

# A preliminary mixing model for Fe isotopes in soils

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## Abstract

Iron partitioning data and whole soil  $\delta^{57}\text{Fe}$  values were combined to calculate the isotopic composition of Fe mixing end-members in profiles of a Czech forest soil and an Israeli semi-arid soil. A least-squares method was used to estimate the Fe isotopic composition of the end-members representing the three main Fe reservoirs in the Czech soil: (1) silicates ( $\delta^{57}\text{Fe} = -0.02 \pm 0.17\text{‰}$ ), (2) organically bound Fe ( $\delta^{57}\text{Fe} = -0.48 \pm 0.27\text{‰}$ ), and (3) pedogenic Fe-oxides ( $\delta^{57}\text{Fe} = -1.07 \pm 1.02\text{‰}$ ). A lack of variation in the isotopic and chemical partitioning patterns in the Israeli soil prevented the application of the least-squares technique, although an Fe-oxide end-member is proposed using a similar mixing model ( $\delta^{57}\text{Fe} = -1.72 \pm 1.16\text{‰}$ ). Combination of the isotopic values for the different reservoirs with published fractionation data from previous studies suggests that the isotopic signature of the silicate fraction in the Israeli soil is dominated by lithogenic sources, while the Fe-oxide pool is influenced mainly by pedogenic precipitation/dissolution processes. The results demonstrate the potential for Fe isotopes as a tool to quantify Fe cycling in soils.

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## 1. Introduction

Iron is a critical nutrient in soils and its availability for plant uptake is determined both by its absolute concentration in the soil and by the way in which it is partitioned between the different mineral and organic

phases (Murad and Fischer, 1988). Understanding Fe partitioning mechanisms is therefore crucial in order to fully assess the bioavailability of Fe in soils, as well as its biogeochemical cycling. Although numerous studies have examined Fe partitioning, new analytical techniques, such as stable iron isotope methods, have the potential to shed additional light on the behaviour of Fe in soils

While a growing body of literature exists concerning Fe isotopes in natural waters, sediments, as well as igneous and extraterrestrial rocks (see Beard et al., 2003b; Anbar, 2004 for recent reviews), only a limited

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number of studies have reported values for Fe isotopes in soil profiles. von Blanckenburg (2000) examined Podzol soil profiles, while Wiederhold and von Blanckenburg (2002) examined the lateral variation in Fe isotope composition in a natural soil catena. More recently, Fantle and DePaolo (2004) reported data on a Californian forest soil. In these studies, it was suggested that the observed isotopic patterns were the result of biotic and abiotic fractionation coupled with transport processes within the soil profiles. Irrespective of whether such fractionation is of organic or inorganic origin, the reduction and oxidation cycles of Fe are likely to be the key controls of isotopic composition. However, the complexity of soil systems means that Fe isotopic signatures on their own are limited with respect to what they can reveal about soil processes. In order to fully understand the isotopic patterns found in soils, and to correctly interpret them in terms of soil processes, the relationship between Fe isotopic composition and Fe partitioning must first be determined. Studies examining Pb isotopes in soils have demonstrated that such an approach can yield important additional information concerning soil processes (Teutsch et al., 2001; Emmanuel and Erel, 2002), and a similar integrated approach should prove rewarding when applied to the study of iron.

In this paper, Fe isotope techniques are coupled with a method of selective sequential dissolution to examine the relationship between Fe isotopes in whole soil samples and Fe partitioning. Samples from a Czech forest soil and an Israeli semi-arid soil are examined and the data are used to calculate the average isotopic composition of Fe in other soil fractions. Possible implications concerning Fe partitioning processes are explored and suggestions for future studies are discussed.

## 2. Methodology

### 2.1. Site description, sample preparation, and laboratory processing

The forest soils examined in this study were sampled from the Načetín site in the Krušné hory Mountains of the northwestern Czech Republic. Načetín falls within the “Black Triangle”, a region on the German–Czech–Polish border which has been

severely polluted by emissions from heavy industry and coal burning power stations. The sampling site is situated in a forested plot isolated from heavy road traffic and the soil is classified as Haplorthods. The base-rock at the site consists of quartzite and biotite–sillimanite gneiss. The semi-arid soil samples were collected in Israel from the Shaar Hagay area in the Judean Mountains. The soil in the sampling area is a shallow Terra Rossa (Haploxerept) and overlies a bedrock of limestone and dolomite. The climate is typical of the Southern Mediterranean region with little or no rainfall during the summer months.

All soil samples were dried at 45 °C to constant weight, passed through clean polyethylene sieves to remove particles larger than 2 mm, and homogenized using standard splitting techniques. Care was taken to prevent contamination of the samples, and much of the subsequent laboratory processing was conducted in clean-room conditions.

To determine total Fe content and Fe isotope composition in the samples, 0.1 g of homogenized powdered soil was totally digested using a mixture of concentrated HF, HCl, and HClO<sub>4</sub> in a Teflon® beaker. The chemical partitioning of Fe in the soils was determined using a selective sequential dissolution (SSD) technique that was adapted from the method first described by Tessier et al. (1979). The SSD procedure treats the soil samples with six consecutive dissolution stages, with each step targeting metals associated with a different soil component. After each step, the suspension is centrifuged, and the supernatant extracted for the determination of trace and major element concentrations. For further details of the SSD method, the reader is referred to Han and Banin (1997) and Teutsch (1999).

