Clays and Clay Minerals, Vol. 30, No. 5, 337–340, 1982.

INFLUENCE OF RELATIVE HUMIDITY ON THE CRYSTALLIZATION OF Fe(III) OXIDES FROM FERRIHYDRITE

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Abstract—Ferrihydrite prepared in different manners was kept under relative humidities ranging from 75 to 100% and at temperatures of 45° and 55°C for 180 days. Ferrihydrite transformed to hematite and goethite at relative humidities close to 100%, but at lower relative humidities the transformation was less pronounced and hematite was highly favored over goethite. Increasing temperature also favored hematite over goethite, and Al substitution completely prevented goethite formation. These results suggest that hematite can form in relatively dry, warm soils or sediments, although more slowly than in moister environments.

Key Words—Ferrihydrite, Goethite, Hematite, Iron oxides, Relative humidity, Synthesis.

INTRODUCTION

Hematite is common, and generally more abundant than goethite in soils of warm and temperate areas where the relative humidity (RH) is markedly lower than 100% for prolonged periods (e.g., the soils of warm deserts and Mediterranean areas (Duchaufour, 1977)). Synthesis from aqueous suspensions in which the activity of water is nearly equal to one have shown that hematite forms from ferrihydrite, which appears to be its necessary precursor (Fischer and Schwertmann, 1975) and that goethite can also form from ferrihydrite via solution (Schwertmann and Fischer, 1966; Knight and Sylva, 1974). However, there is no evidence for the formation of hematite or goethite from ferrihydrite that has been dried and stored under the usual relative humidities and temperatures found in the laboratory. Consequently it is of interest to know whether the transformation of ferrihydrite can take place at higher RHs, such as those found in soils, and, if so, what are the final products. This paper answers these questions on the basis of experiments with synthetic ferrihydrite kept at different RHs and at nearly pedogenic temperatures, thereby attempting to explain in part the common presence of hematite in such soils.

MATERIALS AND METHODS

Pure ferrihydrite (100 mmoles Fe in a final volume of 1 liter) was precipitated from 0.1 M $Fe(NO_3)_3$ solutions and aluminous (2 mole % Al) ferrihydrite from 0.1 M $Fe(NO_3)_3$ + $Al(NO_3)_3$ solutions using either 10% NH_3 or 3 M KOH for the precipitation. All chemicals were Merck Analytical Grade; the same batch was used for all preparations. Precipitation was accomplished while stirring the solution vigorously until a final pH of 7 was reached. This process took approximately 10 min. The pH was readjusted to 7, if necessary, after stirring the suspension for an additional period of 15 min. The ferrihydrite products were then either dialyzed against deionized water for 40 days or rapidly washed (3–5 hr) with deionized water by successive centrifugations and decantations until dispersed. The final pH was found to be 6.5–7 and it was not further adjusted. Table 1 summarizes all preparations.

After dialysis or washing, the ferrihydrite products were freeze-dried from suspensions having about 100 mmoles Fe in 200 ml. The resulting granular, brittle product was ground to a fine powder and placed in humidity chambers in which saturated solutions of KH_2PO_4, $BaCl_2$, KCl, and NaCl kept a constant RH (O'Brien, 1948; Young, 1967). These solutions covered a range of about 75–93% RH. Additional subsamples were placed in pure water. The experiments were carried out at 45° and 55°C, and samples were taken out periodically for analysis.

The amount of hematite or goethite formed was determined quantitatively by X-ray powder diffraction using CoKα radiation in a Philips instrument. Self-supporting mounts were prepared by back-filling about 200 mg of sample into aluminum frames and then pressing the material against filter paper to minimize orientation. The amount of hematite or goethite formed was determined by comparison with external standards that were prepared by mixing known amounts of ferrihydrite, hematite, and goethite having peak widths similar to those of samples being studied. The 110 and 111 reflections of goethite and the 102 and 110 reflections of hematite were used for comparison.

RESULTS AND DISCUSSION

Effect of relative humidity

Figures 1 through 4 show the effect of RH on the transformation of ferrihydrites after 180 days and at temperatures of 45° and 55°C. The crystalline final products were either hematite or a mixture of hematite

Table 1. Summary of ferrihydrite preparations.

