THE INFLUENCE OF SILICATE ON THE TRANSFORMATION OF LEPIDOCROCITE TO GOETHITE

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Abstract—The mechanism of the transformation of lepidocrocite (γFeOOH) to goethite (αFeOOH) has previously been established and the effect of silicate on the transformation was investigated. Rather than completely inhibiting the reaction, as had been suggested, the presence of Si was found to merely retard the nucleation stage of the transformation. There was found to be no decrease in the dissolution rate of the lepidocrocite due to surface adsorption of Si.

Si has no effect if introduced after the nucleation stage, and under conditions of pH and temperature where the dissolution rate of the lepidocrocite largely determines the rate of transformation, the presence of Si has a reduced effect. The results show that Si is adsorbed and incorporated into the goethite structure, and due to its retarding effect on the nucleation, larger crystals of goethite are formed, many of which are twinned.

It is inferred from the results that the apparent stability of lepidocrocite occurring in soils in association with goethite cannot be attributed solely to the presence of Si in the soil system.

INTRODUCTION

In an earlier paper (Schwertmann and Taylor, 1972) the mechanism and kinetics of the transformation of lepidocrocite (γFeOOH) to its more stable polymorph, goethite (αFeOOH) have been described. It was concluded that this transformation consists of a dissolution of the lepidocrocite, a nucleation of goethite from the resultant Fe in solution and the crystalline growth of these nuclei. Any one of these three steps can be rate determining, depending on the conditions under which the transformation is being conducted.

Since lepidocrocite, although less stable than goethite, exists in soils and sediments for long periods of time it is thought that soil constituents might be capable of retarding or even inhibiting the transformation. In this connection the observation of Hiller (1966) is interesting that the transformation of lepidocricite to goethite "can be completely inhibited by traces of silicate, aluminate and stannate". In our first paper (Schwertmann and Taylor, 1972) a similar observation has been mentioned. The following experiments were conducted to elucidate the influence of silicate on the various phases of the transformation.

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MATERIALS AND METHODS

Synthetic lepidocrocites used in these experiments were prepared by bubbling O_2 through an aqueous solution of $FeCl_2$ at approximately pH7. The conversions to goethite were carried out in stoppered polyethylene bottles in high concentrations (0·1 and 1·0 M) KOH.

The conversion with time was followed by determining the relative amounts of goethite and lepidocrocite by quantitative X-ray diffractometry using the (120) lepidocrocite peak and the (130) goethite peak. CoK_α radiation was used. Si in solution was determined photometrically by the molybdenum blue method (Boltz and Mellon, 1947) and iron colorimetrically as the *o*-phenanthroline complex (Asami and Kumada, 1960). For both these determinations an aliquot of the strongly alkaline solution was firstly neutralised. (For further details of these methods see Schwertmann and Taylor, 1972).

RESULTS AND DISCUSSION

Si influence on conversion rate

Figure 1 shows that at 80°C and in M KOH the presence of Si in solution considerably retards the conversion of a well crystalline lepidocrocite (surface area 58 m²/g) to goethite, the retardation increasing with increasing Si concentration in the initial solution. However, the mechanics of the conversion appear to be the same as evidenced by the similar shape of the conversion-time curves.
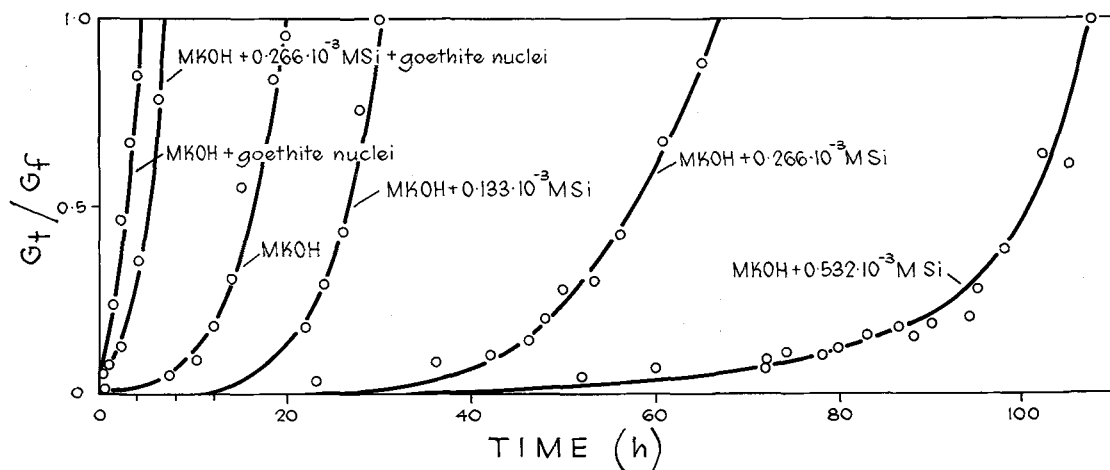
Fig. 1. Variations in the transformation–time curves for the conversion of lepidocrocite to goethite in M KOH at 80°C with variations in Si solution concentrations and the presence of goethite nuclei. The solid lines were drawn from the best linear fits of $\ln (G_t/G_f) = kt + c$.