Although there has been debate concerning the selectivity of sequential dissolution methods (e.g., Nirel and Morel, 1990; Tessier and Campbell, 1991), such extraction techniques remain a useful tool in determining metal partitioning in soils. As the chemical association of the metal ions released at the different stages of the SSD procedure employed in this study has been discussed in previous works (Teutsch, 1999; Teutsch et al., 2001; Emmanuel and Erel, 2002), only a brief review will be given here.

The sequential extraction method used in the present study was initially developed for semi-arid soils, and a summary of the procedure and the chemical

association of the different stages is presented in Table 1. In the Israeli soils, all the dissolution stages, with the exception of the third step ( $OM_{\text{ERO}}$ ), displayed adequate selectivity concerning the targeted soil phases (Teutsch, 1999). When applied to the Czech samples, the method proved to be less selective during the first three dissolution steps (Emmanuel and Erel, 2002), requiring a different interpretation for the source of Fe released into solution.

The first stage of dissolution ( $OM_{\text{EX}}$ ) targets the exchangeable fraction, ions that are bound to surfaces by outer-sphere binding. As free ion  $Fe^{2+}$  and  $Fe^{3+}$  is expected to participate in inner-sphere binding, Fe released during this stage is likely to have been bound to the surface of solid phases via organic complexes. In the Czech soils, such ternary complexes should be relatively common and may be soluble at the exchangeable stage, thereby introducing Fe into solution.

The second step of dissolution was initially intended to dissolve carbonate minerals. Given the absence of carbonate in the Czech soils, Fe released at this stage must obviously be associated with a different phase, and the relatively low concentrations of major ions suggest that no significant mineral phases undergo dissolution. Thus, the Fe released is likely to be bound to solid surfaces, and is probably organically bound in the O-horizon samples.

The third stage of dissolution ( $OM_{\text{ERO}}$ ) was designed to target Mn oxides, although only minor concentrations of Mn were measured during this step in the Czech soils. Concentrations of Fe and Al were often no higher than concentrations in the preceding

stage, and the similar behaviour of the  $OM_{\text{SB}}$  and  $OM_{\text{ERO}}$  fractions suggests a similar origin. Thus, it is concluded that Fe released during the first three stages in the Czech soils in samples containing high concentrations of organic matter is most likely to be organically bound. Although some uncertainty remains concerning the chemical association of Fe during these dissolution steps, in the Czech soils the cumulative Fe associated with these stages typically represents <5% of the total Fe in the soil and never exceeds 7%. In the Israeli soils, Fe released during these steps is always far less than 1% of the total iron.

Subsequent steps of the SSD procedure specifically target Fe that is organically bound ( $OM_{\text{ORG}}$  fraction), Fe-oxides (OX fraction), and silicate-bound iron (RES fraction), and these stages demonstrated adequate selectivity in both the Israeli and Czech soils. The organically bound fraction includes Fe that is sorbed to organic surfaces, complexed by organic ligands or incorporated into organic macromolecules as amorphous oxides. The term Fe-oxides is used throughout this paper to refer to both Fe-oxides and hydrous Fe-oxides that are not associated with the organic matter fractions. Silicate-bound Fe is considered to be incorporated into the crystalline structure of the primary and secondary silicate minerals.

## 2.2. Analytical methods and isotopic analyses

Sample solutions were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 3300) to determine Fe and other major element concentrations. Calibration of the ICP-AES

Table 1  
Summary of the SSD procedure

Stage	Conditions	Fe association in Czech soils	Fe association in Israeli soils
$OM_{\text{EX}}$	1 M $NH_4NO_3$ buffered to pH 7 with $NH_4OH$	Exchangeable, complexed by organic ligands or sorbed to organic particles	Exchangeable
$OM_{\text{SB}}$	1 M NaAc buffered to pH 5	Bound to surfaces of organic particles	Carbonate bound
$OM_{\text{ERO}}$	0.04 M $NH_2OH-HCl$ in 25% HAc at room temperature	Bound to surfaces of organic particles	Carbonate bound
$OM_{\text{ORG}}$	0.01 M $HNO_3$ and 30% $H_2O_2$ at 80 °C	Bound to organic matter or incorporated into organic macromolecules as amorphous Fe-oxides and hydrous Fe-oxides	Bound to organic matter or incorporated into organic macromolecules as amorphous Fe-oxides and hydrous Fe-oxides
OX	0.04 M $NH_2OH-HCl$ in 25% HAc at 90 °C	Fe-oxides and hydrous Fe-oxides	Fe-oxides and hydrous Fe-oxides
RES	Total digestion with $HF-HNO_3-HCl-HClO_4$	Bound within crystalline structure of silicate minerals	Bound within crystalline structure of silicate minerals

was conducted using commercial aqueous standards of the various elements and short time variability and matrix effects were reduced by the addition of an internal Sc standard.

At the onset of the study, measurement of the isotopic composition of the various SSD fractions was considered, but uncertainties concerning isotopic fractionation during the extractions rendered the value of such measurements questionable. There has been only limited work on the application of selective dissolution techniques to the study of Fe isotopes (e.g., Brantley et al., 2004), and additional work is required in order to determine protocols that can reliably measure Fe isotopic compositions in the various soil fractions. Thus, the analytical focus of the present study was restricted solely to whole soil samples.

