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CRYSTALLIZATION OF IRON OXIDES ON CALCITE SURFACES IN STATIC SYSTEMS

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Abstract—Iron salts react readily with calcite in oxidizing calcareous environments to produce solid phase Fe-oxides. These reactions represent important processes in aqueous, geologic, and pedogenic environments. In the present investigation, Fe-oxides were precipitated from $Fe(ClO_4)_2$ solutions on undisturbed calcite grains in aqueous suspension. In this way it was possible to investigate the sequence of events in the crystallization process. Following an initial precipitation on the calcite grains, a period of slow growth of lepidocrocite was noted wherein 4-μm euhedral platelets formed with uniform orientation perpendicular to the calcite surface. The slow growth and highly crystalline nature of the Fe-oxide product may be partially due to the diffusion barrier formed by the growing oxide crystal mass which influenced rate of movement of HCO_3^- to the dissolved Fe phase and Fe ions and H^+ towards the calcite surface. Upon continued aging, the supernate became noticeably opaque. As the suspended nuclei settled, new surfaces for crystal growth were provided which resulted in somewhat less crystalline lepidocrocite and goethite.

Key Words—Calcite, Crystallization, Goethite, Iron oxide, Lepidocrocite, Synthesis.

INTRODUCTION

Solution phase Fe^{3+} (or Fe^{2+} in oxidizing environments) reacts readily with $CaCO_3$ to produce solid phase Fe-oxides. These reactions may be considered as simple acid/base reactions (Loeppert and Hossner, 1984) as summarized below:

$$2Fe^{3+} + 3CaCO_3 + 3H_2O \rightarrow 2Fe(OH)_3 + 3Ca^{2+} + 3CO_2,$$

and

$$4Fe^{2+} + O_2 + 4CaCO_3 + 2H_2O \rightarrow 4FeOOH + 4Ca^{2+} + 4CO_2.$$

The precipitation of Fe-oxides in the presence of calcite represents an important soil-forming process and also has implications concerning the availability of Fe to plants in calcareous soils.

The above reactions were previously studied under rapidly stirred and aerated conditions (Loeppert *et al.*, 1984; Loeppert and Hossner, 1984). The mineralogy and crystallinity of the products were influenced by P_{CO_2} and P_{O_2}, as well as by the oxidation state and concentration of solution phase Fe. The rate of reaction under stirred conditions was shown to be dependent on surface area of the $CaCO_3$. Under stirred conditions the reaction was fast, and the poorly crystalline Fe-oxide product was readily abraded from the calcite surface.

The objective of the present study was to investigate the reaction of $Fe(ClO_4)_2$ with calcite under static conditions which would favor a slow rate of reaction and preclude the possibility of mechanical abrasion of Fe-oxide from the calcite surface. In this way it was possible to investigate the sequence of events in the precipitation process.

MATERIALS AND METHODS

Preparation of calcite

Iceland spar calcite was crushed and dry sieved to obtain 20–40-, 100–120-, and 200–270-mesh fractions. Individual size fractions were reacted in aqueous suspension at pH 3.6, using a pH-stat titrator, to dissolve 5% of the crystal mass. This procedure ensured that surface-adsorbed crystallites were removed from the calcite crystals prior to the reaction with Fe salts.

Reactions of Fe^{2+} with calcite under static conditions

Two grams of calcite crystals was placed as a mound at the bottom of a beaker, and 1.0 liter of 0.01 M $Fe(ClO_4)_2$ solution was carefully added so as not to disturb the calcite. The desired purge gas was bubbled at a rate of 10 ml/min into the solution above the calcite in a manner that did not disturb the calcite grains. The pH of the solution above the calcite was monitored by periodically inserting a combination pH electrode. The pH within the calcite mound was monitored by implanting a 4-mm diameter Microelectrode glass electrode within the mound and determining pH relative to a calomel electrode placed in the suspension above the mound at the time of measurement. Redox potentials within and above the mound were similarly determined by placing Pt electrodes in the bulk solution, at the mound surface, and within the mound and measuring potential relative to a calomel electrode placed in the suspension above the mound at the time of measurement.

A related experiment was carried out in which the Fe and calcite phases were placed in Plexiglas chambers separated by a semi-permeable cellulose membrane.