The rate of conversion increases with time throughout the whole process and a plot of $\ln G_t/G_f$ vs. time yields a linear relationship, where G_t is the concentration of goethite formed at time t, and G_f is the final concentration of goethite after complete conversion. This indicates the autocatalytic nature of the reaction although a decrease in conversion rate towards the end of the reaction due to consumption of lepidocrocite as expected from an autocatalytic reaction could not be detected. An interpretation of this observation was given elsewhere (Schwertmann and Taylor, 1972).

Table 1 contains the correlation coefficients for the linear relationships and also indicates that the half conversion time (HCT), where $G_t/G_f = 0.5$, increases almost linearly with the Si concentration of the original solution. The retardation is clearly reflected in a slower overall apparent conversion rate, k, where $\ln G_t/G_f = kt + c$. These k values are also seen to decrease with increasing Si concentration. The interpretation of the intercept of this linear relationship is doubtful (see Schwertmann and Taylor, 1972). It may or may not indicate a certain amount of goethite (G_0) at time zero. The average value of G_0/G_f for unseeded systems is extremely low (0.00032) and therefore, analytically not different from zero. Also, it is believed that goethite nucleation is possible without seeding the system with goethite. The linear relationship found is therefore only valid after a certain minimum amount of goethite was formed or in seeded systems. Here the average value of G_0/G_f as deter-

Table 1. Parameters of the conversion of lepidocrocite (~ 60 m²/g) in M KOH at various Si concentrations and with and without seeding*

Si-conc. (M × 10³)	Seeded	Temp. (°C)	HCT (hr)	k_a† min⁻¹ × 10³	$\log G_t/G_f$ $= kt + \log G_0/G_f$ (t in hr)	r
0		80	16.2	4.06	0.106t–2.02	0.982
0.133		80	28	3.48	0.916t–2.74	0.990
0.266		80	58	1.26	0.0328t–2.29	0.975
0.532		80	102	0.95	0.0248t–2.91	0.965
0	*	80	2.4	10.8	0.280t–0.973	0.993
0.266	*	80	4.9	7.6	0.198t–1.28	0.998
0.0266		40	170	0.32	0.00834t–1.72	0.988
0.266		40	770	?	?	?

*Seeded with 6·8% goethite.
†$\ln G_t/G_f = k_G t + c$.

mined from the linear relation, was 0·075 which is reasonably close to the actual value of 0·068.

A linear relationship between the HCT and the initial Si concentration also exists in the conversion of poorly crystalline lepidocrocites, providing the conversion is carried out at low temperatures, e.g. 20°C. In a solution M in KOH and $0·332 \times 10^{-3}$ M in Si a lepidocrocite with a surface area of 152 m²/g gave a HCT of 520 hr, whereas the same sample in the absence of Si had a HCT of only 190 hr. A similar observation was made for another poorly crystalline lepidocrocite, (135 m²/g) where the HCT times were 275, 480 and 950 hr for Si concentrations of 0, $0·123 \times 10^{-3}$ and $0·246 \times 10^{-3}$ M, respectively.

