

Stable Fe isotopes - a prospective tool for investigating soil processes

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Abstract

Soil preservation for the future is one of the major objectives of the present-day research. Variations of the isotopic signatures of major elements recorded in soils can bring information about the nature and behaviour of major soil constituents in response to climatic changes and human-induced pressures. We have analysed variations of the Fe isotopic compositions in soils with the objective of (i) investigating mechanisms that control soil development and (ii) examining the impact of various factors, such as climate, topography and intensive human activity on the soil evolution. Our results show significant vertical variations of Fe isotopic composition within redoximorphic soils (Luvisol-Gleysol and Gleysol) but only limited variations within the well-drained Cambisol. No simple relationship can be established between the Fe isotopes variations and pedogenic Fe transfer. Although redox-controlled Fe-mobilization appears to be the main process, additional mechanisms (i.e., primary mineral alteration or other in situ transformations) and factors (i.e. topography) need to be examined, in order to decipher and interpret the Fe isotopes record in soils.

Key Words

Soil conservation, iron isotopes, agriculture, climate

Introduction

Soil durability is continually tested by ongoing climatic changes and by human-induced pressures. In order to insure soil preservation for the future, understanding mechanisms and processes that control soil evolution is among the major scientific challenges. In addition to frequently used methods, isotopes of major elements represent a powerful tool for studying soil processes and can bring helpful information about the nature and dynamics of major soil constituents and their behaviour in response to climatic and anthropogenic changes. Iron is the fourth most abundant element on Earth, it is present in all geological and biological materials and plays an important role in soil structure. Studies of the Fe isotopic compositions of various materials have been made possible by recent progress in analytical techniques, such as multi-collector inductively coupled-plasma mass spectrometry (MC-ICP-MS) (e.g., Beard *et al.*, 2003; Albarède and Beard, 2004; Dauphas and Rouxel, 2006). Thus, investigation of the Fe isotopes variations in soils can help shed light on the mechanisms that play dominant roles in the behaviour of soil constituents in response to various human- and climate-induced pressures.

Fe isotopes variations in redoximorphic soils

Among the most important mechanisms that control Fe isotope fractionation in soils are: modification of the oxidation-reduction state, complexation with organic matter, dissolution and precipitation of Fe minerals. Previous studies demonstrated that there exist systematic variations of Fe isotopic compositions in soils (e.g., Fantle and DePaolo, 2004; Thompson *et al.*, 2007; Wiederhold *et al.*, 2007a; Wiederhold *et al.*, 2007b; Johnson *et al.*, 2008). However, the relationship between the Fe isotopes variations and pedogenic Fe-translocation remains unclear and is complicated by further biochemical mechanisms such as plant uptake and production, and transfer and biodegradation of organo-metallic complexes.

Redox-related transformations and Fe transfer are important processes in redoximorphic soils. We have studied vertical and lateral variations of the Fe isotopic composition of the soils affected (i) by seasonal modifications of water-saturation conditions and (ii) by human activity (intensive agriculture). The aim of our work is to shed light on the dominant mechanisms that control the evolution of redoximorphic soils and to examine the impact of various factors, such as climate, topography and intensive human activity on soil evolution.

Sampling area

Soil samples were collected in the Kervidy-Naizin catchment basin located in Brittany, western France. The sampling area belongs to the Environmental Research Observatory AgrHyS (ERO) designed to study the response time of hydro-chemical fluxes to the evolution of agro-hydrosystems (ORE AgrHyS, 2007a). The

region is characterised by oceanic, humid and temperate climate with mean annual precipitation of 909 mm and monthly mean temperature ranges from 5.4°C to 17.4°C (ORE AgrHyS, 2007b). The soils developed on weathered upper Proterozoic schists. They are locally dominated by silt, clay or sandstone materials and contain a large number of secondary minerals such as Fe-oxides and oxi-hydroxides (hematite, goethite), Mn-oxides, illite, smectite, kaolinite, etc. Soil evolution in the area was influenced mainly by climate with an important short-term variability and by human activity through an intensive agriculture.

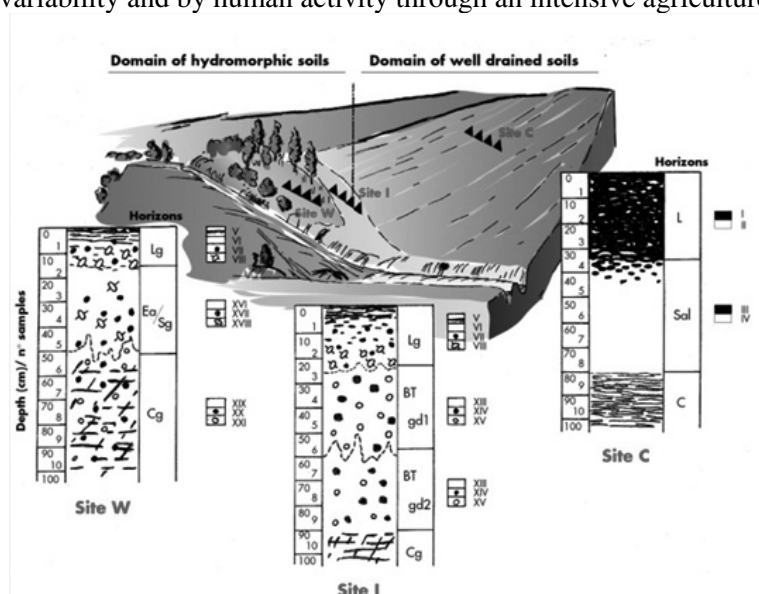


Figure 1. Drawing of the sampling area (from Trolard and Bourrié, 2008).