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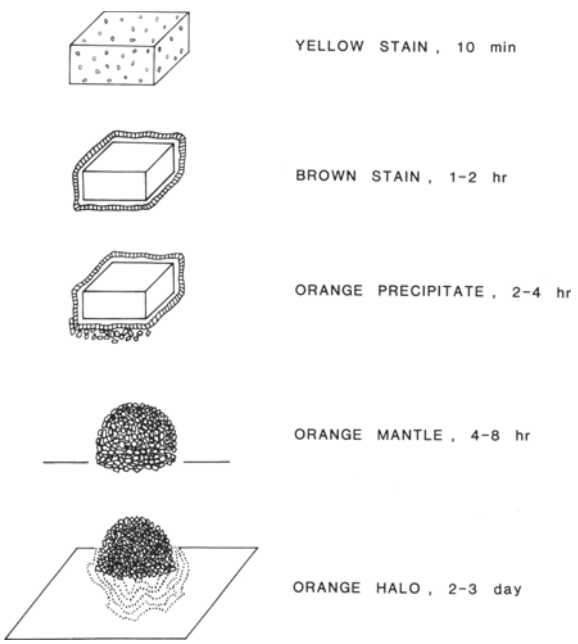


Figure 1. Sequence of precipitation events during reaction of Fe^{2+} with calcite in static aqueous suspension.

Purge gas was bubbled on both sides of the membrane at a rate of 10 ml/min and in a manner that did not disturb the calcite grains.

Analysis of products

The Fe-oxide product was identified by X-ray powder diffraction (XRD) analysis using a Philips diffractometer with CuKα radiation and a graphite crystal monochromator. Crystallinity values are reported as the half-height peak widths of the major diagnostic peaks. Corrections for instrument line broadening were made by subtracting the half-height peak width for the nearest major peak of 5–20-μm size quartz. XRD patterns were obtained using scan speeds of 0.25°2θ/min.

Samples for scanning electron microscopy (SEM) were attached to Al stubs with plastic double-adhesive tape and coated with 200 Å of Au-Pd with a Hummer I sputter coater. Samples were rimmed with carbon conductive paint, and electron micrographs were obtained with a JEOL JSM 25 scanning electron microscope operated at 15 keV.

RESULTS

Visual observations of the precipitation process, following the addition of $Fe(ClO_4)_2$ and with air as the purge gas, provided an indication of the sequence of crystallization events (Figure 1). Initial precipitation in the non-agitated system in both the Plexiglas chamber and in the glass beakers occurred directly on the calcite surface. A yellow stain developed within 30 min on the calcite surface and progressed first to a red stain and then to a well-defined brown precipitate after an additional 2 hr of reaction. With continued precipitation, the Fe-oxide transformed to a dense brown crust on the calcite crystals. During the initial phases of precipitation, the solution was clear; however, following the formation of the dense crust, the suspension became slightly opaque. Suspended Fe-oxides began to settle onto the calcite grains to form an additional mantle. Initially, the flocculated materials were evident as a halo around the encrusted calcite grain. Growth of the mantle was faster in more concentrated Fe^{2+} solution and in more rapidly aerated systems. In the latter systems the increased rate of reaction was due to the increased agitation of the solution surrounding the calcite grains. In no case did the Fe-oxide precipitate on the walls of the glass beaker.

For systems in which the calcite and solution-phase Fe were separated by a semi-permeable membrane, Fe-oxides precipitated predominantly on the calcite side of the membrane with only trace quantities of X-ray-amorphous gel on the Fe side. These results are in agreement with those of Loeppert and Hossner (1984) in which solutions were vigorously agitated on both sides of the membrane.

