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COMMENT

Comment on “On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C” by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg

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Abstract—Within the scope of a planned update of the Nagra/PSI thermochemical database (Pearson and Berner, 1991; Pearson et al., 1992) we are currently reviewing data concerning the carbonate complexation of trace metals (Hummel et al., 2000). The investigation of Bruno et al. (1992) attracted our attention because it is to our present knowledge the only publication exploring the carbonate complexation of ferric iron. The lack of stability constants of Fe(III) carbonate complexes is regarded as a serious deficiency in our database, and therefore, the work of Bruno et al. (1992) has been carefully reviewed with the aim of including their results into the next version of the Nagra/PSI database. The important findings of Bruno et al. (1992) unfortunately are disguised by some inconsistencies in the treatment of their experimental data that, in turn, hide an unresolved ambiguity in their experiments: The stability constants of the complexes as reported by Bruno et al. (1992), and as already included into the IUPAC database (IUPAC, 1997), are such small numbers that Fe(III) carbonate complexes are predicted to be completely negligible in any aqueous system. On the other hand, their experimental findings point to the fact that Fe(III) carbonate complexes might be important in many groundwater systems. This comment aims at resolving this enigma and clarifying the importance of Fe(III) carbonate complexation. *Copyright © 2000 Elsevier Science Ltd*

1. TREATMENT OF THE DATA

The results of solubility measurements of hematite in $NaHCO_3$ solutions were interpreted by Bruno et al. (1992) in terms of two aqueous complexes, $Fe(OH)CO_3(aq)$ and $Fe(CO_3)_2^-$. The influence of these complexes in the Fe_2O_3–H_2O–$CO_2(g)$ system is explored graphically in a predominance diagram (Fig. 7 in Bruno et al., 1992). This predominance diagram shows that “the Fe(III) speciation changes from $Fe(OH)_3(aq)$ to $Fe(CO_3)_2^-$ in the high pH, high p_{CO_2} range.” An examination of the diagram reveals that below pH 6 the complex $Fe(OH)_3(aq)$ dominates the system up to a CO_2 partial pressure of 1 bar. This result does not match with experimental findings of Bruno et al. (1992). They state that at $pH < 6$ “the measured Fe(III) concentrations at $p_{CO_2} = 0.97$ atm are 1000 times larger than expected assuming equilibrium with $Fe(OH)_3(aq)$ only.” Consequently, they interpreted all their experimental data in terms of Fe(III) carbonate complexes.

I attempted to reproduce this predominance diagram using the stability constants reported by Bruno et al. (1992), $\log \beta_{11} = -3.83 \pm 0.21$ and $\log \beta_2 = 7.40 \pm 0.11$ for $Fe(OH)CO_3(aq)$ and $Fe(CO_3)_2^-$, respectively. The data for the H_2O–$CO_2(g)$ system and the Fe(III) hydrolysis data were taken from Nordstrom et al. (1990). However, this recalculation neither could reproduce Figure 7 of Bruno et al. (1992) nor did it remedy the contradiction between the predominance diagram and the experimental findings. To the contrary, speciation calculations using the above mentioned thermodynamic constants predict that Fe(III) carbonate complexes are completely negligible even at pH 14 and $p_{CO_2} = 1$ bar. The entire parameter space is predominated by Fe(III) hydrolysis.

A closer examination of the data treatment by Bruno et al. (1992) seemed to be necessary at this stage. All experimental data had been interpreted in terms of two solubility equilibria

$$0.5\ Fe_2O_3(s) + 0.5\ H_2O + CO_2(g) = Fe(OH)CO_3(aq) \tag{1}$$

$$0.5\ Fe_2O_3(s) + 0.5\ H_2O + 2\ CO_2(g) = Fe(CO_3)_2^- + H^+ \tag{2}$$

Their equilibrium constants as determined by Bruno et al. (1992) are $\log K_3 = -4.9 \pm 0.2$ and $\log K_4 = -11.40 \pm 0.10$, respectively. The constants finally reported by Bruno et al. (1992) refer to the equilibria

$$Fe^{3+} + H_2O + CO_3^{2-} = Fe(OH)CO_3(aq) + H^+ \tag{3}$$

$$Fe^{3+} + 2\ CO_3^{2-} = Fe(CO_3)_2^- \tag{4}$$

with $\log \beta_{11}$ and $\log \beta_2$, respectively. To transform equilibrium 1 into 3 and 2 into 4 two auxiliary constants are needed, namely the solubility equilibrium for hematite