Three dominant soil types were described in the Kervidy-Naizin catchment site (e.g., Jaffrezic, 1997):

- (i) Cambisol located on the hill slope (site C, Figure 1) is used as cropland and is characterised by dominantly well-drained, oxic conditions. It consists of three horizons: Ap-B-C.
- (ii) Luvisol-Gleysol located in the transition zone (wasteland) between the well-drained cropland and poorly-drained lowermost part of the landscape (site I, Figure 1). The soil consists of a horizon sequence Apg-Btg-Cg and contains redoximorphic features such as mottling and rust accumulations in root spaces.
- (iii) Gleysol located in the bottomland (wasteland) (site W, Figure 1), at proximity to a small river. It is characterised by poorly-drained conditions, shallow water table and waterlogged environment. The soil consists of a horizon sequence Apg-E-Cg and is characterised by typical redoximorphic features that have developed due to an excess of water of topographical origin.

Samples and methods

We collected samples using an auger from profiles in the Cambisol (cropland on the hill slope), in the Luvisol-Gleysol (transition zone) and in the Gleysol (downslope redoximorphic zone). One sample was taken every 10 cm in order to obtain high spatial vertical resolution. An aliquot of each sample was dried and ground into fine powder using an agate mortar. For the isotopic measurements, approximately 300 mg of sample powder was treated with 30% H₂O₂ in order to eliminate organic matter and then dissolved using a mixture of concentrated HF-HNO₃ acids, at high temperature (~130°C). Iron and other trace metals (Cu, Zn) were separated and further purified using ion exchange resins (AG MP1, AG1X8). Iron concentrations were analysed using ICP-AES (Icap 6300) at the Laboratoire de Sciences de la Terre, Ecole Normale Supérieure de Lyon, France. Iron isotopic compositions were analysed using high-resolution MC-ICP-MS Nu1700 (national instrument at the Laboratoire de Sciences de la Terre, Ecole Normale Supérieure de Lyon, France). A standard-bracketing approach was used to correct for instrumental mass bias and isotope data are reported in delta notation: $\delta^{56}\text{Fe} = [({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}/({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] * 10^3 (\text{‰})$.

Results and discussion

The iron concentration remains constant within the Cambisol profile (hill slope), indicating no significant vertical transfer of iron with depth (Figure 2 a). Moreover, the Fe isotopic compositions are uniform, within the analytical error, but we observe a slight increase in $\delta^{56}\text{Fe}$ in the B-horizon. In contrast, the Luvisol-Gleysol (transition zone) and Gleysol (bottomland) show significant variations of the Fe concentrations and Fe isotopic compositions with depth (Figure 2 b, c). The surface horizons (Apg) of both the Luvisol-Gleysol and Gleysol are depleted in Fe compared to the surface horizon of the Cambisol and the Fe content increases

with depth. The $\delta^{56}\text{Fe}$ ranges vertically from -0.1 to +0.2 ‰ within the Luvisol-Gleysol (Figure 2 b) and from -0.2 to 0.2 ‰ within in the Gleysol (Figure 2 c).