pH and redox potential

The pH of 0.01 M $Fe(ClO_4)_2$ solutions was ~3.0. After addition of the Fe salt above the calcite grains, the suspension pH increased from 3.0 to pH 4.2–4.8 (Figure 2). The rate of increase during the first 24-hr period was greatest with the smallest calcite particle size. The faster rate may be attributed to the higher surface area of the carbonate phase which resulted in a more rapid neutralization of traces of H^+ and Fe^{3+} in the original Fe^{2+} salt solution (Loeppert *et al.*, 1984). Following this initial increase, the pH remained essentially constant at 4.0–5.0 and then gradually increased to the equilibrium pH of calcite. The pH of the mound interior tended to increase more rapidly to the equilibrium pH of calcite (Figure 2), and following formation of the dense crust, the pH within the mound was controlled largely by the solid phase $CaCO_3$. The pH of the Fe suspension was controlled predominantly by the Fe solution phase until the Fe was completely neutralized at which time the pH of the suspension was also determined by the $CaCO_3$. These results are similar to those obtained in the stirred system (Loeppert *et al.*, 1984), except that in the former system, reaction was completed in hours compared to weeks in the present system. Also, the reaction pH of the Fe solution phase was 4.0–5.0 in the static system compared to 5.0–6.0 in the stirred system, as influenced by rate of release of HCO_3^-.

The redox potentials within the mound and in the supernate dropped to negative millivolt values as the Fe^{2+} salt was added, and in the supernate equilibrated

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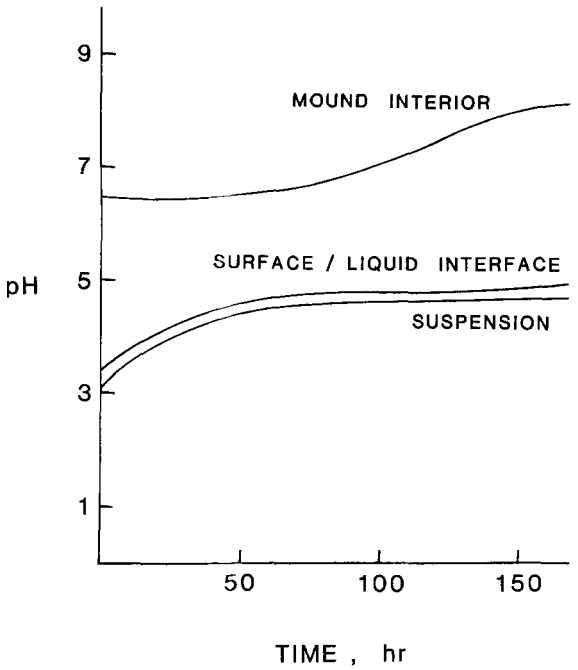


Figure 2. Plot of pH during the reaction of 0.01 M $Fe(ClO_4)_2$ with an excess of calcite.

to a nearly constant value of approximately −200 mV within 20 hr. Therefore, as calculated from the Nernst relation, $\log(Fe^{2+})/(Fe^{3+})$ was maintained at a steady-state level of approximately 16.4 during the bulk of the reaction. These results indicate that the Fe^{3+} that formed from the oxidation of Fe^{2+} was maintained within the system in trace quantities. Presumably, the rate of hydrolysis of Fe^{3+} to $Fe(OH)_3$ was as fast as the rate of oxidation of Fe^{2+} to Fe^{3+}.

Electron microscopy

Cross-sectional views of the Fe-oxide coatings on individual calcite grains revealed that an oxide layer of small crystals was located directly at the calcite surface (Figure 3A and 3B). It is suspected that this layer formed during early stages of the process, inasmuch as indications are that precipitation during later stages of the process likely occurred at the outer surface of the crust. The innermost layer likely resulted from the initial rapid precipitation at the calcite surface. Adjacent to and overlying this initial surface was formed a dense monolayer (crust) of large platy lepidocrocite crystals with an orientation approximately perpendicular to the calcite surface (Figure 3B and 3C). Individual lepidocrocite crystals had regular angular features. Platelets were about 4 μm in length and 0.1 μm in thickness. Above this monolayer, platy crystals with edge-to-edge or edge-to-face orientation were clustered, but not in association with the calcite surface. The individual crystals composing the clusters generally had less well-defined features in comparison to the well-defined platy crystals found in the monolayer, though well-defined lepidocrocite crystals as large as 5 μm (Figure 3D) were locally present. Polymeric materials which had nucleated at a distance from the calcite surface and which had settled in a halo zone around the base of the encrusted calcite grain had subspherical morphology and bore no resemblance to the crystalline platy materials (Figure 3E).