$$0.5\ Fe_2O_3(s) + 3\ H^+ = Fe^{3+} + 1.5\ H_2O \tag{5}$$

with $\log K_{s0} = -1.62 \pm 0.05$ (Bruno et al., 1992) and the carbonate equilibrium

$$CO_2(g) + H_2O = CO_3^{2-} + 2\ H^+ \tag{6}$$

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with $\log K_{a2} = -18.15 \pm 0.01$ (Nordstrom et al., 1990).

Combining equilibria 1, 3, 5, 6, and 2, 4, 5, 6 yield

$$\log \beta_{11} = \log K_3 - \log K_{s0} - \log K_{a2} \tag{7}$$

and

$$\log \beta_2 = \log K_4 - \log K_{s0} - 2 \log K_{a2} \tag{8}$$

The results, $\log \beta_{11} = 14.9$ and $\log \beta_2 = 26.5$, differ by about 19 (!) orders of magnitude from the values reported by Bruno et al. (1992).

Note that $\log K_3$ and $\log K_4$ are concentration constants valid for 0.2 mol/L $NaClO_4$/$NaHCO_3$ solutions. Bruno et al. (1992) report that they used the extrapolated values to the infinite dilution standard state of the constants K_3 and K_4 by applying the SIT approach. They do not give any numbers or further explanation of the extrapolation procedure. However, we may infer the procedure applied by Bruno et al. (1992). According to the usual practice, the SIT ϵ parameters representing specific ion interactions, are considered to be zero for neutral species (Grenthe et al., 1992). This means that no ionic strength dependence of equilibrium 1 is expected and thus, $\log K_3^0 = \log K_3$. In equilibrium 2 we have two charged species, $Fe(CO_3)_2^-$ and H^+. Their SIT ϵ parameters are $\epsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ and $\epsilon(Na^+, Fe(CO_3)_2^-) \approx \epsilon(Na^+, Am(CO_3)_2^-) = -0.05 \pm 0.05$ (Silva et al., 1995). The latter parameter is only an estimate, but the correction for ionic strength effects in 0.2 mol/L solutions is governed by the Debye-Hückel term of the SIT equation and the contribution of specific ion interactions to the total ionic strength effect sums up to $\Delta \log K = 0.03$ at maximum. The total ionic strength correction is $\log K_4^0 = \log K_4 - 0.25$. The expected ionic strength effects are within the range of statistical uncertainties of the derived constants. In our further discussion considering orders of magnitude they are completely negligible.

A predominance plot using the correctly derived stability constants reveals the stunning picture of carbonate complexes dominating the entire aqueous chemistry of ferric iron (Fig. 1). According to this diagram it would be virtually impossible to observe Fe(III) hydrolysis in natural aquatic systems and in the neutral pH range the mixed carbonate hydroxide complex is predicted to dominate down to a CO_2 partial pressure of 10^{-9} bar. It is rather unlikely that such tremendous effects would have remained unnoticed in all experimental investigations and field observations so far. Moreover, a comparison of $\log \beta_2 = 26.5$ with well-established constants, e.g., $\log \beta_2 = 16.94 \pm 0.12$ for $UO_2(CO_3)_2^{2-}$ (Grenthe et al., 1992) or $\log \beta_2 = 12.3 \pm 0.4$ for $Am(CO_3)_2^-$ (Silva et al., 1995), shows that the Fe(III) constant is unrealistically high.