Sample	Precipitated with: NH$_3$	KOH	Salts eliminated by: Washing	Dialysis	2 mole % Al: Yes	No
ND	×			×		×
NDA	×			×	×	
KD		×		×		×
KDA		×		×	×	
NW	×		×			×
NWA	×		×		×	
KW		×	×			×
KWA		×	×		×	

and goethite. In all products the total amount of hematite + goethite that formed increased with RH, indicating that water plays a role in the transformation. Pure ferrihydrites yielded goethite plus hematite when stored in liquid water at either 45° or 55°C. Samples KD, NW, and KW yielded only traces or no goethite when stored at ≤93% RH. Therefore, lowering the water activity favored hematite over goethite. Because the water activity must control the dissolution of ferrihydrite, the former results support the idea of Feitknecht and Michaelis (1962), Schwertmann and Fischer (1966), and Fischer and Schwertmann (1975) that goethite forms by the dissolution of ferrihydrite and subsequent crystallization from solution, whereas, in a competitive reaction, hematite forms within the ferrihydrite aggregates and does not require an external solution phase.

Sample ND yielded similar amounts of goethite at all RHs (about 15% of the original ferrihydrite for 55°C and 10% for 45°C). The crystallinity of this goethite was very poor (width at ½ height was 1.2°2θ for the 110 reflection) and it probably formed because incipient goethite crystals were already produced during the initial sample dialysis. Traces of poorly crystalline goethite were also detected in the other dialyzed sample (KD).

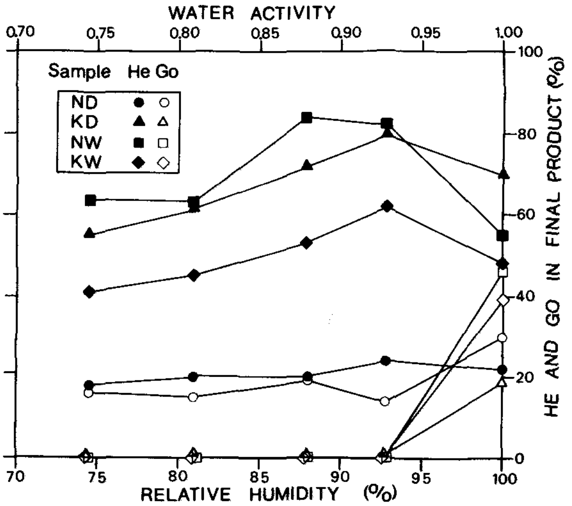

Figure 1. Effect of RH on the crystallization of hematite (He) and goethite (Go) from pure ferrihydrite kept at 55°C for 180 days.

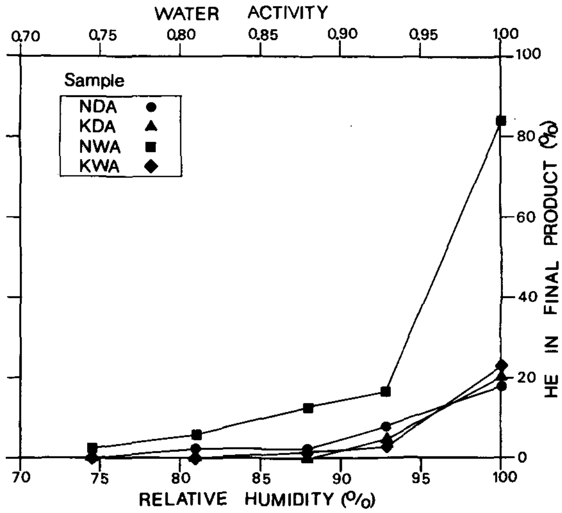

Figure 2. Effect of RH on the crystallization of hematite (He) from aluminous ferrihydrite kept at 55°C for 180 days. No goethite formed in this experiment.

No precise quantitative relationships can be established between RH and amount of goethite + hematite because the degree and type of transformation is influenced by other factors discussed below.

Effect of Al substitution

Al-containing ferrihydrite yielded, at all RHs, and after 180 days, a smaller amount of crystalline products than the corresponding Al-free ferrihydrite (cf. Figure 1 with Figure 2; Figure 3 with Figure 4). The retarding effect of Al on the crystallization of ferrihydrite is known for aqueous suspensions (Wolska, 1976; Schwertmann *et al.*, 1979) and, in the present experiments, this effect increased with decreasing RH. At 75% RH substantial amounts of hematite were formed from pure ferrihydrite, but negligible amounts or no hematite formed from aluminous ferrihydrite. Thus, both low RH and Al substitution delay the transformation of ferrihydrite to hematite.