The method used to prepare Fe solutions for iron isotopic analysis is described in detail by Matthews et al. (2004) and only a brief account is given here. A portion of the acid digested solution (Section 2.1) containing 100 mg Fe was placed in a Teflon<sup>®</sup> beaker with 1 drop of 30% H<sub>2</sub>O<sub>2</sub> and evaporated to dryness. The solid was then redissolved in 1 ml 6 M HCl to produce a 100 ppm Fe solution that was then subjected to double chromatographic separation procedure with a precleaned Biorad Macropore anion exchange resin MP1 100–200 mesh in chloride form. Recovery of Fe from the column was found to be >99%. The final eluted sample was evaporated to dryness with 1 drop of 30% H<sub>2</sub>O<sub>2</sub> to ensure that all the

Fe was in ferric form. The dry sample was then redissolved in 0.1 M HCl to produce a 10 ppm solution suitable for mass spectrometry.

Isotopic measurements were made by adopting a sample bracketing method using a standard solution (1000 ppm Fe in 1 M HCl) prepared from the IRMM-14 Fe standard. Prior to analysis, 1 drop of 30% H<sub>2</sub>O<sub>2</sub> was added to 0.5 ml of the IRMM-14 stock solution, which was evaporated to dryness and dissolved in 50 ml 0.1 M HCl to produce a 10 ppm ferric ion working standard. In addition to the precautions to ensure that the Fe in both standards and samples was in the ferric state, the analysis was made within a few days of preparation of the 10 ppm Fe solutions. Iron isotopic measurements were carried out using a Nu Instruments MC-ICP-MS and sample and standard Fe solutions were introduced to the plasma through a desolvating nebulizer without N<sub>2</sub> flow. All analyses reported in the present study are given in the  $\delta^{57}\text{Fe}$  notation relative to the IRMM-14 standard:

$$\delta^{57}\text{Fe} = \left[ \left( \frac{{}^{57}\text{Fe}/{}^{54}\text{Fe}}{\left( \frac{{}^{57}\text{Fe}/{}^{54}\text{Fe}}{\right)_{\text{IRMM-14}}} - 1} \right) \right] \times 1000. \quad (1)$$

Mass spectrometric reproducibility was tested by running the IRMM-14 standard both as sample and as standard. Procedural errors were determined by processing IRMM-14 solution samples using the same double chromatographic separation protocol as the

Table 2  
Selected soil parameters

Sample	Soil	Depth (cm)	Pedogenic horizon	pH <sup>a</sup>	Organic matter <sup>b</sup> (mass%)	HWC <sup>c</sup> (mass%)	Silicates (mass%)
SE-2-3	Forest	2–3	O	3.1	71.5	7.8	25
SE-2-5	Forest	4–5	O	3.1	50.8	6.3	37
SE-2-7	Forest	6–7	O	3.1	25.2	3.5	57
SE-2-9	Forest	8–9	OA	3.1	14.1	2.2	76
SE-2-14	Forest	39	BC	4.1	6.0	1.2	93
SE-2-12	Forest	58	BC	4.1	5.7	1.1	94
SHO-2-4	Semi-arid	0–6	A	6.8–7.9	10.8	8.1	73
SHO-2-3	Semi-arid	6–11	C	6.8–7.9	4.2	6.7	84
SHO-2-2	Semi-arid	11–18	C	6.8–7.9	3.9	7.0	85

<sup>a</sup> Values for the forest soils have been supplied by T. Paces, Czech Geological Survey, while the range for the semi-arid soils is from Koyumedziski et al. (1988).

<sup>b</sup> Determined by loss-on-ignition.

<sup>c</sup> Hygroscopic water content.

soil samples. This method yielded a value for IRMM-14 samples of  $\delta^{57}\text{Fe}=0.06\% \pm 0.09$  ( $1\sigma$ ). Replicate analyses of samples using repeat extractions in different runs and/or isotopic analyses on different days also indicate that external ( $1\sigma$ ) errors are typically less than 0.1% (Matthews et al., 2004). Two soil samples were processed and analyzed in duplicate (SE-2-9 and SHO-2-3) in this study and demonstrated errors within those reported here.

### 2.3. Determination of soil characteristics

A number of soil parameters, including hygroscopic moisture, organic matter content, and soil pH, were determined in order to more fully characterize the soils studied (Table 2). Hygroscopic water content was measured by weight loss at 105 °C (Topp, 1993), while the loss-on-ignition method was used as a proxy for organic matter content (Kirel, 1993). The mass of the residual fraction of SSD procedure was used to estimate silicate content according to the method described by Emmanuel and Erel (2002).

X-ray diffraction (XRD) was used to identify the main mineral phases in the Czech and Israeli soils. At Načetín, quartz, muscovite, kaolinite, vermiculite, and plagioclase were identified, while the Israeli soil contained carbonates, K-feldspar, plagioclase, quartz, and various clays including montmorillonite and mixed layer illite–smectite. Fe and Al oxides were not detected in the soils during the XRD analyses, presumably due to their low concentrations in the soils.