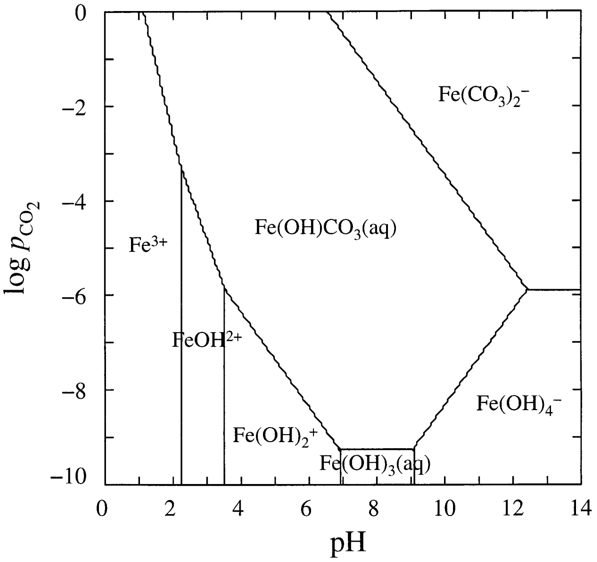

Fig. 1. Calculated predominance area diagram of the Fe(III) hydroxide–carbonate system in the range $0 \leq pH \leq 14$ as a function of the $CO_2(g)$ partial pressure, at I = 0 and 25°C. Equilibrium constants of $\log \beta_{11} = 14.9$ and $\log \beta_2 = 26.5$ have been used for the complexes $Fe(OH)CO_3(aq)$ and $Fe(CO_3)_2^-$, respectively. The precipitation of solids is suppressed.

These results prompted me to closely examine the experimental data presented in Bruno et al. (1992). Figure 1 in Bruno et al. (1992) presents the data in the form log [Fe(III)] as a function of pH + 2 log p_{CO_2} "in order to bring together the data obtained at different p_{CO_2}." The rationale of choosing this representation is not obvious. In terms of the speciation model of Bruno et al. (1992),

$$[Fe(III)] = K_3 \cdot p_{CO_2} + K_4 \cdot p_{CO_2}^2 \cdot [H^+]^{-1} \tag{9}$$

the experimental data are only under certain circumstances on the same scale, namely in the parameter range where the $Fe(CO_3)_2^-$ complex dominates. Here, the experimental data are expected to follow a straight line of slope 1 (and intercept $\log K_4$) in a log [Fe(III)] versus pH + 2 log p_{CO_2} diagram according to Eqn. 9. In the parameter range of $Fe(OH)CO_3(aq)$ predominance the experimental data are expected to be independent of pH, but on different levels of log Fe(III) = $\log K_3 + \log p_{CO_2}$ according to the CO_2 partial pressure of the experiments. A better choice of parameters would have been a plot of log [Fe(III)] − log p_{CO_2} versus pH + log p_{CO_2} representing the speciation model of Bruno et al. (1992) on an overall common scale according to the equation:

$$[Fe(III)]/p_{CO_2} = K_3 + K_4 \cdot p_{CO_2}/[H^+] \tag{10}$$

Anyway, Figure 1 in Bruno et al. (1992) is used for qualitative arguments only, and the agreement between the experimental and calculated data is shown in Figure 2 of their paper. According to the labeling, this figure is a linear–linear plot of [Fe(III)] vs. $p_{CO_2}/[H^+]$ or $p_{CO_2}/[H^+]^2$. However, neither version can represent the speciation model by just a single straight line as shown in Figure 2 in Bruno et al. (1992). Neither the figure caption nor the text provides further help to resolve this enigma. Following the above discussion I assumed that the correct labels might be $[Fe(III)]/p_{CO_2}$ vs. $p_{CO_2}/[H^+]$ (Eqn. 10). Reading the data from Figure 2 in Bruno et al. (1992) under this assumption and doing a linear regression analysis, the equilibrium constants given by Bruno et al. (1992) can be reproduced with sufficient accuracy: $\log K_4 = -11.33 \pm 0.09$ and $\log K_3 \approx -5.5$. However, K_3 has a large uncertainty and cannot be distinguished from zero on the 95% confidence level, that is, $K_3 = (2.9 \pm 5.4) \cdot 10^{-6}$.

A close match between the two data sets given in Figures 1 and 2 of Bruno et al. (1992) has been achieved, but only under

