9. Natural Rust on Stone

9.1. Iron Content of Minerals

The iron content of the earth’s crust averages 5%. At the earth’s surface iron is tied up as green or black ferrous-ferric iron in the ferromagnesian silicates, as the black ferrous-ferric oxide magnetite, as the yellowish ferrous sulphides, pyrite and marcasite; as the grey to dark-brown ferrous carbonate siderite, and as the red or black ferric oxide hematite. The last is not only a common pigment in rock but can also accumulate as our most important iron ore. In humid atmospheres the brown to ochre-brown ferric hydroxide, goethite, is the most important mineral of the common “rust”, alpha-FeOOH. Goethite is usually accompanied by amorphous (not yet crystallized) ferric hydroxide of the same color. Natural rust is summarized as the “mineral” limonite which is not a mineral in the true sense. All the minerals mentioned here tend to adjust to the humid or semi-humid atmospheric surface conditions as they weather to ferric hydroxide or limonite. Metallic iron also changes to rust, mostly amorphous ferric hydroxide with some magnetic brown maghemite, gamma-Fe₂O₃. Crystallization or aging of the non-crystalline ferric hydroxide leads to the formation of submicroscopic goethite. In some rare instances deep orange gamma-FeOOH, lepidocrocite, can form.

The stone industry is much interested in the stability of the iron minerals and minerals containing iron, especially in their rate of oxidation to ferric oxide and ferric hydroxide which may show as undesirable discoloring of existing colors. The minerals and their behaviour are as follows:

9.2. Ferromagnesian Silicates

Biotite, the black mica, loses its ferrous-ferric iron from the silicate lattice at the beginning of the weathering process because the iron is only loosely built into the lattice. Iron almost immediately precipitates as a natural rust halo nearby the biotite flakes. The presence of larger quantities of biotite flakes evenly distributed across the rock substance may spread an almost even ochre cast over the rock. The release of iron from mica is about 500 times greater in distilled water than from other ferromagnesian silicates leached under identical conditions (KELLER, et al. 1963). The presence of exposed black mica appears to be a source for the rapid release of iron.

Hornblende, augite: These minerals include a variable amount of iron, about 7—15%, as black or green ferrous-ferric iron. Weathering of this mineral group also
releases iron, but at a much slower rate than black mica does; it would take several human generations to notice discoloring. The presence of fresh minerals of this group does not appear to threaten discoloring of the surroundings of the mineral grains for at least a century.

9.3. Pyrite, Marcasite

Both iron sulfides, FeS₂, pyrite can occur in almost all types of rocks, whereas marcasite is restricted to sedimentary rocks. Both minerals when exposed to air dissociate and oxidize equally fast to rust, releasing sulfurous or sulfuric acid or both. Surface etching by released sulfuric acid can be frequently observed in marbles and other carbonate rocks. (See photo of marble cross with pyrite-quartz vein Fig. 118 in the chapter on Chemical Weathering.) Greenish tarnish on pyrite is rare under strictly oxidizing conditions, but may show up if an abundance of pyrite is exposed by which the forming rust is reduced again by the pyrite. SINGER and STUMM (1970) summarize the oxidation process of the iron sulfides in respect to the development of acid mine waters which process readily applies to exposed stone surfaces. The basic reactions are as follows:

Stage 1: FeS₂ (solid) plus O₂ goes to Fe²⁺ plus sulfur compound.
Stage 2: Fe²⁺ plus O₂ (aqueous) oxidizes to Fe³⁺.
Stage 3: Fe³⁺ plus H₂O precipitates as FeOOH (solid rust).
Stage 4: Fe³⁺ plus FeS₂ (solid) reduces to Fe²⁺ plus SO₄⁻² (green tarnish on pyrite surface).

Stage 1: The solid ferrous sulfide takes up oxygen as soon as the sulfide is in contact with rainwater and the atmosphere, leading to both ionized ferrous and ferric iron plus the sulfate ion. This process continues as oxidation of the ferrous iron takes place in the next stage.

Stage 2: Oxidation of the ferrous iron (Fe²⁺) takes place from oxygen present in rainwater. But before such oxidation occurs, migration of the ionized Fe³⁺ may occur to a short distance from its source where it then becomes oxidized to the more stable but still-ionized Fe⁵⁺.

Stage 3: Fe³⁺ precipitates, first as amorphous ferric hydroxide (rust). This slowly crystallizes to the microcrystalline ochre-brown mineral goethite, rarely to the deep red-orange mineral lepidocrocite. The solubility of ferric hydroxide in water is extremely small, only about 0.0005 ppm at pH = 5, and still less at pH = 7 (0.000005 ppm). Fig. 134 presents the solubility of ferric hydroxide against the pH of the solvent. The release of sulfuric acid during weathering of pyrite may temporarily lower the pH of the attacking rainwater to near pH = 3, at which acidity the solubility of ferric hydroxide increases rapidly to about 5 ppm, and 550 ppm at a pH of 2; this acidity, however, is not believed to be reached in nature on a stone surface. The rapid dissipation of the iron away from the dissolving pyrite does generally not permit the contact of the precipitated ferric hydroxide with the still unoxidized portions of the pyrite grains. The observed halos up to 3 to 4 inches away from the source material suggest that some iron had to travel despite the practical insolubility of the ferric hydroxide at average rain-