## 3. Results and discussion

### 3.1. Fe partitioning and isotopic patterns in forest soils

An examination of Fe concentrations and Fe partitioning highlights a number of features typical of forest soils. In Table 3, it can be seen that total concentrations of Fe in the Czech samples generally increase down the profile. As Fe is primarily associated with the oxide and silicate phases, such behaviour simply reflects the decreasing organic matter content and increasing presence of primary and secondary minerals with depth. The change in soil composition through the profile also causes a shift in the association of Fe, and this can be seen in an examination of Fig. 1 and Table 3. In the O-horizon, Fe is predominantly associated with organic matter (~30–50%; OM<sub>EX</sub>, OM<sub>SB</sub>, OM<sub>ERO</sub>, and OM<sub>ORG</sub> fractions) and silicates (~40–60%; RES), while in deeper horizons, silicates and oxides (OX) represent the main Fe reservoirs (>80% and 9–16%, respectively). These trends are similar to those observed in other forest soils (Blume, 1988).

The profiles of  $\delta^{57}\text{Fe}$  of the soil samples as a function of depth are given in Fig. 2. In contrast to the Fe concentration and partitioning patterns in the soil samples, the factors controlling the isotopic patterns in the soil are not readily apparent. An initial value for  $\delta^{57}\text{Fe}$  of  $-0.28\%$  at a depth of 2–3 cm decreases to a minimum of  $-0.46\%$  at 6–7 cm at the base of the O-horizon. In deeper horizons,  $\delta^{57}\text{Fe}$  increases to values of around  $-0.1\%$ . By comparison,

Table 3  
Iron content per unit mass of soil associated with the different SSD fractions and  $\delta^{57}\text{Fe}$  of whole soil samples

Sample	Depth (cm)	OM <sub>EX</sub> (mg g <sup>-1</sup> )	OM <sub>SB</sub> (mg g <sup>-1</sup> )	OM <sub>ERO</sub> (mg g <sup>-1</sup> )	OM <sub>ORG</sub> (mg g <sup>-1</sup> )	OX (mg g <sup>-1</sup> )	RES (mg g <sup>-1</sup> )	Sum (mg g <sup>-1</sup> )	$\delta^{57}\text{Fe}$
SE-2-3	2–3	0.05	0.06	0.18	3.83	1.20	8.22	13.54	-0.28
SE-2-5	4–5	0.07	0.24	0.30	5.99	1.73	4.89	13.22	-0.30
SE-2-7	6–7	0.08	0.94	0.49	7.25	3.82	9.60	22.18	-0.46
SE-2-9a	8–9	<0.01	1.18	0.69	7.44	6.58	18.66	34.55	-0.33
SE-2-9b									-0.42
SE-2-14	39	0.01	0.09	0.12	0.39	3.72	37.22	41.54	-0.17
SE-2-12	58	0.01	0.14	0.19	0.42	6.30	33.01	40.05	-0.11
SHO-2-4	0–6	0.01	0.02	0.05	0.41	6.30	37.00	43.79	-0.32
SHO-2-3a	6–11	<0.01	0.02	0.07	0.12	6.70	44.60	51.50	-0.22
SHO-2-3b									-0.25
SHO-2-2	11–18	<0.01	0.01	0.07	0.11	7.20	46.70	54.10	-0.20

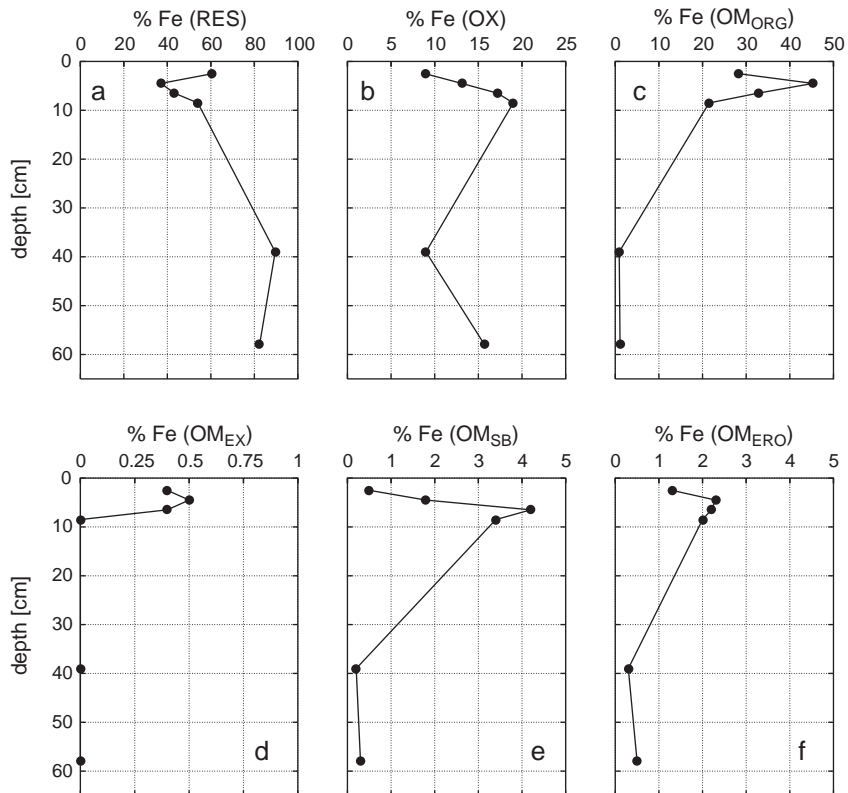


Fig. 1. Percentage of Fe associated with the different SSD fractions versus depth for the Czech forest soils. (a) Silicate; (b) Fe-oxides; (c–f) organic fractions. The average depth of each sample is indicated.

von Blanckenburg (2000) noted an isotopic variation of 1‰ in the profiles of Podzol soils, while Fantle and DePaolo (2004) reported a variation of 0.8‰ in a Californian forest soil. As with the present study, both von Blanckenburg (2000) and Fantle and DePaolo (2004) found the most negative samples at the base of the O-horizon.