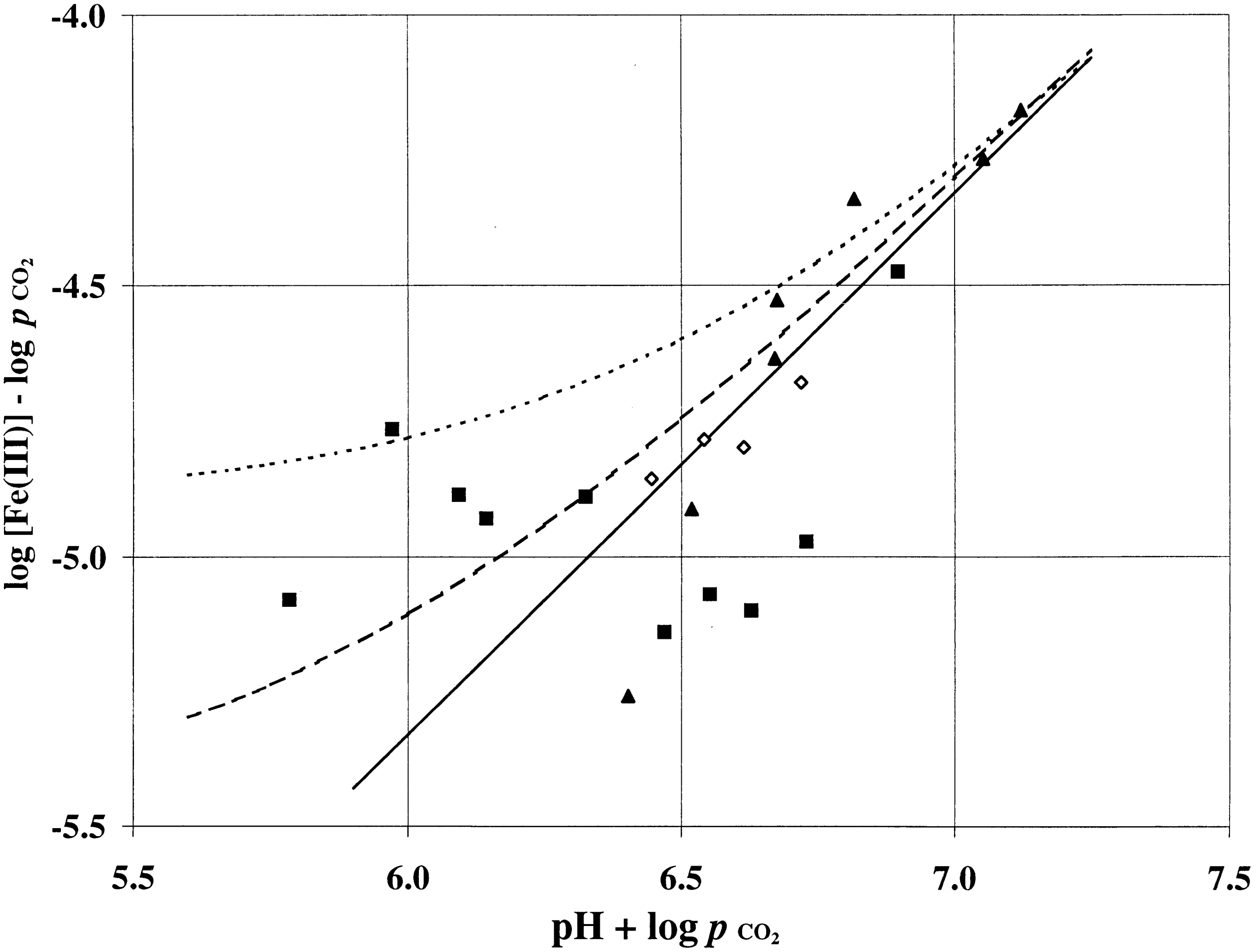

Fig. 2. Synopsis of experimental data and thermodynamic model calculations in the form of a plot log [Fe(III)] − log p_{CO_2} vs. pH + log p_{CO_2} representing all data on a common scale. Filled symbols represent experimental data derived from Fig. 1 in Bruno et al. (1992), squares: p_{CO_2} = 0.30 bar, triangles: p_{CO_2} = 0.97 bar. Open symbols show data from Fig. 2 in Bruno et al. (1992) at variance with the data set of their first figure. The solid line has been calculated using log $K_4 = -11.33$, the dashed line shows the effect of adding log $K_3 = -5.5$ to the model. The dotted line represents the data given by Bruno et al. (1992), log $K_3 = -4.9$ and log $K_4 = -11.4$.

