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The effect of ill-defined ferric oxides on the redox characteristics of flooded soils

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Summary

Preliminary determinations of redox potential (Eh), pH and Fe^{2+} activity in the interstitial solution of two flooded soils indicate that the equilibria between ferric and ferrous iron are governed largely by ill-defined ferric oxides, which are intermediate between amorphous $Fe(OH)_3$ and α-FeOOH as far as stability is concerned. This partly explains the many unsuccessful attempts to interpret the Eh of flooded soils in terms of iron redox systems for which theoretical E_h^0 values can be calculated.

Introduction

Most Eh measurements in reduced media could be correlated with general characteristics such as the content of organic matter, the presence of large amounts of nitrate and manganese and the appearance of sulphate reduction (cf. Ponnamperuma, 1964; Starkey and Wight, 1946). Attempts to interpret these data in terms of several well established ferric-ferrous and manganic-manganous redox systems, were generally unsuccessful (cf. IRRI, 1964; Bohn, 1968). Important progress has been made by Ponnamperuma and others (IRRI, 1964; IRRI, 1965; Ponnamperuma et al., 1967). They performed Eh-pH measurements in a soil solution drawn by gravity through a sintered glass tube from a pot with water-saturated soil and transferred into a N_2-filled cell, constructed for Eh-pH determination. In contrast to 'soil potentials', which often showed differences in the order of 100 to 300 mV, the 'solution Eh' values were highly reproducible. They were positive throughout the inundation period and, in the last stages of reduction, were 100 to 300 mV higher than the redox potentials measured in the soil. The results could be explained quantitatively by considering the equilibria between Fe^{2+} and the amorphous hydroxides $Fe(OH)_3$ and $Fe_3(OH)_8$. However, it is questionable whether the precautions to prevent oxydation by O_2 were sufficient, particularly because oxygen can be absorbed on the surface of Pt-electrodes (Bohn, 1968).

Experimental

An alternative procedure for Eh- and pH determination in the soil solution has been made by placing two 15 cm^3 porous pots (equipped with Pt and graphite electrodes, and a devise for collecting the soil solution by applying suction) in a 3-litre pot filled with water-saturated soil. Three Eh-electrodes were placed in the soil at the same depth as the porous pots. Periodically, Eh was measured after collecting 'fresh' soil solution in the porous pots by applying a pressure difference of 20 to 30 cm Hg. In the same way this (clear) solution was further transferred through a narrow plastic tube into a 30 cm^3 beaker vessel (previously filled with 5 cm^3 paraffine oil) for pH determination, Fe^{2+} analysis and measurement of the specific conductance to estimate the Fe^{2+} activitty coefficient (cf. Ponnamperuma, Tianco and Loy, 1966).

Besides the Eh-electrodes, a 52A Electrofact pH meter, a commercial glass electrode and a saturated calomel electrode were used for the Eh-pH measurements. The plastic tube was closed very tightly in between the measurements.

The soils used include an illitic clay soil from the Netherlands with 45% clay; $pH_{water} = 7.0$; 0.47% organic C; 0.86% 'free Fe' and 0.06% 'free Mn' (Soil 1) and one reddish brown soil from Kenya with 25% clay; $pH_{water} = 4.9$; 1.84% organic C; 2.18% 'free Fe' and 0.08% 'free Mn' (Soil 2). Soil 2 was enriched with $^1/_4$% $CaCO_3$ and, in one case, $^1/_2$% C as cellulose powder was added to Soil 1 to speed up reduction.

Results and discussion

The pH values of the soil solution were similar to those measured by means of a glass electrode pressed into the soil. This indicates that CO_2 loss during transference of the solution was negligible.

After 20 to 50 days the 'solution Eh' and the 'soil Eh' reached values in the order of —100 to —250 mV. The course of the 'solution Eh' did not show any irregularities during or after collection of the solution. This indicates that artificially induced oxidation did not influence the measured 'solution Eh'.

In all soils the Fe^{2+} concentration increased steadily throughout the inundation period. As this was likely to be the result of solution reduction of any form of ferric oxide, $Fe_2O_3.nH_2O$, this process probably can be represented by the reaction (neglecting the hydratation of the oxide):

$$Fe_2O_3(s) + 6H^+ + 2e \rightleftharpoons 2Fe^{2+} + 3H_2O.$$

for which:

$$Eh = E^o_h - 0.059 \log [Fe^{2+}] - 0.177 \text{ pH} \qquad (1)$$

In Equation 1 the value of E^o_h will depend on the form and hydratation of the ferric oxide.

