Fe(III) reduction in soils from South China

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Abstract
The content of Fe in soils in South China is high and the Fe reduction process is important for contaminants transformation in this region. In this study, 23 soil samples from South China were used to study the effects of soil characteristics and weathering parameters on the Fe reduction processes. The total Fe reduction rates ranged from 5.8% to 38.4% and the dissolved Fe reduction rates ranged from 0.04% to 7.9% in different soils. The high soil weathering intensity would inhibit Fe reduction. Both the total Fe reduction rate and dissolved Fe reduction rate were positively linear related with the weathering coefficients SiO_2/Al_2O_3 and Al_2O_3/Fe_2O_3. High soil pH would accelerate the dissolved Fe reduction rate, and there was positive linear relationship between them. The content of organic matter in soils had no obvious effect on the Fe reduction process. The key relationships identified between soil properties and Fe reduction processes in this study should be generally applicable to this region for understanding the Fe cycle in soils.

Key Words
Fe cycle, reduction, soil weathering, subtropical soils, South China.

Introduction
The redox cycling of Fe plays pivotal roles in geochemical cycles of contaminants in natural environments. Redox transformations of Fe(III) oxides and oxyhydroxides in soils, which are important reaction interface for many metals and metalloids, can affect the environmental fate and transport of contaminants (Tas and Pavlostathis 2007). Fe(III) reduction produces Fe(II), which is an effective reductant when present at Fe(III) oxide surfaces (Li *et al*. 2008a). Contaminants that are amenable to surface-mediated reduction in soils by solid-associated Fe(II) include chlorinated aliphatic and nitroaromatic hydrocarbon compounds and certain heavy metals and radionuclides (Li *et al.* 2008b).

Several factors may control the rates of Fe reduction, especially in soils, in which there are numerous complex components. The soils in South China were developed under subtropical monsoon climate, which resulted in the high-degree weathered extent with the main type of red soils (Schoonen *et al.* 1998). The minerals such as iron oxides are enriched in these soils, and the Fe cycle is the important geochemical process for the contaminants transformation in soils in South China (Liu 1993). More important is that Fe reduction is pivotal for stimulate the detoxification process of contaminated soils and it is also the main step of Fe species cycle in natural environment (Roden 2004). So, it is important and interesting to investigate the Fe reduction in different soils, especially in the soils with high content Fe. And furthermore, the soils developed from different parent materials have different physicochemical properties, and the weathering chronosequence of soils also lead to the different properties, which may be vital for the Fe reduction in the soils.

To better understand the Fe reduction process in the red soils from South China with different properties and weathering chronosequence, in this study, we conducted a laboratory experiment to investigate the Fe reduction in 23 soils which developed from different parent materials and also with different weathering chronosequence. The obtained results of this study are anticipated to be valuable and important for understanding and adjusting the geochemical process of contaminants, which are now universal in the soils in South China.

Materials and Methods
Study Sites
Twenty-three soil samples, including twelve Ferrosols, six Ferrolasols, three Anthrosols, and two Argosols types, were collected from South China. All of the samples were collected from the soil depth of 0-15 cm. The 23 soils samples were developed from different parent materials, in which three from Granite, three from Basalt, two from Sedimentary rocks, four form Hazle, three from Alluvial deposit, and five from Quaternary Period red earth.

Soil properties analysis and Fe reduction experiments
Please find the detail analysis methods for determining the soil pH, the content of organic matters, the content of total Fe and dissolved Fe, the content of Al and Si in *Handbook of Soil Analysis.*
Standard anaerobic techniques were used for all the Fe reduction experiments. An anaerobic media were boiled and cooled under a constant stream of O_2-free N_2, dispensed into aluminum-sealed culture bottles under the same gas phase, capped with butyl rubber stopper, and sterilized by autoclaving (121 ^oC, 20 min). Besides the sterilized media, inoculation and sampling were conducted by using sterile syringes and needles. All vials were incubated in a Bactron Anaerobic/Environment ChamberII (Shellab, Shedon Manufacturing Inc., Cornelius, OR) at 30 ^oC in dark. Fe (III) reduction in soil was prepared by 0.5 g soil sample and anoxic suspensions including 30 mM PIPES buffer (pH7), 10 mM lactate acid, and washed suspensions S12 which gave a final cell concentration of about 108 cells/mL. The total concentration of Fe(II), including dissolved and sorbed Fe(II), was determined by extracting Fe(II) from the samples using 1.5 M HCl for 1.5h (Fredrickson and Gorby 1996) and assaying the extract using 1,10-phenanthroline colorimetric method. Dissolved Fe(II) was determined by removing the soil and sorbed Fe(II) from the aqueous phase using a 0.22 μm syringe filter by 1,10-phenanthroline (Roden and Zachara 1996).