the assumption that the labels in Figure 1, indicating the experimental p_{CO_2}, are inverted: The squares in Figure 1 seem to represent data measured at p_{CO_2} = 0.30 bar and the triangles data measured at p_{CO_2} = 0.97 bar. However, the only hint in the original text seems to contradict this assumption of exchanged labels. Can we resolve this new enigma? I found an independent check indicating which labeling scheme might be the correct one: Both series of measurements, conducted at constant but different CO_2 partial pressures, are essentially titrations carried out by adding appropriate amounts of 0.2 mol/L $NaHCO_3$ solutions to a 0.2 mol/L $NaClO_4$ starting solution. The end point of the titration is reached when the solution is converted to pure 0.2 mol/L $NaHCO_3$. Taking the maximum values x = pH + 2 log p_{CO_2} of both series of measurements from Figure 1 in Bruno et al. (1992) and combining them with the well-known equilibrium

$$CO_2(g) + H_2O = HCO_3^- + H^+ \tag{11}$$

with log $K_{a1} = -7.58 \pm 0.01$ (Nordstrom et al., 1990; corrected to ionic strength 0.2 mol/L) the maximum value of $[HCO_3^-]$ reached in the experiments can be estimated according to

$$\log [HCO_3^-] = \log K_{a1} + x - \log p_{CO_2} \tag{12}$$

Assuming that the labels in Figure 1 in Bruno et al. (1992) are correct, we have for the squares x = 6.37 at p_{CO_2} = 0.97 bar, which results in $[HCO_3^-]$ = 0.06 mol/L, and for the triangles x = 7.11 at p_{CO_2} = 0.30 bar, which results in $[HCO_3^-]$ = 1.12 mol/L. The latter result is in clear contradiction to experiments carried out at a constant ionic strength of 0.2 mol/L as described in Bruno et al. (1992). If we assume that the labels are exchanged in Figure 1 of Bruno et al. (1992), we get $[HCO_3^-]$ = 0.20 mol/L for the squares and $[HCO_3^-]$ = 0.35 mol/L for the triangles. Within the uncertainty of the estimation procedure this result is compatible with the experiments.

