
Reactions of Fe²⁺ and Fe³⁺ with Calcite¹

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¹ Contribution from the Texas Agricultural Experiment Station.

Abstract: Ferrous or ferric perchlorate, 0.01 M, was reacted with calcite in stirred aqueous suspensions which were bubbled vigorously with an oxidizing purge gas. Two and three equivalents of CaCO₃ were dissolved per mole of Fe²⁺ and Fe³⁺ neutralized, respectively. With Fe(ClO₄)₂, the crystalline Fe oxide products partially coated the calcite surface. The dominant products were lepidocrocite and goethite when the purge gas was air or 20% CO₂ (balance air), respectively. After reaction with Fe²⁺ the edges and corners of the calcite crystals were generally rounded and the faces were non-uniformly pitted; however, after reaction with Fe³⁺, a mosaic pattern with distinct ridges and channels was evident on the calcite. These ridges were somewhat pitted, but distinct stepped dislocations were present leading to a featureless and generally flat channel floor. When the calcite was separated from the Fe solution by a semi-permeable membrane, precipitation occurred predominantly on the calcite side and on the Fe side of the membrane in the Fe²⁺ and Fe³⁺ systems, respectively.

Fe oxyhydroxides precipitated from the Fe(ClO₄)₃ and Fe(ClO₄)₂ solutions by different mechanisms. In the Fe(ClO₄)₃ system, although the initial reaction may have been at the calcite surface, the bulk of the poorly crystalline ferrihydrite was formed by hydrolysis of Fe polymers in suspension. Neutralization occurred by the reaction with basic products of a surface-controlled dissolution of calcite, rather than by a direct reaction of acidic polymers with the calcite surface. In the Fe(ClO₄)₂ system, lepidocrocite or goethite formed by the partial hydrolysis of Fe³⁺ or Fe³⁺ by reaction with calcite or the basic products of calcite dissolution and subsequent precipitation of simple Fe species on existing FeOOH nuclei.

Key Words: Calcite • Dissolution • Goethite • Hydrolysis • Iron • Lepidocrocite • Precipitation

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