Assuming that the measured Eh is determined by this equilibrium condition, the 'apparent E^o_h' can be calculated from the experimentally determined Eh, pH and $[Fe^{2+}]$. This 'apparent E^o_h' can be transformed into a standard free energy change of the reaction $\triangle F^o_r$, which can be used to estimate the 'apparent standard free energy of the formation' of ferric (hydr)oxide ($\triangle F^o_{f\,Fe_2O_3}$) participating in the reaction at a given time:

$$E^o_h = \triangle F^o_r \,/\, 2 \times 23.06 \qquad (2)$$

in which:

$$\Delta F^\circ_r = \Delta F^\circ_{f\,Fe_2O_3} - 2\,\Delta F^\circ_{f\,Fe^{2+}} - 3\,\Delta F^\circ_{f\,H_2O} \qquad (3)$$

Substituting published values for $\Delta F^\circ_{f\,Fe^{2+}}$ and $\Delta F^\circ_{f\,H_2O}$ (Garrels and Christ, 1965) and combining Equations 1, 2 and 3 yield:

$$\Delta F^\circ_{f\,Fe_2O_3} = 46.12\,(Eh + 0.059 \log Fe^{2+} + 0.177\,pH) - 210.7 \text{ kcal/mole } Fe_2O_3 \qquad (4)$$

The ΔF°_f values have been calculated from Eh measurements, averaged for 'soil potentials' on the one hand and for 'solution potentials' on the other hand. The results have been plotted in Fig. 1, together with the ΔF°_f values of the least stable (amorphous $Fe(OH)_3$) and the most stable (α-FeOOH) ferric oxides (taken from Garrels and Christ (1965) and recalculated in terms of kcal/mole Fe_2O_3).

The actual ΔF°_f values are not very reliable because the reproducibility of the Eh readings in each couple of porous pots was not better than 10 to 70 mV, corresponding to 0.5 and 3.2 kcal/mole Fe_2O_3. Nevertheless the results allow some important conclusions.

The calculated ΔF°_f generally shows a gradual decrease from values in the neighbourhood of $\Delta F^\circ_{f\,Fe(OH)_3}$ (—161.9 kcal/mole Fe_2O_3) at the start of the experiment, to values nearby $\Delta F^\circ_{f\,\alpha FeOOH}$ (—177.3 kcal/mole Fe_2O_3) after 66 days. The 'solution Eh' obviously showed a better behaviour than the 'soil Eh'. Sometimes ΔF°_f values calculated by means of the 'soil Eh' followed an irregular course (Soil 1 with cellulose), or were to low for any ferric oxide (Soil 1 with cellulose at 29 days and Soil 2 at 66 days).

The observations indicate the presence of ill-defined ferric oxides ('limonite') with ΔF°_fvalues intermediate between $\Delta F^\circ_{f\,Fe(OH)_3}$ and $\Delta F^\circ_{f\,\alpha-FeOOH}$. The observed course is in accordance with thermodynamic principles, as the least stable ferric oxides will