The difference in overall conversion rate between a system with and without Si for the same poorly crystalline lepidocrocites is much less or even non existent if the conversion is carried out at 80°C. Under these conditions the conversion is extremely rapid due to very high supersaturation of Fe in solution with regard to goethite there-by minimizing the possibility of Si interference. Moreover, at this temperature these poorly crystalline samples give rise to haematite as well as goethite, greater amounts being formed in the presence of Si that in its absence. Like oxalate (Schwertmann, 1969/70), silicate seems to inhibit the via solution formation of goethite to a certain extent and therefore favours the dehydration process of poorly crystalline material to haematite.

In the system seeded with 6·8% goethite the retardation of the transformation of a well crystalline lepidocrocite (57 m²/g) by Si is markedly reduced (Table 1). At the same time the Si uptake by the goethite (to be discussed in the next section) is also considerably decreased.

Si uptake

The Si concentration in solution showed a decrease during the conversion process approaching a final value in equilibrium with the goethite formed. There is a definite initial decrease in the Si concentration probably due to surface adsorption by lepidocrocite. This decrease is more marked in the case of poorly crystalline lepidocrocites but even then only constitutes a small part of the total Si removed from solution.

The major part of the Si removed is highly correlated with the amounts of goethite that have been formed. A linear relationship exists for the equation

$$\ln \frac{Si_t}{Si_0} = -c \frac{G_t}{G_f}$$

where Si_t and Si_0 are the Si concentrations at times t and zero.

This indicates that the goethite formed is responsible for the Si uptake, and furthermore that the relative Si uptake per unit time and per unit amount of goethite formed decreases as the transformation proceeds. This is most likely due to the decreasing Si concentration in solution which governs the uptake of Si by goethite.

Plotting Si uptake per unit weight of goethite Si_u/G_t against Si_t gives a significant positive correlation. However, this relationship has a simple linear form (Table 2) rather than that of a typical adsorption isotherm obtained if ordinary adsorption was involved. This indicates that the Si taken up during the goethite formation is not in a reversible adsorption equilibrium with the Si in solution, but is probably incorporated into the goethite during its crystal growth. From the data in Table 2 it appears that for the same initial Si concentration, the Si uptake per unit weight of goethite increases with half conversion time, i.e. the slower the goethite formation the more Si is taken up. To furnish further evidence on this idea of Si incorporation in goethite some additional experiments were conducted.

An addition of Si after the goethite has formed (in the absence of Si) leads to almost no Si uptake. This is reasonable in view of the high OH concentration of the system (see Hingston *et al.*, 1968).

In a further experiment it was tried to remove

Table 2. Relationship between Si concentration in solution (Si_t) and Si uptake by goethite (Si_u/G_t) during its formation from lepidocrocite at 80°C in M KOH

Initial Si conc. (M × 10³)	Seeding*	HCT (hr)	Linear regression $Si_u/G_t \dagger = k \cdot Si_t + c$	r
0·133		28	$0·194\ Si_t + 0·0076$	0·980
0·266		58	$0·152\ Si_t + 0·0117$	0·998
0·266	*	4·9	$0·113\ Si_t + 0·0059$	0·997

*Seeded with 6·8% goethite.
†m-mole Si per mg of goethite formed at time *t*.

the Si taken up by extractions with fresh M KOH and with 0·2 N KCl adjusted with HCl to pH 2·90, 1·90 and 0·99. Only in the first KOH extraction were measurable amounts of Si released but even in this case less than 1% of the total Si taken up during the goethite formation was extracted. The KCl–HCl mixtures were even less efficient.

These observations suggest that care must be taken in preparing synthetic goethites for such work as cation or anion exchange properties. If the goethite is prepared by ageing gels in glassware at high pH values there is every possibility that Si is dissolved from the glassware and incorporated into the goethite structure.

Effect of Si addition at various times

From the results obtained so far, particularly from the seeding experiments, it can be expected that the induction period due to Si should be shorter the later during the course of the transformation the Si is added. The results of an experiment designed to confirm this idea are given in Fig. 2. Si at a concentration of $2·66 \times 10^{-4}$ M was added 2, 4, 6 and 8 hr after the beginning of a transformation carried out in M KOH at 80°C and the degree of conversion and Si in solution were determined after 21 and 30 hr. After 21 hr complete conversion has taken place in the absence of Si. It can be seen from Fig. 2(b) that the addition of Si 4 hr or later after the start has no retarding influence on the conversion, although at this stage the conversion is just commencing. This is further evidence that the retarding influence of Si occurs mainly during the nucleation stage of the transformation, long before the major part of the Si is taken up by the goethite. This decreasing influence with the time of the Si addition after the start is reflected in a linear cor-

relation (negative) between Si in solution and Si uptake by goethite ($Si_u/G_t = -0·0645\ Si_t + 0·0194$).