Al completely inhibited goethite formation at all RHs, which is in agreement with the experiments of Gastuche *et al.* (1964), Wolska (1977), and Schwertmann *et al.* (1979).

Effect of temperature

The degree of transformation was always higher at 55° than at 45°C (Figure 5). The slope of the regression line of the amount of hematite formed at 55°C vs. the amount of hematite formed at 45°C is much larger than the slope of the regression line of the amount of goethite formed at 55°C vs. the amount of goethite formed at

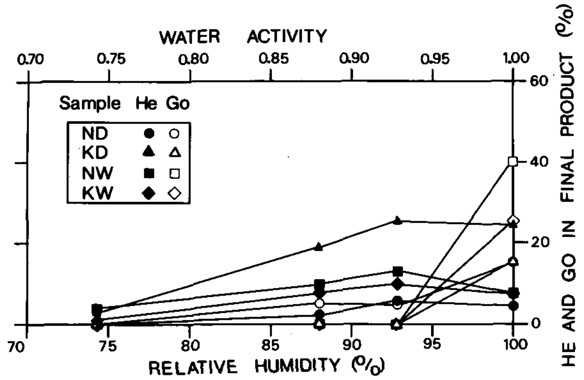

Figure 3. Effect of RH on the crystallization of hematite (He) and goethite (Go) from pure ferrihydrite kept at 45°C for 180 days.

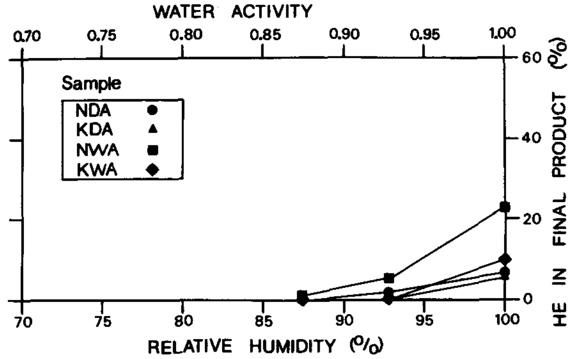

Figure 4. Effect of RH on the crystallization of hematite (He) from aluminous ferrihydrite kept at 45°C for 180 days. No goethite formed in this experiment.

45°C (2.91 vs. 0.99). Thus, increasing temperature appears to favor hematite over goethite in accordance with previous findings (Schwertmann and Fischer, 1966; Lewis and Schwertmann, 1979).

From the above results, the formation of hematite is very slow at lower, pedogenic temparatures. In another experiment, not reported here, hematite crystallizes at a RH above 88% from a ferrihydrite prepared in the same manner as sample NWA and kept at 28°C. For that sample one year of ageing was necessary before hematite could be detected by X-ray powder diffraction.

Effect of pretreatment

Precipitation by NH_3 vs. KOH or washing vs. dialyzing did not affect the crystallization of hematite and goethite from ferrihydrite. However, one of the dialyzed samples (ND) yielded much more goethite at a RH below 100% than its washed counterpart; under liquid water, the washed samples always yielded more goethite than the dialyzed samples.

It is likely that factors that are difficult to control or measure (e.g., ion adsorption, small pH changes, speed of preparation, speed of freeze drying) obscure the effect of pretreatment; thus, no definite conclusions can be drawn from the present results.

CONCLUSIONS

Ferrihydrite can transform to hematite and goethite at RH near 100%. At lower RH, the transformation is less complete and hematite is highly favored over goethite. Increasing temperature favors hematite formation, and Al-substitution prevents goethite formation altogether.

The results support the ideas of Schwertmann and Fischer (1966) and Fischer and Schwertmann (1975) that goethite forms from small entities in solution (preferable $Fe(OH)_2^+$ ions) (Knight and Sylva, 1974) supplied by the ferrihydrite whereas, in a competitive reaction, hematite crystallizes within the ferrihydrite aggregates by internal rearrangement and dehydration. Considerable goethite was formed at 100% vs. ≤93% RH because a liquid phase containing monomers was available. At 100% RH more goethite was formed after quick washing than after long dialysis. This difference can be explained by a higher concentration of monomers after washing than after dialysis. The complete removal of monomers from a hydrolyzed solution of $Fe(NO_3)_3$ inhibited goethite formation as compared to the presence of monomers (D. G. Lewis, Department of Soil Science, University of Adelaide, Adelaide 5064, Australia; unpublished results).