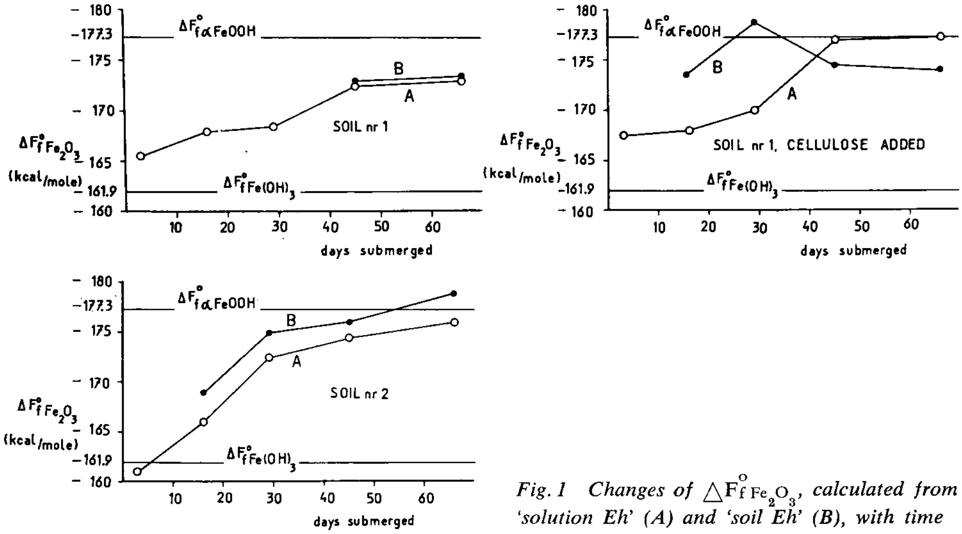

Fig. 1 Changes of $\Delta F^\circ_{f\,Fe_2O_3}$, calculated from 'solution Eh' (A) and 'soil Eh' (B), with time

determine the equilibrium in the first stages of reduction, while, after these compounds have been dissolved completely, the equilibrium will be shifted to involve oxides of higher stability. Addition of cellulose in Soil 1 induced a stronger reduction and consequently the calculated $\triangle F_f^\circ$ values were lower than those of the untreated soil. This indicates that single Eh-pH measurements are of little value in defining the iron redox system operating in flooded soils. Unless the Eh is determined by a well-defined ferric oxide, a check on the presence of a certain redox system is hardly feasible because the possible $\triangle F_f^\circ$ range ($\triangle F^\circ_{f\,FeOOH} - \triangle F^\circ_{f\,Fe(OH)_3} = -15.4$ kcal/mole Fe_2O_3) corresponds to an Eh variation of 330 mV. These observations may partly explain the many unsuccessful attempts to interpret in situ Eh measurements in terms of iron redox systems with well established E_h° values.

In addition it should be stressed that the approach discussed above could be adapted for a quantitative and qualitative analysis of ferric oxides in soils. Although such a method is probably very time-consuming, no other reliable procedure for the analyses of ill-defined ferric oxides appears to exist.

The difference between the results obtained by this method and the one used by Ponnamperuma et al. (1967) can be explained by considering the effect of very small O_2 impurities in the N_2 applied during collection of the solution. In the absence of a solid phase that participates in the redox reaction, the Eh can be changed easily by the oxidation of very small quantities of ferrous ions into ferric ions, because the ferric ion activity is extremely low under the redox conditions of flooded soils. For example, from the equation

$$Eh = 1.19 + 0.059 \log [Fe(OH_2^+] / [Fe^{2+}] - 0.118\, pH \qquad (5)^{1}$$

it can be calculated that 4×10^{-10} mole O_2 per litre can increase the Eh from -220 to $+80$ mV in a solution with a pH of 6.5 and a Fe^{2+} activity of 10^{-3} mole per litre. In a 'pure' N_2 atmosphere it is almost impossible to maintain an O_2 pressure small enough to prevent this oxidation. When the Eh has risen high enough to permit the oxidation and precipitation of Fe^{2+} to form either $Fe(OH)_3$ or $Fe_3(OH)_8$, the Eh depends on the pH and the Fe^{2+} activity as follows (Ponnamperuma et al., 1967):

$$Eh = 1.06 - 0.059 \log [Fe^{2+}] - 0.177\, pH \ (Fe^{2+} - Fe(OH)_3 \text{ equilibrium}) \qquad (6)$$

or

$$Eh = 1.37 - 0.089 \log [Fe^{2+}] - 0.236\, pH \ (Fe^{2+} - Fe_3(OH)_8 \text{ equilibrium} \qquad (7)$$

In either case the Eh is fairly well buffered because a solid phase of unit activity participates in the reaction.

Equation 5 cannot be applied strictly to actual processes when the ferric ion activity is so small (10^{-9} to 10^{-13} mole per litre), but it probably indicates qualitatively the major source of the difference between the 'soil Eh' and the 'solution Eh', found by Ponnamperuma and co-workers. This consideration also explains why the Eh of a solution collected in a N_2 atmosphere could be defined in terms of the $Fe^{2+} - Fe(OH)_3$ and $Fe^{2+} - Fe_3(OH)_8$ redox systems in a wide variety of soils.

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[1] This equation has been based on the assumption that $Fe(OH)_2^+$ is the predominant ferric ion species under the pH condition of flooded soils (pH 6–7). The E_h° value of 1.19 V has been calculated from standard free energy values listed by Garrels and Christ (1965).

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