Morphology and surface area of final goethites

Goethites formed in the presence of Si differ somewhat in crystal morphology and surface area from those grown in Si free systems. As shown in Fig. 3a, goethites grown in the absence of Si consist of needles of various length and thickness. However, if Si is initially present in the system the goethite also occurs as large rod-like crystals which are quite often twinned, Fig. 3b, as well as the variable acicular forms mentioned above, the larger crystals being more prevalent at 80°C than at 20°C. The higher proportion of larger crystals is reflected in consistently lower surface areas as shown in Table 3.

Table 3. Surface area of goethites grown from lepidocrocite in M KOH with and without Si

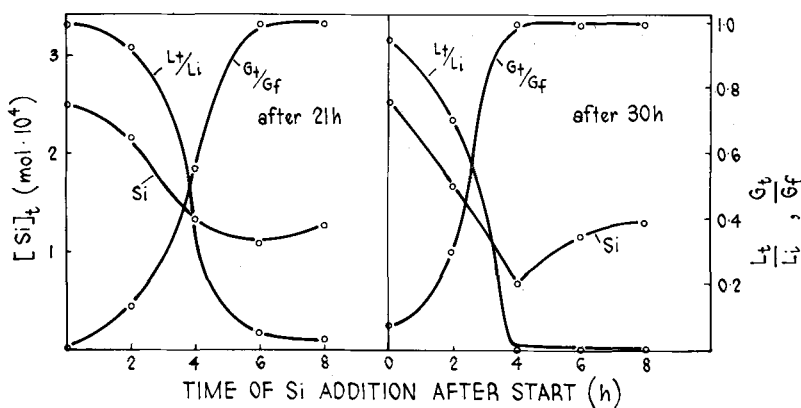| Surface area of lepidocr. (m^2/g)	Si conc. ($M \times 10^3$)	Temp. (C)	Surf. area of goethite (m^2/g)
50	0	80	17
50	0·246	80	14
58	0	80	23
58	0·266	80	12
152	0	80	25
152	0·266	80	23
152	0	20	53
152	0·322	20	34
135	0	20	127
135	0·123	20	89
135	0·246	20	70