The results also illuminate the mechanism of hematite formation from ferrihydrite. It is obvious that some water is necessary for hematite to form within the fer-

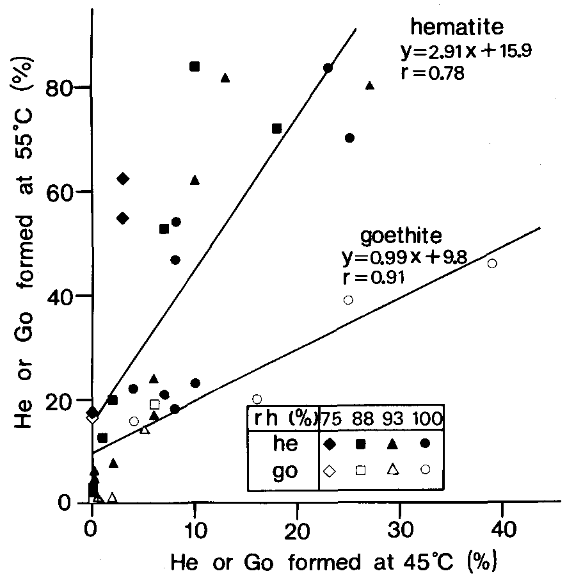

Figure 5. Percent hematite and goethite formed at 55°C vs. percent formed at 45°C.

rihydrite aggregate because the rate of hematite formation increased with increasing RH. Presumably the presence of water facilitated dehydration by proton transfer (tunneling) between OH groups.

Although the results obtained here cannot be applied to natural environments *in toto,* it is likely that ferrihydrite transforms into hematite in relatively dry and warm soils and sediments, such as the soils of the Mediterranean region during the summer season.

ACKNOWLEDGMENT

The authors are indebted to Prof. U. Schwertmann who reviewed the manuscript and provided many valuable comments.

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(Received 7 October 1981; accepted 24 December 1981)

Резюме—Железный-гидрит, подготовленный разными методами, содержался в течение 180 дней в условиях относительной влажности от 75 до 100% и температуры от 45 до 55°C. Железный гидрит превращался в гематит и гетит при относительных вгажностях близких 100%, но при меньших величинах относительной влажности эта перемена происходила в меньшей степени с большим количеством гематита по сравнению с гетитом. Рост температуры также увеличивал количество гематита, а подстановка Al полностью предотвращала формирование гетита. Эти результаты указывают на то, что гематит может формироваться в относительно сухих, теплых почвах или осадках, хотя это происходит медленнее, чем во влажных средах. [E.C.]

Resümee—Ferrihydrit, das auf verschiedene Arten hergestellt wurde, wurde relativen Feuchtigkeiten von 75–100% bei Temperaturen von 45° und 55°C für 180 Tage ausgesetzt. Ferrihydrit wandelte sich bei relativen Feuchtigkeiten nahe 100% in Haematit und Goethit um. Bei niedrigerer relativer Feuchtigkeit war die Umwandlung jedoch schwächer, und es bildete sich wesentlich mehr Haematit als Goethit. Eine Temperaturzunahme begünstigte ebenfalls die Haematitbildung im Vergleich zu der von Goethit. Eine Al-Substitution verhinderte die Bildung von Goethit vollständig. Diese Ergebnisse deuten darauf hin, daß sich Haematit in relativ trockenen, warmen Böden oder Sedimenten bilden kann, allerdings langsamer als unter Feuchten Bedingungen. [U.W.]

Résumé—De la ferrihydtrite preparée de manières différentes a été conservée à des humidités relatives s'étageant entre 75 à 100% et à des températures de 45° et 55°C pendant 180 jours. La ferrihydrite s'est transformée en hématite et en goethite à des humidités relatives près de 100%, mais à des humidités relatives plus basses, la transformation était moins prononcée et la formation d'hématite était fortement favorisée par rapport à celle de goethite. Une température croissante a aussi favorisé la formation d'hematite par rapport à la goethite, et la substitution d'Al a complètement empêché la formation de goethite. Ces résultats suggèrent que l'hématite peut être formée dans des sols ou des sediments relativement chauds et secs, quoique de manière plus lente que dans des environements plus humides. [D.J.]