The faces and edges of the calcite grains at the mound surface were etched as were the individual calcite grains on the beaker floor (Figure 3F). Calcite grains that were more centrally located in the mound showed no visible evidence of surface etching; furthermore, no Fe-oxide was observed to have precipitated within the mound interior. The pattern of precipitation indicates that growth occurred principally on existing FeOOH crystal nuclei at the exterior of the mound. Following the initial stages of reaction, neutralization of acidic species most likely occurred via reaction with carbonate species or OH^- in solution rather than directly with the solid phase $CaCO_3$.

X-ray powder diffraction

XRD analysis showed that the crust formed on the calcite surface contained both well-crystalline lepidocrocite and less-crystalline goethite (Figure 4). In all experiments, lepidocrocite was the dominant phase, even in systems in which 20% CO_2 (balance air) was used as the purge gas. These results are in contrast to those obtained in stirred systems with 20% CO_2 as the purge gas in which goethite was the dominant product phase (Loeppert *et al.*, 1984). Apparently, the CO_2 did not influence the aerated $Fe(ClO_4)_2$/calcite suspensions to form goethite under conditions of slow crystal growth.

The peaks attributed to the trace quantities of goethite indicate that the goethite was more poorly crystalline and/or of smaller particle size than the lepidocrocite. XRD data (Table 1) support the visual observation that the lepidocrocite comprising the crust was more crystalline than that comprising the mantle or suspended sediment. The corrected half-height peak widths of the 120 reflection of lepidocrocite for crust, mantle, and suspension materials were 0.15, 0.23, and 1.43°2θ, respectively. In all materials, the half-height peak widths of the 020 reflections were broader than those of the 200 reflections of lepidocrocite. For example, the corrected peak widths of the suspended sediment were 2.83 and 1.38°2θ for the 020 and 200 reflections, respectively. These results may be partly attributed to a smaller size in the crystalline *b*-dimension (Schwertmann and Taylor, 1979), but may also be due to crystal disorder in the *b* dimension. Schwertmann and Taylor concluded from high-resolution transmission electron microscopy (HRTEM) that XRD line broadening of the 020 reflection of several poorly

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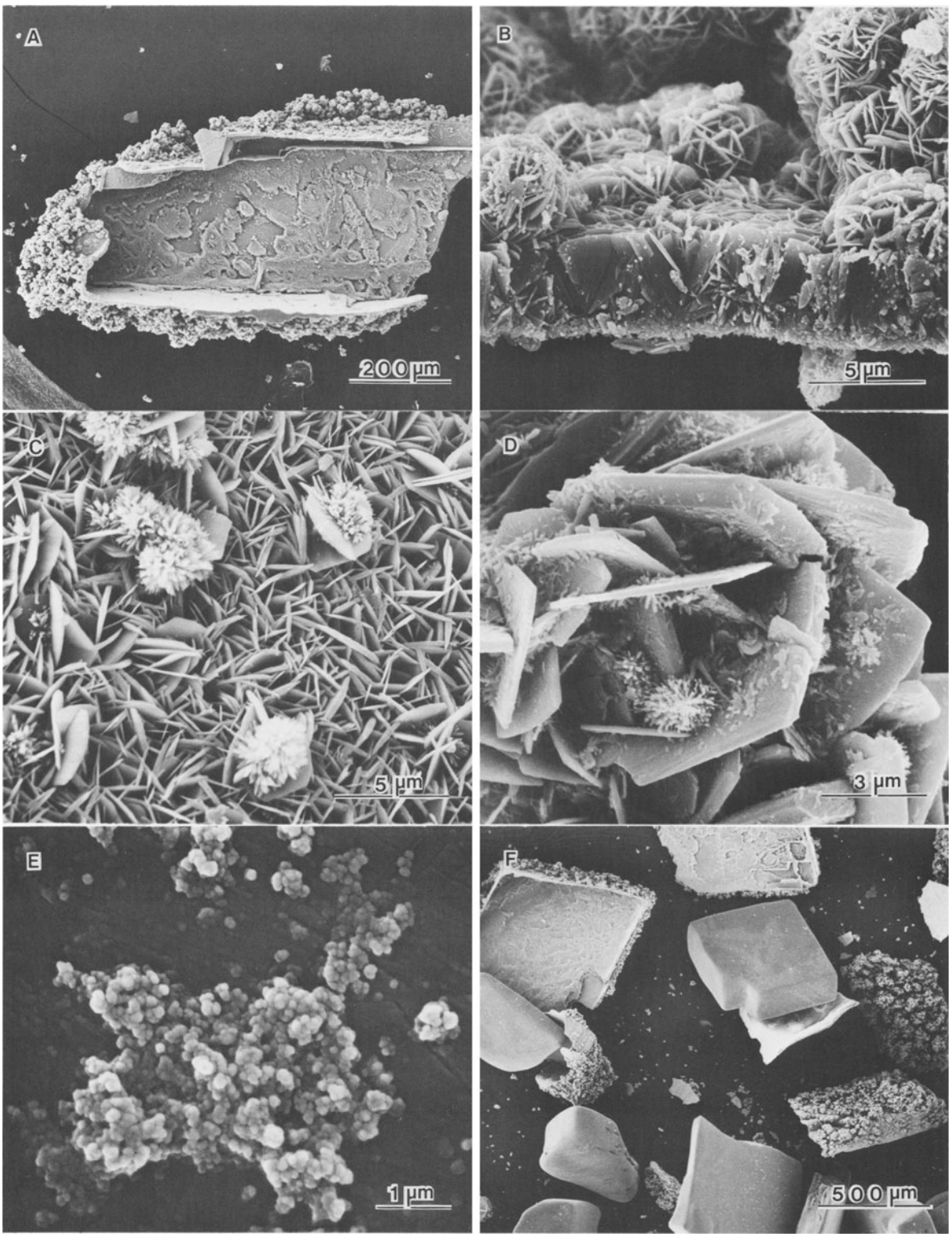