Results

Soil characteristics
A broad range of soil characteristics were represented across the 23 soil samples, and soil pH, soil organic matter, the weathering coefficients were obtained in this study. Soil pH ranged from 4.55 to 7.3. The Ferralosols were significant more acidic (4.55-5.11) than other soils types, including Ferrosols (4.91-7.3), Anthrosols (6.09-6.24), and Argosols (5.64-7.3). The soil organic contents ranged from 0.24% to 6.57%, in which there was no significant difference in organic matter content between the different soil types. The content of Fe standardized as Fe_2O_3 ranged from 1.03% to 19.6%, which differentiated greatly. The three soils developed from Basalt had the highest Fe content that all were more than 10%. The Al and SiO_2 content were also different in these 23 soils samples. The Al content standardized as Al_2O_3 ranged from 7.22% to 29. 75% and the SiO_2 content ranged from 40.0% to 65.8%. The weathering degree were high for the studied soils, in which the weathering coefficients of SiO_2/Al_2O_3 ranged 2.42 to 13.2, and coefficients of Al_2O_3/Fel_2O_3 ranged from 2.06 to 11.5, while there also is no significant difference both between in the soil types and parent materials.

Fe reduction in soil
There were obvious Fe reduction process for all the soil samples, and the difference of Fe reduction rates were significant for the different soil samples. As to the total Fe reduction, Typic Hapli-Udic Ferralosols (S-TF2) and Typic Gleyi-Stagnic Anthrosols (A-TGA2) achieved the highest Fe reduction rates of 38.4% and 31.4%, respectively. The Fe reduction rates of most of the soils (16 samples) ranged from 10.0% to 20.0%. Only five soil samples, including Xanthic Hapli-Udic Ferralosols (B-XF), Typic Rhodi-Udic Ferralosols (B-TF), Rhodic Hapli-Udic Ferrosols (B-RF), Leachic Carbonati-Udic Ferrosols (L-LF2), and Xanthic Hapli-Udic Ferrosols (G-XF1), achieved the low Fe reduction rates, which were all lower than 10%. Fe reduction occurred mainly on the surface of the soils. However, some of Fe can be easily dissolved when the soils were suspended with water, and the dissolved Fe can also be reduced. The dissolved Fe reduction rates ranged from 0.03% to 7.94%, which were much lower than those of total Fe for every soil. And also, varied Fe reduction rates were obtained in different soils. S-TF2 also achieved the highest dissolved Fe reduction rate of 7.94%, while the dissolved Fe almost can not occurred in Typic Ari-Udic Ferrosols (Q-TF) only with the rate of 0.03%.

Discussion

The 23 soil samples used in this study represent a diversity of physicochemical properties typical of red soils from South China in subtropical area. Thus, key relationships identified between soil properties and Fe reduction processes should be generally applicable to this region. Owing to the high content of Fe in the soils from South China, the geochemical processes of the contaminants in these soils can be relevant with the Fe cycle, especially the Fe reduction. However, the characteristics and the weathering intensity of the soils are important for determining the Fe reduction process.

