slabs used as building facings and cemetery markers. The type of feldspar in the chosen granite, the selection of particular blocks from a variable rock face in a quarry, the type of mechanical treatment to prepare a slab, the nature of the heat/cold/wet/dry cycling on site, and the particular exposure to atmospheric gases are recognized as important variables (10). Chemical microscopy of the entire range of architectural and monumental granites is needed to determine the textural features at the weathered surfaces. In addition, the chemical processes developed by industrial chemists for molecular sieve zeolite catalysis might be tested on feldspar surfaces. Even small improvements in longevity of the initial sheen could prove valuable. The huge literature on ceramics and their glazes (including ones containing silica powder) will be con-

sidered elsewhere. Various chemical processes are used to increase resistance to heat and acids and to reduce porosity (98, 99). Silica-rich regions of many ceramics tend toward disordered glass, whose nanometer porosity is negative for many applications. Ideas for deliberate physicochemical modification of ceramic surfaces based on understood processes from industrial zeolite and natural feldspars will be given later. In particular, a chemically silicified feldspar glaze might be even more refractory and strongly resistant to chemical staining than present commercial ceramic pottery, including porcelain. Perhaps the chemical composition of a feldspar-rich monolith for automobile catalytic converters might be tailored to maximize mechanical stability and synergy with the catalytic coatings.

To conclude this overview, the present experimental and observational data on feldspars and zeolites lead to ideas on feldspar weathering that should prove testable with advancing technologies. The abstract and the preceding paragraph covers possible simple applications in agriculture, architecture and monumental masonry, and ceramics. Detailed evaluations and implications for human welfare will be covered in later papers.

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