Figure 3. Scanning electron micrographs of lepidocrocite precipitated on calcite surfaces during the reaction of 0.01 M $Fe(ClO_4)_2$ in static aqueous suspension.

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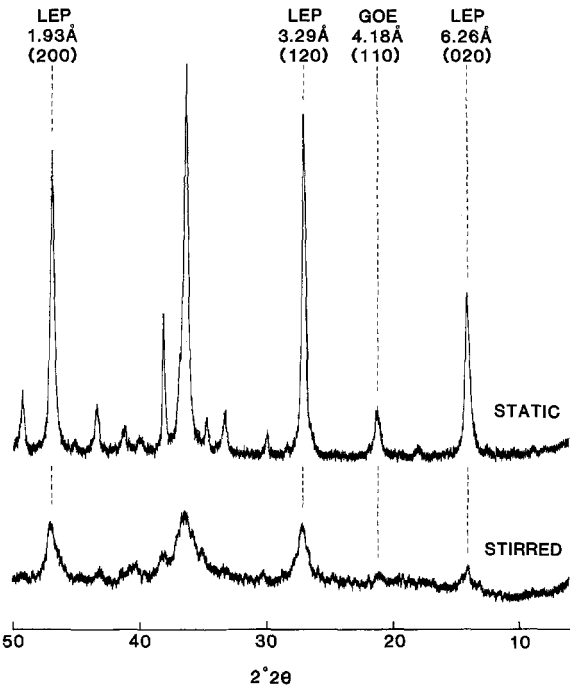


Figure 4. X-ray powder diffractograms (CuKα radiation) for lepidocrocite precipitated in static and stirred calcite suspensions from 0.01 M $Fe(ClO_4)_2$. Goe = goethite, Lep = lepidocrocite.

crystallized lepidocrocite samples was due to small size along the *b*-dimension of coherently scattering crystals.

Because in this study even the well-crystallized lepidocrocite with crystal widths in the *b*-dimension approaching 0.5 μm (Figure 4) showed wider 020 than 200 diffraction peaks, the possibility that crystal disorder influenced the differential band broadening cannot be dismissed. The d-spacing of the 020 reflection of lepidocrocite obtained from suspension was 6.55 Å compared to 6.26 Å for the well-crystalline crust (Table 1). Schwertmann and Taylor (1979) concluded from HRTEM micrographs, which showed no substantial variation in interlayer distance along the *b*-dimension, that the higher spacings were *not* likely due to intercalation of H_2O between the rows of FeOOH octahedra. They instead suggested that the larger spacings may have been due to reduced strength of H-bonds between the adjacent layers of the lepidocrocite structure in very thin crystals. Yet, in the current study the possibility exists that the higher spacings of the 020 reflection of poorly crystalline lepidocrocite may be at least partially due to incomplete dehydration of structural Fe and/or occlusion of CO_2.