Fig. 2. Influence of time of Si addition of the conversion of lepidocrocite to goethite and Si uptake in M KOH at 80°C after 21 and 30 hr.
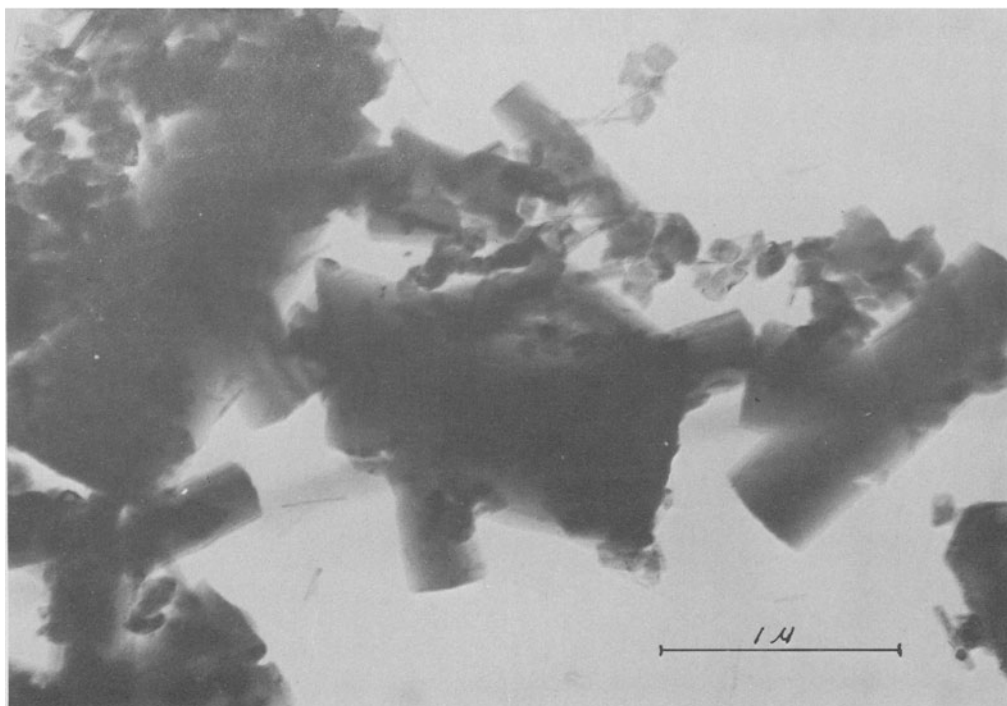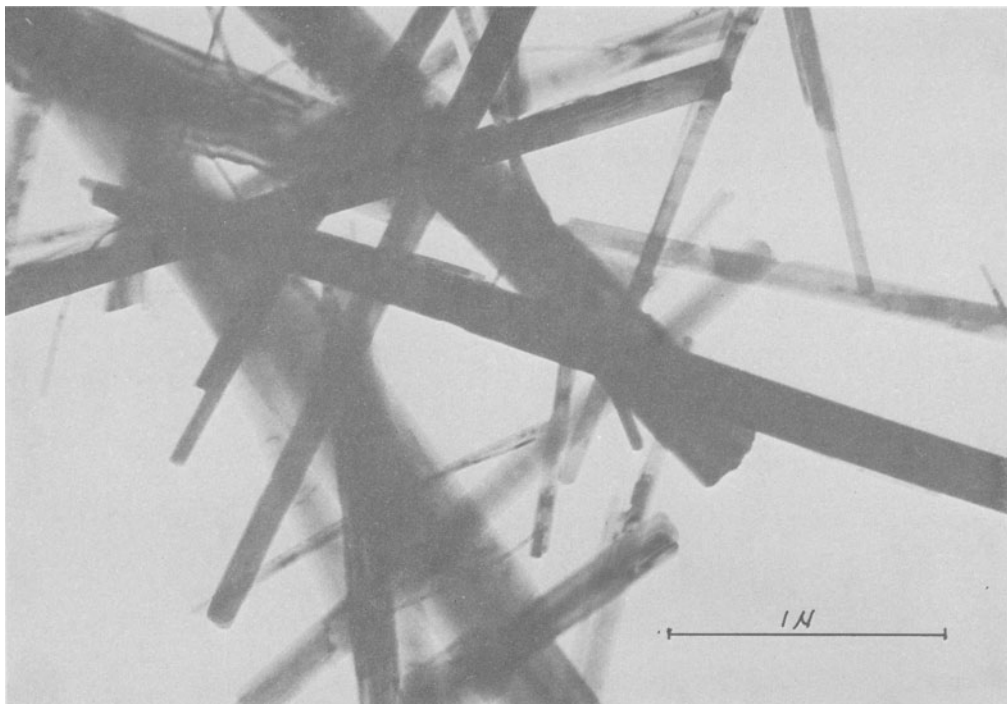
Fig. 3a–b. Goethite formed from lepidocrocite at 80°C in M KOH (3a) and M KOH $+ 0{\cdot}266 \times 10^{-3}$ M Si (3b).

These results are consistent with the idea that Si interferes particularly during the nucleation phase resulting in the formation of fewer crystals which subsequently grow to a larger crystal size.

CONCLUSIONS

Without changing the principal mechanism of the conversion the addition of Si at low concentrations ($0-0.5 \times 10^{-3}$ M) drastically retards, but does not completely inhibit, as suggested by Hiller (1966), the conversion of lepidocrocite to goethite in a strongly alkaline solution. The results suggest that the retardation is not due to the reduction of the rate of dissolution of the lepidocrocite by adsorption of Si. From additional experiments it is rather concluded that Si interferes mainly at the nucleation stage of the conversion. At this stage the relative Si concentration per unit area of goethite nuclei is high and the surface therefore has to cope with the tendency of Si to be taken into the goethite lattice leading to slowed formation and growth of nuclei. The more goethite surface formed during nucleation the less serious will be this tendency so that the later Si is introduced into the system after the start of the conversion the smaller will be its retarding effect.

