

# 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 Načétin site in the Krušné hory Mountains of the northwestern Czech Republic. Načétin 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<sup>®</sup> 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

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