The lepidocrocite prepared under non-stirred conditions in the presence of $CaCO_3$ in this experiment is more crystalline than the natural lepidocrocite obtained from a South African hydromorphic soil (Schwertmann and Taylor, 1979) or that observed in a well-drained calcareous soil (Ross and Wang, 1982); moreover, it is considerably more crystalline than the lepidocrocite synthesized in stirred systems (Loeppert *et al.*, 1984). The high degree of crystallinity is likely due to the slow rates of crystal formation, low Fe redox potential, slow release of HCO_3^-, and the absence of impurities (e.g., SiO_3^-) which may influence product crystallinity.

DISCUSSION

The overall reaction of solution phase Fe^{2+} with calcite in the static system occurred in several distinct steps. An initial precipitation of Fe-oxide on the calcite grains was followed by a period of slow crystal growth. The slow growth may be attributed to a diffusion barrier formed by the growing Fe-oxide crystal mass, which influenced the rate of movement of CO_3^{2-} or HCO_3^- to the dissolved Fe phase, and Fe^{3+} and H^+ towards the calcite surface. The barrier had the effect of reducing the pH in the Fe solution and increasing the pH

Table 1. Corrected half-height peak widths from X-ray diffraction patterns of selected samples of natural and synthetic lepidocrocite.

Preparation procedure	Peak position (°2θ)	Corrected half-height peak width (°2θ)		
	(020)	(020)	(120)	(200)
Reaction of 0.01 M $Fe(ClO_4)_2$ with non-agitated 20–40-mesh calcite				
Suspension	6.55	2.83	1.43	1.38
Mantle	6.27	0.45	0.23	0.21
Crust	6.26	0.27	0.15	0.16
Agitation of 0.01 M $Fe(ClO_4)_2$ with 200–270-mesh calcite while bubbling with air (Loeppert *et al.*, 1984)	6.32	1.8	1.0	0.9
Oxidation of 0.01 M $FeCl_2$ at pH 6.0, PT 63 (Schwertmann and Taylor, 1979)	6.31	2.8	1.5	1.1
Natural lepidocrocite from hydromorphic soil, SA59 (Schwertmann and Taylor, 1979)	6.27	0.55	0.55	0.50

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within the mound as diffusion of reactants was retarded. The decreased pH in the solution phase resulted in a reduced rate of oxidation of Fe^{2+} and reduced rate of crystal formation. As a consequence, this decreased rate of reaction resulted in a more crystalline Fe-oxide product which is especially evident in comparison of the half-height peak widths of products formed in stirred systems and static systems. The rate of release of soluble base probably decreased as the Fe-oxide coating matured, because the oxide barrier likely served as both a barrier to diffusion and to the agitation of the bulk solution caused by bubbling of the purge gas. Yet, in spite of the presence of the oxide barrier, soluble base continued to diffuse into the Fe solution as was evidenced by the continued precipitation of Fe-oxide.

With time, the solution became noticeably opaque, and the suspended nuclei settled onto the crystal mass and beaker bottom. These nuclei provided new surfaces for crystal growth which resulted in tufts of mantle material. In the presence of excess $CaCO_3$ and an oxidizing environment, the Fe^{2+} was eventually completely oxidized, and the Fe^{3+} was completely hydrolyzed.

The mechanism of precipitation of Fe from solution onto a calcite surface may be compared to the precipitation of ferrihydrite, lepidocrocite, and/or goethite from the mixture of aqueous solutions of Fe^{2+} and KOH (e.g., Atkinson *et al.,* 1968). The rate of precipitation is controlled by the rate of oxidation of Fe^{2+}, which is influenced by pH, rate of aeration, and concentration of Fe^{2+}. With 20–40-mesh calcite, the rate of release of HCO_3^- was sufficiently slow to favor low suspension pH and to promote the slow growth of lepidocrocite. The potential exists for the synthesis of even larger lepidocrocite crystals on calcite grains if the rate of precipitation can be controlled carefully at an even slower rate.

The reactions discussed in this paper have implications to soil pedogenic processes and certain soil-management situations. For example, in acid mine spoils in which the acidity is derived from pyritic materials, neutralization may be achieved by addition of limestone. The results of these experiments suggest that the neutralization efficiency of applied calcite may be reduced but not completely inhibited due to the formation of Fe-oxide coatings on calcite particles.