Further evidence that Si is taken into the goethite lattice rather than adsorbed at the surface was given by the unsuccessful attempts at Si extraction.

The overall amount of Si taken up amounts to only one Si atom per 300–1000 Fe atoms. This marked influence of traces of Si at first appears to offer an explanation for the relative stability of lepidocrocite in soils and sediments where the Si in soil solutions may often be at higher concentrations than those used in these experiments. However, at room temperatures and lower pH values the conversion rate is mainly controlled by the dissolution rate of the lepidocrocite rather than the nucleation rate, which is the rate determining process at higher temperatures and pH values (Schwertmann and Taylor, 1972). Thus in natural systems where the lepidocrocite is often intimately associated with goethite, i.e. the system is already nucleated, the apparent stability of the lepidocrocite cannot be attributed to the presence of Si.

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Résumé – Le mécanisme de la transformation de la lépidocrocite (γFeOOH) en goethite (αFeOOH) a été établi précédemment et l'effet des silicates sur la transformation a été étudié. On a trouvé que plutôt que d'inhiber complétement la réaction, comme cela avait été suggéré, la présence de Si retarde simplement l'étape de nucléation de la transformation. On a trouvé qu'il n'y a pas de diminution de la vitesse de dissolution de la lépidocrocite, due à une adsorption superficielle de Si.

Si n'a pas d'effet s'il est introduit après l'étape de nucléation; dans des conditions de pH et de température où la vitesse de dissolution de la lépidocrocite détermine principalement la vitesse de transformation, la présence de Si n'a qu'un effet réduit. Les résultats montrent que Si est adsorbé et incorporé dans la structure de la goethite; à cause de son effet retardateur sur la nucléation, de plus grands cristaux de goethite se forment, un grand nombre d'entre eux étant maclés.

On infère de ces résultats que la stabilité apparente de la lépidocrocite présente dans les sols en association avec de la goethite ne peut pas être attribuée uniquement à la présence de Si dans le système sol.

Kurzreferat – Im Gegensatz zu bisherigen Vermutungen vermag die Anwesenheit von Si ($0.03-0.53 \times 10^{-3}$ mol/l) die Umwandlung von Goethit in Lepidokrokit im alkalischen Bereich zwar nicht zu unterbinden aber doch stark zu hemmen. Die Lösungsgeschwindigkeit des Lepidokrokit wird durch Si nicht vermindert. Si hat nur einen geringen Einfluß, wenn es nach Abschluß der Keimungsphase eingeführt wird sowie unter pH- und Temperaturbedingungen, bei dem die Lösungsrate des Lepidokrokits und nicht die Keimbildungsrate des Goethits geschwindigkeitsbestimmend ist.

Daraus wird geschlossen, daß Si vorwiegend die Bildung von Goethitkeimen erschwert, was zur

Bildung weniger, aber größerer Kristalle führt, die häufig verzwillingt sind. Si wird offenbar in den Goethitkristall eingebaut.

Die relativ hohe Persistenz des Lepidokrokits in Böden gegenüber dem stabileren Goethit kann demnach nicht allein dem Si in der Bodenlösung zugeschrieben werden.

Резюме — Механизм превращения лепидокрокита (γ FeOOH) в гетит (α FeOOH) был установлен раньше и исследовано влияние силикатов на превращение. Оказалось, что присутствие Si только задерживает стадию образования ядер при превращении, а не тормозит реакцию совершенно, как предполагалось раньше. Найдено также, что вследствие поверхностной адсорбции Si уменьшение скорости растворения лепидокрокита не происходит.

Si, введенный после стадии образования ядер, не влияет на реакцию, а при некоторых условиях pH и температуры, когда растворение лепидокрокита в большой степени определяет скорость превращения, влияние присутствия Si уменьшается. Результаты показывают, что Si адсорбируется и включается в структуру гетита, а вследствие его замедляющего влияния на образование ядер, образуются более крупные кристаллы гетита, часто сдвоенные.

Из результатов сделан вывод, что кажущаяся стабильность лепидокрокита в почвах в связи с гетитом, не может быть целиком приписана присутствию Si в почвенной системе.