Despite the complexity of soil systems, the factors controlling Fe isotopic composition can be understood by examining the plots of isotopic composition versus the proportion of Fe associated with each of the three primary soil fractions (Fig. 3). The linear regression lines for both the silicate ( $R^2=0.67$ ) and organic fractions ( $R^2=0.59$ ) suggest that the isotopic profiles are influenced by mixing between reservoirs with different isotopic signatures. The linear relationship between the proportion of Fe associated with the oxide component and the isotopic signatures is weaker (Fig. 3b). However, this does not indicate that Fe-

oxides play a minor role in the mixing process. Firstly, a lower correlation is anticipated due to the relatively small variation in the proportions of Fe associated with the oxide fraction (Fig. 3b). Second, an examination of isotopic mass balance equations shows that strictly linear relationships between partitioning and isotopic composition can only occur in two component mixtures, and not in ternary mixtures as is likely in the case of forest soils.

Clearly, the  $\delta^{57}\text{Fe}$  signature of the different Fe reservoirs may change with depth due to transport, precipitation/dissolution, and redox processes. Nevertheless, interpreting the Fe isotopic compositions recorded in the forest soils in terms of mixing between three distinct fractionated reservoirs is useful as a preliminary model. In the following section a systematic approach is presented for calculating the average isotopic compositions of the proposed mixing end-members.

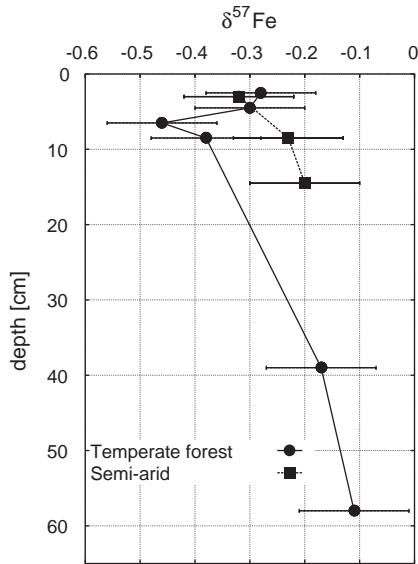


Fig. 2. Profiles of  $\delta^{57}\text{Fe}$  in the Czech temperate forest soils and the Israeli semi-arid soils. The mean depth of each sample is indicated and the error bars represent the  $1\sigma$  uncertainty of the isotopic measurements.

### 3.2. Multicomponent mixing models and end-member identification

An isotopic mass balance equation involving silicate, Fe-oxide, and organically bound Fe can be written for each sample:

$$a_{\text{silicate}}\delta^{57}\text{Fe}_{\text{silicate}} + a_{\text{ox}}\delta^{57}\text{Fe}_{\text{ox}} + a_{\text{org}}\delta^{57}\text{Fe}_{\text{org}} = \delta^{57}\text{Fe}_{\text{sample}} \quad (2)$$

where  $a$  is the fraction of Fe associated with each component, and the subscripts silicate, ox, and org refer to silicate, oxide, and organically bound Fe, respectively. If it is further assumed that the isotopic compositions of the mixing end-members do not change throughout the soil profile, the system of mixing equations representing the set of different samples from 1 to  $n$  can be written in matrix form

$$\mathbf{Ax} = \mathbf{b} \quad (3)$$

where

$$\mathbf{A} = \begin{pmatrix} a_{\text{silicate } 1} & a_{\text{ox } 1} & a_{\text{org } 1} \\ a_{\text{silicate } 2} & a_{\text{ox } 2} & a_{\text{org } 2} \\ \vdots & \vdots & \vdots \\ a_{\text{silicate } n} & a_{\text{ox } n} & a_{\text{org } n} \end{pmatrix} \quad (4)$$

$$\mathbf{x} = \begin{pmatrix} \delta^{57}\text{Fe}_{\text{silicate}} \\ \delta^{57}\text{Fe}_{\text{ox}} \\ \delta^{57}\text{Fe}_{\text{org}} \end{pmatrix}, \quad (5)$$

and

$$\mathbf{b} = \begin{pmatrix} \delta^{57}\text{Fe}_{\text{sample } 1} \\ \delta^{57}\text{Fe}_{\text{sample } 2} \\ \vdots \\ \delta^{57}\text{Fe}_{\text{sample } n} \end{pmatrix}. \quad (6)$$

When the number of samples,  $n$ , is equal to 3, the system of equations can be solved by Gaussian elimination. However, when  $n > 3$ , the system of equations is overconstrained and needs to be solved using the least-squares method (Stoer and Bulirsch,