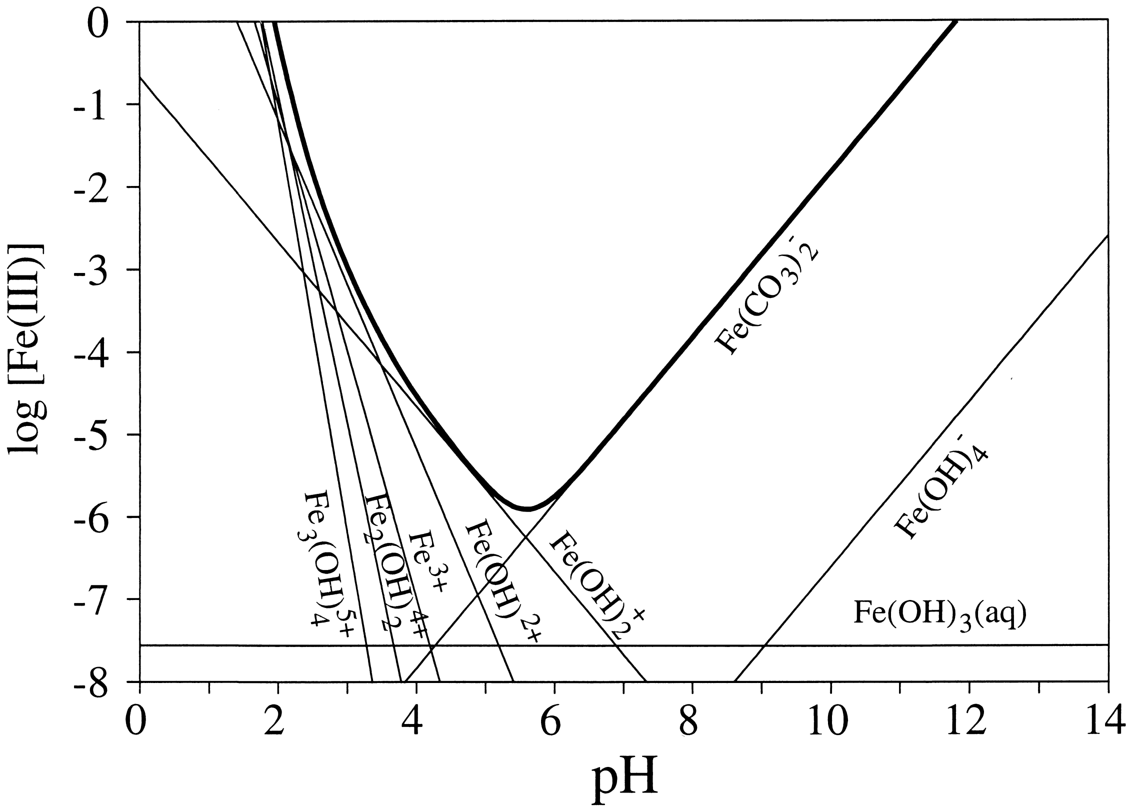

Fig. 3. The solubility of freshly precipitated amorphous ferrihydrite in a system open to the atmosphere ($p_{CO_2} = 10^{-3.5}$ bar) as a function of pH, at I = 0 and 25°C. The solubility constant of ferrihydrite and the Fe(III) hydrolysis data were taken from Nordstrom et al. (1990), and log $\beta_2 = 26.5$ has been used for the complex $Fe(CO_3)_2^-$.

Despite all these efforts to reconstruct the most probable data set, a small inconsistency remains unresolved. Four data points are systematically shifted by a factor of exactly 2 in [Fe(III)] concentration comparing the (corrected) data sets of Figures 1 and 2 in Bruno et al. (1992). The consequences of this inconsistency are minor. Fitting the speciation model to the data set of Figure 1 does not change K_4 (log $K_4 = -11.34 \pm 0.12$) compared with the data set of Figure 2, but the constant $K_3 = (1.0 \pm 7.3) \cdot 10^{-6}$ is now totally insignificant on the 95% confidence level.

Figure 2 summarises my efforts to clarify the treatment of data in Bruno et al. (1992). We see that assuming solely a $Fe(CO_3)_2^-$ complex explains the experimental findings with a constant log $K_4 = -11.3$ (solid line in Figure 2) in agreement with the value given by Bruno et al. (1992). However, the existence of a mixed complex $Fe(OH)CO_3(aq)$ remains a matter of debate. The value given by Bruno et al. (1992), log $K_3 = -4.9$, is too large in any case (dotted line in Fig. 2). If we consider the data set of Figure 1 in Bruno et al. (1992), a constant of log $K_3 \approx -5.5$ can be derived (dashed line in Fig. 2). If we consider the data set of Figure 2 in Bruno et al. (1992), an even smaller fit parameter results. However, the data scatter in the relevant parameter region prevents any statistically significant result in both cases. Thus, in the further discussion we will ignore a mixed complex $Fe(OH)CO_3(aq)$ and rely solely on the complex $Fe(CO_3)_2^-$.

2. RUMINATIONS ABOUT SOLID PHASES

Even if we ignore the mixed complex $Fe(OH)CO_3(aq)$, the strong complex $Fe(CO_3)_2^-$ remains to be discussed. If we interpret the experimental findings of Bruno et al. (1992) as solubility controlled by hematite, the exceptionally high constant log $\beta_2 = 26.5$ remains unchanged. What are the predicted consequences of this strong ferric iron carbonate complexation for a simple beaker experiment in the laboratory? For example, we may predict the solubility of freshly precipitated amorphous ferrihydrite in a beaker open to the atmosphere ($p_{CO_2} = 10^{-3.5}$ bar) as a function of pH (Fig. 3). A range of ferrihydrite solubility constants, $3 \leq \log K_{s0} \leq 5$, is given by Nordstrom et al. (1990), representing the different stages from freshly precipitated to aged ferrihydrite. According to these data, the solubility in the alkaline region is controlled by the $Fe(CO_3)_2^-$ complex and the concentration of dissolved Fe(III) reaches 1 mol/L at pH 12 in the case of freshly precipitated ferrihydrite (Fig. 3). Even in the case of aged ferrihydrite the Fe(III) concentration reaches 1 mol/L at pH 14. Thus, the prediction is that ferrihydrite precipitated in the neutral pH range will completely dissolve by addition of strong base due to the formation of $Fe(CO_3)_2^-$ from atmospheric CO_2. This is in striking contradiction to experimental evidence. Several long-term studies have been conducted in the past to explore in detail the slow transformation of ferrihydrite to goethite or hematite in alkaline solutions (Schwertmann and Murad, 1983; Cornell and Gio-