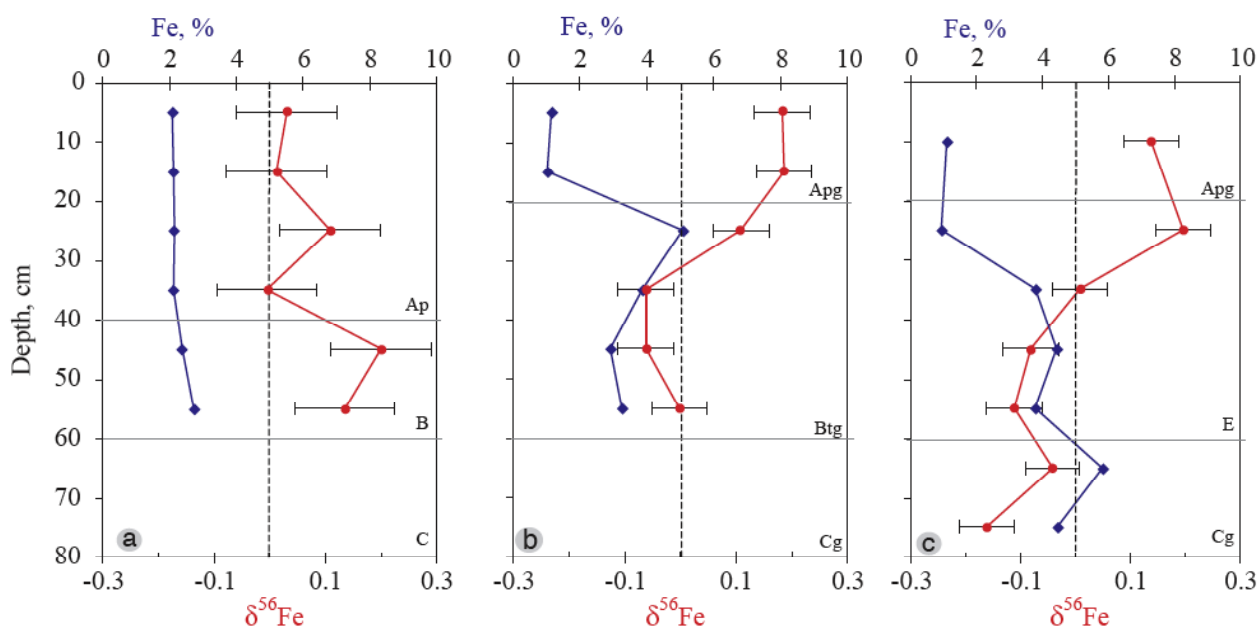


Figure 2. Vertical variations of the Fe concentration (blue diamonds) and Fe isotopic composition (red circles) in the three soils: (a) Cambisol (hill slope), (b) Luvisol-Gleysol (transition zone) and (c) Gleysol (bottomland). Error bars indicate 2σ for the Fe isotopic analyses and range from 0.05 to 0.09 ‰. Grey horizontal lines with abbreviations indicate horizon limits.

Uniform Fe concentrations and Fe isotopic compositions were previously described by Wiederhold *et al.* (2007a) in a freely drained Cambisol and indicated that Fe remained immobile due to dominant oxic conditions in well-aerated soils. Our results are consistent with the absence of vertical Fe transfer in the Cambisol (Figure 2 a). However, we observe a slight increase of $\delta^{56}\text{Fe}$ in the B-horizon, which suggests enrichment in heavy Fe isotopes at depth. This enrichment is likely to be linked to the in situ mineral transformation, rather than to Fe mobilization.

Significant vertical variations in the Fe concentrations and Fe isotopic compositions observed in the Luvisol-Gleysol and Gleysol (Figure 2 b, c) are consistent with a soil development influenced by important seasonal variations of the water regime, and consequently, by modifications of the oxidation-reduction conditions. The lowest Fe concentrations observed in the surface horizons (Apg) are associated with the highest $\delta^{56}\text{Fe}$ within both, Luvisol-Gleysol and Gleysol profiles. In waterlogged environment, increased accumulation of organic matter and weathering of clay minerals lead to remobilization of Fe as organo-metallic complexes or dissolved Fe^{II} (e. g., Fritsch *et al.*, 2009). Light Fe isotopes preferentially released during bacterially mediated dissolution in reducing conditions or during ligand-controlled dissolution are transferred either vertically or laterally, by the excess runoff water. Our results, i.e. high $\delta^{56}\text{Fe}$ in the topsoil and low $\delta^{56}\text{Fe}$ in depth, are consistent with the preferential release of the light Fe isotopes during Fe-oxi-hydroxides dissolution and depletion of light Fe in the surface horizons of the waterlogged soils. Iron content increases gradually with depth indicating accumulation of the Fe removed from the upper horizons. At the same time, the $\delta^{56}\text{Fe}$ decreases with depth and show progressive enrichment of deeper horizons in light Fe isotopes. Furthermore, we observe several particularities in the soil affected by waterlogging. In the Luvisol-Gleysol (Figure 2 b), there is a peak of Fe concentration on the top of the Btg horizon corresponding to the seasonal water table-level variations. However, the lowest $\delta^{56}\text{Fe}$ does not correspond to the maximum Fe content but is located deeper in the soil profile, suggesting that processes other than Fe translocation are involved in the Fe isotopes fractionation within this soil.

In addition, in the Gleysol we observe development of the eluvial (E) horizon, which should show depletion in Fe because of Fe-leaching under reducing conditions. Instead we observe a gradual increase of Fe content with depth associated with a decrease of $\delta^{56}\text{Fe}$. The light Fe accumulation within E horizon might indicate temporary oxidizing conditions leading to Fe fixation (lateral input from the uphill and Fe accumulation).

Conclusions

Vertical and lateral variations of the Fe isotopic composition (i) record spatial and temporal changes of soil conditions and (ii) reflect dominant mechanisms that play a role in the soil evolution. Thus, the Fe isotope studies could bring helpful information for understanding the soil processes. However, mechanisms that fractionate Fe isotopes in soils are complex (modification of redox conditions, complexation, plant uptake, etc.) and the relationship between Fe isotope fractionation and pedogenic Fe transfer is not straightforward. In order to interpret the Fe isotope record in soils, we need to decipher small-scale variations (e. g. sampling and analyses of individual soil minerals and redoximorphic features), and particularly those related to in situ mineral transformations. Also, additional comprehensive investigations are necessary on soils developed under different conditions. Alternatively, combined studies using isotopes of other metallic elements with geochemical behaviour differing from that of Fe (Zn or Cu) should help discriminate between dominant soil processes.

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