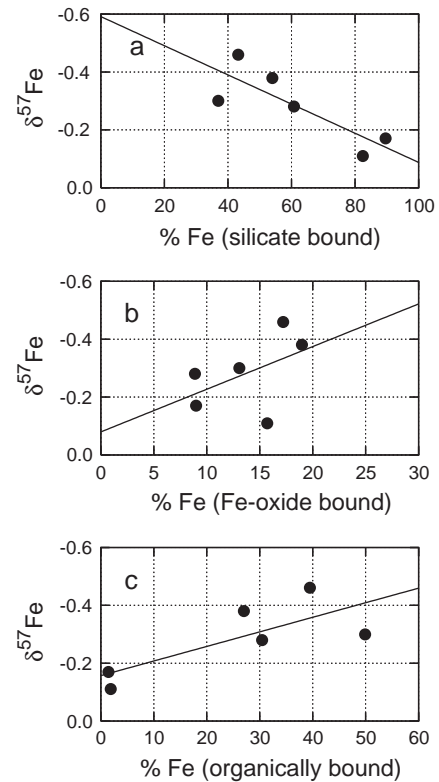


Fig. 3. Values of  $\delta^{57}\text{Fe}$  versus the percentage of Fe associated with the three main soil components for the Czech forest soils. (a) Silicates (RES fraction); (b) Fe-oxides (OX fraction); (c) organically bound (OM<sub>EX</sub>, OM<sub>SB</sub>, OM<sub>ERO</sub>, and OM<sub>ORG</sub> fractions). The straight lines represent linear regressions. Values of  $R^2$  for the three components are 0.67, 0.23, and 0.59 for the silicate, Fe-oxides, and organic fractions, respectively.

1980). Multiplying both sides of the equation by the transform of  $\mathbf{A}$ ,  $\mathbf{A}^T$ , such that

$$\mathbf{A}^T \mathbf{A} \mathbf{x} = \mathbf{A}^T \mathbf{b}, \quad (7)$$

a square system of equations is obtained that can then be solved by ordinary Gaussian elimination to yield “average” values for the isotopic end-members. This method avoids the need for direct determination of the different isotopic pools by methods such as selective dissolution and can be generalized to any number of mixing end-members.

The partitioning data presented in Table 3 are used to calculate values for the elements of  $\mathbf{A}$ . The proportions of Fe associated with organic matter are taken as the sum of the  $\text{OM}_{\text{EX}}$ ,  $\text{OM}_{\text{SB}}$ ,  $\text{OM}_{\text{ERO}}$ , and  $\text{OM}_{\text{ORG}}$  fractions, while the oxides and silicate proportions are represented by the  $\text{OX}$  and  $\text{RES}$  fractions, respectively. Using this approach, the following system of equations is obtained

$$\begin{pmatrix} 0.607 & 0.089 & 0.304 \\ 0.370 & 0.131 & 0.499 \\ 0.433 & 0.172 & 0.395 \\ 0.540 & 0.190 & 0.270 \\ 0.896 & 0.090 & 0.015 \\ 0.824 & 0.157 & 0.019 \end{pmatrix} \begin{pmatrix} \delta^{57}\text{Fe}_{\text{silicate}} \\ \delta^{57}\text{Fe}_{\text{ox}} \\ \delta^{57}\text{Fe}_{\text{org}} \end{pmatrix} = \begin{pmatrix} -0.28 \\ -0.30 \\ -0.46 \\ -0.38 \\ -0.17 \\ -0.11 \end{pmatrix}. \quad (8)$$

Solving using the least-squares method yields the following isotopic end-members:  $\delta^{57}\text{Fe}_{\text{silicate}} = -0.02 \pm 0.17\text{‰}$ ,  $\delta^{57}\text{Fe}_{\text{ox}} = -1.07 \pm 1.02\text{‰}$ , and  $\delta^{57}\text{Fe}_{\text{org}} = -0.48 \pm 0.27\text{‰}$ . The uncertainties indicated represent the standard deviation of Monte Carlo simulations with normally distributed errors for the isotopic measurements ( $\sigma = 0.1\text{‰}$ ) and the Fe partitioning data ( $\sigma = 2\%$ ), accounting for analytical and procedural errors. The relatively large calculated uncertainties reflect the sensitivity of the mixing equations to small deviations in isotopic composition, and error estimation must be recognized as an integral part of the least-squares method. As analytical methods improve, however, such errors should be reduced.

While these values represent average isotopic compositions, a number of important observations can be made. Firstly, the  $\delta^{57}\text{Fe}$  value for the silicate fraction is consistent with the values usually reported in oxidized lithogenic silicate materials (Beard and Johnson, 1999; Beard et al., 2003b). Secondly, the oxide frac-

tion possesses a negative isotopic signature, in contrast to lithogenic iron oxides which previous studies have shown to have  $\delta^{57}\text{Fe}$  values on average of approximately  $0.2 \pm 0.2\text{‰}$  relative to IRMM-14 (Beard et al., 2003b; Matthews et al., 2004). However, isotopically negative values for Fe-oxides have been observed in low temperature subsurface systems, where Fe has undergone redox cycling (Matthews et al., 2003). Furthermore, as the SSD procedure cannot distinguish between lithogenic and pedogenic Fe-oxides, the pedogenic Fe-oxide signature could be even more fractionated due to the presumably higher  $\delta^{57}\text{Fe}$  of the lithogenic Fe-oxides. A third important observation is that the calculated value for the organic matter fraction is also negative. Brantley et al. (2001) report a value of  $\delta^{56}\text{Fe} = -0.85\text{‰}$  for the exchangeable fraction of the soil examined in their study, and in organic horizons Fe associated with this fraction is predominantly associated with organic matter. The  $\delta^{57}\text{Fe}$  value for organic matter calculated here represents one of the first values reported for natural organic matter.

Thus, the differing signatures calculated in the silicate, pedogenic oxide, and organic matter fractions are likely to be the result of the reductive dissolution of silicates coupled with transport, oxidation, and oxide precipitation. These processes will be explored in greater depth in the following sections.