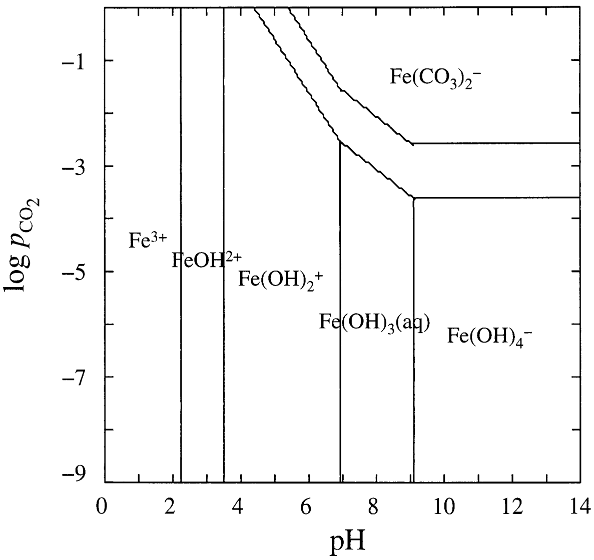

Fig. 4. Calculated predominance area diagram of the Fe(III) hydroxide–carbonate system in the range $0 \le pH \le 14$ as a function of the $CO_2(g)$ partial pressure, at $I = 0$ and 25°C. Revised equilibrium constants have been used for the complex $Fe(CO_3)_2^-$. The small predominance area of $Fe(CO_3)_2^-$ corresponds to $\log \beta_2 = 20$, the extended one to $\log \beta_2 = 22$. The precipitation of solids is suppressed.

vanoli, 1985). Even experiments in 6 mol/L KOH solutions containing suspensions of 0.01 mol/L ferrihydrite could be carried out without loss of ferrihydrite due to dissolution. The kinetics of the transformation was followed by taking subsamples from the suspension during an experiment. The unconverted ferrihydrite had to be dissolved by shaking the subsamples with a pH 3 mixture of 0.2 mol/L oxalic acid and 0.2 mol/L ammonium oxalate for 2 h in the dark (Cornell and Giovanoli, 1985).

The slow transformation kinetics of ferrihydrite to goethite or hematite may provide the resolution of this contradiction. Bruno et al. (1992) carefully prepared and checked their starting material, a monodisperse suspension with spherical hematite particles of 50 nm in diameter. Then they started their solubility experiments by adding $NaHCO_3$ solution and report that "typical equilibrium times were one week for the first point of the solubility titration and 1 to 2 days for the successive additions." Did they still have hematite at the surface of their particles controlling the "equilibrium" state in their experiments? Dissolution and reprecipitation effects of 50 nm particles may result in a significant surface covering of the particles by freshly precipitated amorphous ferrihydrite, which subsequently transforms back to goethite and hematite at a very slow rate. Experiments at 24°C (Schwertmann and Murad, 1983) showed that the time of half conversion of ferrihydrite to goethite and hematite exceeds 100 days at pH 7 and 200 days at pH 5.

Following the hypothesis of final "equilibrium" states with ferrihydrite and using the range of ferrihydrite solubility constants given by Nordstrom et al. (1990), $3 \le \log K_{s0} \le 5$, the stability constant of the $Fe(CO_3)_2^-$ complex can be reevaluated as $20 \le \log \beta_2 \le 22$. Note that this range of values now is compatible with the well-known β_2 constants of U(VI) and Am. A predominance diagram shows the influence of this revised constant (Fig. 4): Fe(III) carbonate complexation has no effect on surface waters in equilibrium with CO_2 of the atmosphere ($p_{CO_2} = 10^{-3.5}$ bar), and at low pH the usual Fe(III) hydrolysis effects are shown. However, in carbonate-rich groundwater (e.g., $p_{CO_2} = 10^{-2}$ bar) we expect Fe(III) carbonate complexes to predominate. Hence, even assuming a worst case scenario, that is, freshly precipitated ferrihydrite as solubility controlling phase in the experiments of Bruno et al. (1992) and ignoring the possible existence of a mixed complex $Fe(OH)CO_3(aq)$, we can conclude that the findings of Bruno et al. (1992) reveal a prominent role of ferric iron carbonate complexes in groundwater systems. It would be worthwhile to resolve the ambiguity concerning the solubility controlling solid phase, and the resulting uncertainty of the derived complexation constants, by conducting additional experiments, for example, with freshly precipitated ferrihydrite or goethite.

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