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Резюме—Соли железа охотно реагируют с кальцитом в окисляющих известковых средах с образованием твердых фаз Fe-окисей. Эти реакции представляют важные процессы в водных, геологических и почвообразовательных средах. В настоящей работе Fe-окиси осаждались из растворов $Fe(ClO_4)_2$ на невозмущенных зернах кальцита в водных суспензиях. Таким образом, было возможно изучать порядок явлений в процессе кристаллизации. После первоначального осаждения на кальцитовых зернах наблюдался период медленного роста лепидокрокита с образованием 4-μм идиоморфных пластинок с однородной ориентацией перпендикулярной к поверхности кальцита. Медленный рост и высококристаллическая природа продукта Fe-окиси частично могут быть вызваны диффузным барьером, образованным растущей массой кристаллов окисей, что влияет на скорость движения HCO_3^- к растворенной фазе Fe, а также ионов Fe и H^+ по направлению к поверхности кальцита. С продолжающимся старением поверхность раствора становится заметно непрозрачной. По мере того, как взвешенные зародыши оседали, новые поверхности были обеспечены для кристаллического роста, что в результате давало менее кристалические лепидокрокит и гетит. [E.G.]

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Resümee—Eisensalze reagieren sehr leicht mit Calcit in oxidierenden kalkhaltigen Milieus unter der Bildung fester Eisenoxide. Diese Reaktionen stellen wichtige Prozesse in wässrigen geologischen und bodenbildenden Bildungsmilieus dar. In dieser Untersuchung wurden Eisenoxide aus $Fe(ClO_4)_2$-Lösungen auf ungestörten Kristallkörnern in wässriger Suspension ausgefällt. Auf diese Art war es möglich, die Abfolge der einzelnen Akte des Kristallisationsprozesses zu untersuchen. Anschließend an die ursprüngliche Ausfällung auf die Calcitkörner wurde eine Periode des langsamen Wachstums von Lepidokrokit beobachtet, wobei 4 μm große idiomorphe Blättchen gebildet wurden, die eine einheitliche Orientierung senkrecht zur Calcitoberfläche aufwiesen. Das langsame Wachstum und die gute Kristallinität des Eisenoxid-Produktes kann z.T. durch die Diffusionsbarriere verursacht werden, die durch die wachsende Oxidkristallmasse gebildet wurde, die die Bewegungsgeschwindigkeit von HCO_3^- zu der gelösten Fe-Phase sowie die der Fe-Ionen and H^+-Ionen in Richtung auf die Calcitoberfläche beeinflußte. Nach fortgesetzter Alterung wurde der Überstand merklich opak. Wenn sich die suspendierten Keime abgesetzt hatten, dann war eine neue Oberfläche für ein Kristallwachstum vorhanden, worauf sich ein etwas weniger gut kristallisierter Lepidokrokit und Goethit bildete. [U.W.]

Résumé—Des sels de fer réagissent aisément avec la calcite dans des environements calcareux oxidants pour produire des oxides-Fe à phase solide. Ces réactions représentent des procédés importants dans des environements aqueux, géologiques et pédogéniques. Dans l'investigation présente, les oxides-Fe ont été précipités de solutions $Fe(ClO_4)$ sur des grains de calcite non-dérangés dans une suspension aqueuse. De cette façon, on a pu investiguer la séquence d'évenements dans le procédé de cristallisation. Suivant une précipitation initiale sur les grains de calcite, une période de croissance lente de lépidocrocite a été notée dans laquelle des plaquettes euhédrales 4 μm se sont formées avec une orientation uniforme perpendiculaire à la surface calcite. La croissance lente et la nature fortement cristalline du produit oxide-Fe peuvent être partiellement dues à la barrière de diffusion formée par la masse de cristal oxide croissante qui a influencé la vitesse de mouvement de HCO_3^- à la phase Fe dissout et des ions Fe et H^+ vers la surface calcite. Lors d'un vieillissement continué, le supernate est devenu remarquablement opaque. La déposition des noyaux suspendus a produit de nouvelles surfaces pour la croissance de cristaux, ce qui a resulté en de la lépidocrocite et de la goethite quelque peu moins cristallines. [D.J.]

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