### 3.3. Iron partitioning and Fe isotopes in semi-arid soils

In contrast to the Czech forest soil, the variation in Fe isotope composition in the Israeli samples is slight and within the analytical error (Table 3; Fig. 2). Furthermore, it can be seen that nearly all the Fe in the Mediterranean soils is associated with the silicate fraction (~85%) with the Fe-oxides representing the minor component (~15%). The organic matter fraction does not represent a significant sink for Fe in the soils as only a small amount of organic matter is present in the soils.

Due to the lack of variation in soil composition and partitioning patterns, the least-squares method outlined in the previous section cannot be applied directly to these samples. However, if it is assumed that the silicate end-member possesses the same lithogenic signature as that found in the Czech forest soils (i.e.,

$\delta^{57}\text{Fe} = -0.02 \pm 0.17\text{‰}$ ), an average value of  $\delta^{57}\text{Fe} = -1.72 \pm 1.16\text{‰}$  is calculated by mass balance for the Fe-oxide fraction.

The isotopic composition of the silicates and Fe-oxides can be discussed in light of the soil's aeolian origin (Yaalon, 1987; Teutsch et al., 2001). While the isotopic composition of the silicates reflects their crustal provenance (Beard et al., 2003b), the strongly negative  $\delta^{57}\text{Fe}$  value in the oxide fraction suggests that the oxides are not rock derived, but are instead precipitated during a cycle that involves the weathering of silicate minerals during pedogenic processes including the reduction of ferric Fe, illuvial transport, and oxide formation. Experimental studies of biogenic and abiotic reduction of ferric minerals to ferrous iron show that the ferrous ion will be isotopically depleted in the heavy isotope (Beard et al., 1999; Johnson et al., 2002; Beard et al., 2003a; Welch et al., 2003; Brantley et al., 2004; Icopini et al., 2004). Thus, reduction is likely to play a major role in this isotope fractionation cycle.

### 3.4. Implications for Fe cycling in soils

Although the uncertainties are large, the calculated isotopic compositions of the Fe-oxides in the Israeli

and Czech soils are quite different. Such differences could reflect varying proportions of lithogenic versus pedogenic Fe-oxides and/or the different mechanisms by which Fe-oxides form in the two soils. How these pathways might affect the isotopic signatures of Fe in the various soil reservoirs and conversely what can be learned from Fe isotopes about these processes will now be explored using a simplified model that illustrates the primary fractionation processes involved in Fe cycling in soils.

Provided that reliable data is available on isotopic fractionations and the isotopic composition of the different Fe pools, important information can be retrieved regarding the interactions between the various reservoirs of Fe in soils. A schematic model, based on that of Murad and Fischer (1988) describing some of the main pedogenic processes involved in Fe cycling, shows the isotopic composition of the three main pools and the fractionation processes acting on each of the reservoirs (Fig. 4). The model includes both inorganic and organic interactions. Examples of inorganic processes include the weathering of silicate minerals to produce coprecipitated Fe-oxides, the release of Fe into solution by mineral dissolution, or the precipitation of Fe-oxides from the aqueous iron.

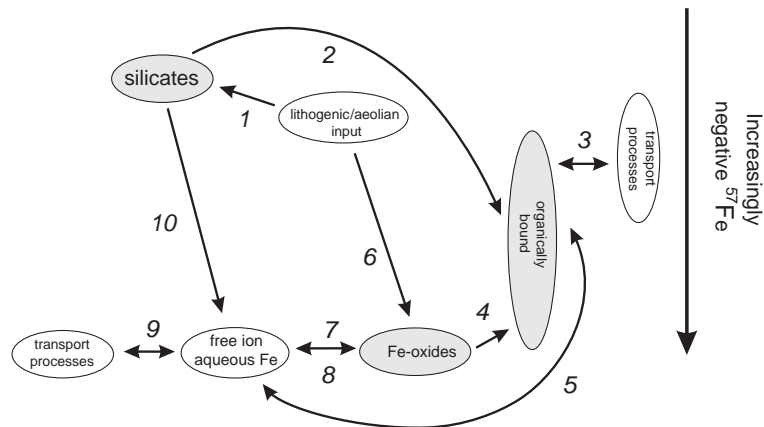


Fig. 4. Schematic representation of the main processes involved in Fe cycling in soils. In the Czech soils, the relative values for  $\delta^{57}\text{Fe}$  are constrained for the shaded reservoirs. The different processes described by the model can be summarised as follows: (1) Direct lithogenic/aeolian input into the soil silicate pool, (2) Dissolution of soil silicates by organic molecules and/or bacterial reduction to produce organically bound Fe, (3) Advective and diffusional transport processes of organically bound Fe, (4) Dissolution of Fe-oxides by organic processes, (5) Reversible transfer of Fe between the organic pool and the free aqueous state, (6) Direct input of lithogenic oxides into soil Fe-oxide pool, (7) Precipitation from free ion state, (8) Dissolution of Fe-oxides to free ion state, (9) Advective and diffusional transport processes of free Fe, (10) Incongruent dissolution of soil silicates to produce aqueous free Fe. The input reservoir of lithogenic material is taken as the average of crustal material ( $-0.06\text{‰}$ ; Beard et al., 2003b), while the equilibrium fractionation between aqueous Fe and Fe-oxides is taken as  $0\text{‰}$  (Skulan et al., 2002). The range of values spanned by the organic reservoir is intended to reflect the range of different processes that contribute to this pool.