The soil pH mainly affected the reaction activity in the solution while the surface of soils was only slightly affected by it. The organic matter in soils were constitute of complicated components, in which only those with the function of electron transformation can accelerate the Fe reduction rates (Chacon *et al.* 2006, Peretyazhko and Sposito 2005). However, the organic matters in the soils used in this study were mainly the cellulose which was not active. So, as shown in Table 1, the total Fe reduction rates were not relevant with either the soil pH or the content of organic matters. The weathering process had significant action on the soils, and the soils with high weathering intensity can resulted in the high crystal extent, which were more difficult to be reduced than that of amorphous and complex Fe in the soils. As shown in Table 1, the total Fe reduction rates were positive related with the weathering coefficients of both of SiO_2/Al_2O_3 and Al_2O_3/Fe_2O_3, with the relationships of y=0.82x+4.76 and y=1.04x+3.15, respectively. This indicated that the Fe in the soils with lower weathering degree can be more readily to reduce. However, the reduction potential of dissolved Fe was mainly affected by the soils solution, and increase the soil pH can reduce the reduction potential of the dissolved Fe species. Furthermore, increase the soil pH can lead to the integration of Fe to the surface of soil, which was more readily to be reduced. So, the dissolved Fe reduction rates of the different soils were positively related with the soil pH, with the R^2 of 0.544 and p of 0.007. And the weathering intensity also has the negative effect on the reduction process of the dissolved Fe, in which the reduction rates of the dissolved Fe were linearly related with the weathering coefficients as presented in Table 1, with the relationships of y=0.31x+0.60 and y=0.43x-0.21, respectively with SiO_2/Al_2O_3 and Al_2O_3/Fe_2O_3.

Table 1. The parameters of the linear relationship between the soils characteristics and the Fe reduction rates.

	Total Fe reduction		Dissolved Fe reduction	
	R^2	p	R^2	p
pH	0.29	0.19	0.54	0.01
Organic matters	0.11	0.63	0.19	0.38
Fe_2O_3	0.55	0.01	0.52	0.01
Al_2O_3	0.39	0.07	0.35	0.11
SiO_2	0.25	0.49	0.17	0.44
SiO_2/Al_2O_3	0.36	0.09	0.43	0.04
Al_2O_3/Fe_2O_3	0.44	0.04	0.57	0.01

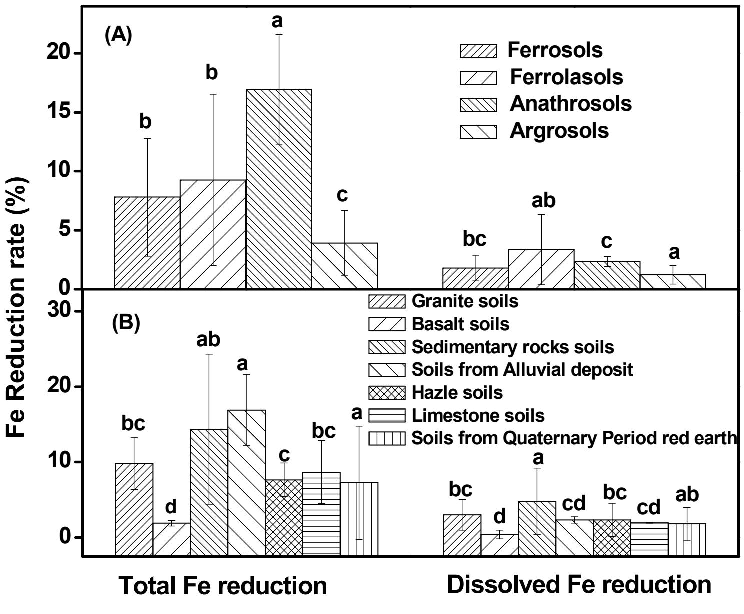

Figure 1. The average Fe reduction rates in different soil types (A), and in the soils developed from different parent materials (B).

The soil types can also affect the Fe reduction process. As shown in Figure 1A, The Fe in the Anathrosols conducted a higher reduction rates than in the other three types of soil, i.e. Ferrosols, Ferrolasols, and Argrosols. Anathrosols were affected by the activities of human being, which give the soils more ploughing and caused higher surface area. So, more reactive sites can be provided for Fe reduction, resulting in the higher total Fe reduction rates than the other soils. And Fe in soils developed from different parent materials also had different Fe reduction rates. Fe in soils developed from sedimentary rocks soils and from Alluvial deposit had the higher total Fe reduction rates than the soils from other parent materials (Figure 2B).

Conclusion

The Fe reduction processes of different soils in South China were affected by the soil characteristics and the weathering coefficients. The high weathering intensity of the soils can inhibit the reduction rates of the total Fe in soils, while the soil pH and content of organic matters was not related with the total Fe reduction rates. The dissolved Fe reduction rates were positively related with the soil pH, and they were also related with the soil weathering coefficients.

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