Organic processes include the bacterial reduction of soil minerals, as well as mineral dissolution by siderophores and organic ligands.

From the model it can be seen that the overall isotopic signatures of the different pools are the result of the characteristic fractionations associated with the various processes and their respective contributions. If isotopic equilibrium holds, the fractionation processes acting on each reservoir will balance, and for every pool this can be expressed by a separate equation based on the lever law

$$\sum (f_{j-i} \Delta^{57}\text{Fe}_{j-i}) = 0, \quad (9)$$

where  $\Delta^{57}\text{Fe}_{j-i}$  refers to the fractionation induced by pathway  $j-i$  on reservoir  $j$  (i.e.,  $\Delta^{57}\text{Fe}_{j-i} = \delta^{57}\text{Fe}_j - \delta^{57}\text{Fe}_i$ ), and  $f_{j-i}$  indicates the relative contribution of each of these steps, such that  $\sum f_{j-i} = 1$ .

If the fractionations of the different processes are known, this equation can be applied to the different soil reservoirs to assess their relative influence on the isotopic signatures. This point can be illustrated using data from the silicate pool in the Israeli soils. As the organic content in the soils is low, organically mediated dissolution should be small. Thus, two major processes will govern fractionation: (1) direct lithogenic/aeolian input (pathway 1), and (2) weathering of silicates (pathway 10). With these simplifications, Eq. (9) can be written as

$$f_1 \Delta^{57}\text{Fe}_1 + f_{10} \Delta^{57}\text{Fe}_{10} = 0, \quad (10)$$

and the influence of pathway 1 can be calculated by

$$f_1 = \frac{\Delta^{57}\text{Fe}_{10}}{\Delta^{57}\text{Fe}_{10} - \Delta^{57}\text{Fe}_1}. \quad (11)$$

Estimates for the fractionation of the different pathways can be made from previous studies. A value for  $\Delta^{57}\text{Fe}_1$  can be estimated from the difference between the bulk signature for clastic sediments of  $\delta^{57}\text{Fe} = -0.06\text{‰}$ , (Beard et al., 2003b) and the isotopic composition of the silicates, yielding a fractionation of  $-0.04\text{‰}$ . From Skulan et al. (2002) pathways 7 and 8 are estimated to have fractionations close to  $0\text{‰}$ , allowing  $\Delta^{57}\text{Fe}_{10}$  to be estimated from the difference between the Fe-oxide and silicate reservoirs ( $1.70\text{‰}$ ). Substitution of these values into Eq. (11) yields a value of only 2% for the contribution of weathering to the signature of the soil silicates.

A similar approach can be applied to the Fe-oxide reservoir in the semi-arid soil. Again, organic dissolution is assumed to be insignificant, and the reservoir should be influenced by direct lithogenic input (pathway 6;  $\Delta^{57}\text{Fe}_6 = -0.06 + 1.72\text{‰} = 1.66\text{‰}$ ) and precipitation/dissolution from the free ion state (pathways 7 and 8, respectively;  $\Delta^{57}\text{Fe}_7 = \Delta^{57}\text{Fe}_8 = 0\text{‰}$ ). By substituting the appropriate values into the following equation

$$f_6 \Delta^{57}\text{Fe}_6 + f_7 \Delta^{57}\text{Fe}_7 + f_8 \Delta^{57}\text{Fe}_8 = 0, \quad (12)$$

it is apparent that lithogenic sources must contribute only minimally to the isotopic signature of the oxides.

In principal, this method can also be applied to the Czech soil. However, the dominant role that organic cycling plays in forest soils prevents the use of some of the simplifications applied in the treatment of the semi-arid soil. Thus, future studies need to adopt additional methods in order to fully understand the roles played by the different fractionation processes in organic soils. While the values obtained for the contributions of Fe from different processes are highly speculative, the calculations serve to demonstrate the potential contribution that Fe isotopes can make to the study of Fe in soils. In order to verify such calculations, and to apply this approach to the additional Fe reservoirs in soils, more information is clearly required concerning the individual partitioning processes.

#### 4. Conclusions

The goal of this study has been to assess the feasibility of combining Fe partitioning data and whole soil isotopic analyses to calculate the isotopic composition of Fe mixing end-members in soils. The isotopic ratio obtained for the silicate end-member is consistent with previous mineralogical studies, suggesting that the least-squares method adopted in the current study can be used as an alternative to more time consuming techniques involving the analysis of all the partial dissolution fractions. In both the Czech and Israeli soils, Fe-oxides were found to have significantly negative  $\delta^{57}\text{Fe}$  signatures, suggesting that this may be a common feature in soils. Furthermore, the determination of the relative contribution of dif-

ferent processes to Fe-oxide formation and soil silicates demonstrates the potential for combining partitioning and isotopic fractionation data in the study of Fe cycling in soils.

While the present study has attempted to shed light on the fate of Fe in soils, additional work is required to independently verify the isotopic compositions of the soil fractions, as well as the relative contributions of organic and inorganic processes to the formation of Fe-oxides. Future research might extend the approach described here to other forest soils and soil types, as well as to different soil fractions. In addition, the introduction of partial dissolution techniques that avoid artificial fractionation is likely to lead to greater insight into Fe partitioning in soils. At present, more information is needed concerning the Fe isotopic fractionation of the reversible and irreversible processes that occur during soil formation.

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