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Iron isotope systematics of shale-derived soils as potentially influenced by small mineral particle loss

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Abstract

Loss of small mineral particles from soil has been suggested as a process that can produce net isotopic fractionation in the remaining soil. We extracted water dispersible colloids (WDCs) from bulk soil collected at the Susquehanna/Shale Hills Critical Zone Observatory (SSHO) and measured their Fe isotopic composition for comparison to published data from the site. The goal was to explain soil δ^{56}Fe values that become lighter as Fe is lost from soil. The range of δ^{56}Fe values for WDCs was 0.22 to 0.59 ‰, barely intersecting the value of ~0.8 ± 0.3‰ predicted by mass balance for particulate Fe loss by a previous study. The WDCs extracted likely represent a mixture of unfractionated Fe inherited from shale minerals and secondary Fe fractionated by weathering zone processes. Thus, although the WDC compositions do not confirm small mineral particle losses as causing overall Fe isotope fractionation in SSHO soils, they are compatible with that interpretation.

Introduction

Iron isotope systematics in soils at the Susquehanna/Shale Hills Critical Zone Observatory (SSHO) have proven difficult to decipher. Soils form under oxidizing conditions from the Rose Hill Shale parent material (δ^{56}Fe = 0.31‰) and isotopic values in bulk soil decrease to a range of -0.12 to 0.29 ‰ (Yesavage et al., 2012). The decrease in soil δ^{56}Fe correlates loosely with the loss of total Fe from soils and somewhat with decreases in Fe(II) (Fig. 1). Iron in secondary, poorly crystalline forms, extractable by 0.5 N HCl, is generally isotopically lighter, with values that range from -0.17 to 0.00 ‰, and the δ^{56}Fe of bulk soil generally decreases as the fraction of extractable Fe increases (Fig. 1).

Although the poorly crystalline secondary Fe is clearly the primary means by which isotopically light Fe is retained in SSHO soils, the means by which isotopically heavy Fe is lost is less clear. Concentrations of Fe in stream and "macropore" samples were ~1 µM in filtered (<0.45 µm) samples and 2–10 µm in unfiltered samples, and approximately 0.01 µM in lysimeter samples from hill slope soils (Yesavage et al., 2012). Therefore little Fe appears to be lost from soils in dissolved form.

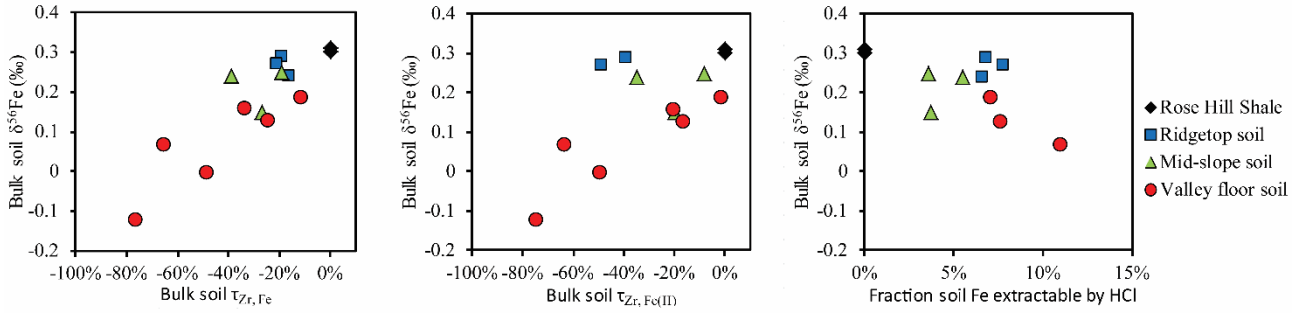

Fig. 1. Variation of δ^{56}Fe with depletion of total Fe, depletion of Fe(II), and fraction of Fe in poorly crystalline (0.5 N HCl-extractable) forms in SSHO soils. Depletion of Fe in soil relative to the parent shale was calculated using traditional mass balance methods and using zirconium as an index. The three soil profiles are ridgetop (SPRT2; 0–25 cm), middle slope (SPMS2; 0–47 cm), and valley floor (SPVF(FS1); 0–67 cm). All data from Yesavage et al. (2012).

Elemental mass balance studies of the SSHO soils have concluded that mobilization of micron-sized and smaller mineral particles is a significant contributor to elemental losses (Jin et al., 2010). The fine grained nature of minerals in the shale parent material suggests that both inherited (from shale) as well as secondary (pedogenic) minerals could be removed as they are translocated through a matrix of larger material. This same process may also influence isotope systematics in these soils. A study of Mg isotopes at the same sites concluded that a combination of isotopically light Mg being sequestered during clay dissolution–precipitation reactions, and

losses of isotopically heavy particulate Mg in micron-sized particles, explained the generally lighter isotopic values in bulk soil compared to parent shale (Ma et al., 2015). Isotopically heavy stream sediments in the watershed were seen as consistent with this loss of isotopically heavy Mg as suspended, micron-sized particles from the hillslope.

A similar mechanism of preferential losses of small mineral particles with heavier Fe isotope compositions may explain the decrease in bulk soil δ^{56}Fe at SSHO. Yesavage et al. (2012) indicated that loss of micron-sized particles with a δ^{56}Fe of ~0.8 ± 0.3‰ would be predicted by mass balance. To assess this idea, we measured the δ^{56}Fe values of generally micron-sized and smaller mineral particles from SSHO soils. Water dispersible colloids (WDCs) were dispersed from bulk soil in the laboratory and refined by a three-step procedure of centrifugation, filtration, and benchtop settling. The resulting materials were analyzed for their iron isotopic compositions for comparison to the δ^{56}Fe values from Yesavage et al. (2012).

Methods

The WDCs were extracted from depth increments of soils collected at the same three locations as the soils described above from Yesavage et al. (2012). Dried bulk soil (23g) and 207 mL of ultrapure water (18.2 MΩ/cm) were placed in a 250-mL plastic bottle (1:10 soil:solution). Bottles were shaken on a table shaker for 10 minutes at ~100 rpm. The bottles were centrifuged for 4 minutes at 2,000 rpm in a RC5C Sorvall® Instruments centrifuge with a swinging bucket HS-4 Sorvall® rotor to settle sand- and silt-size material. The upper 170 mL from each bottle (supernatant) was siphoned to a flask by vacuum. To remove low density root material and larger mineral particles, the supernatant was then passed through a 1-µm nylon mesh (Elko Filtering Co., Miami, Florida). The mesh was pre-treated by soaking briefly in methanol to remove manufacturing residue and then pre-wetted with deionized water to aid supernatant filtering. Eight rounds of shaking, centrifugation, and siphoning were performed for each 23-g sample to maximize yield.

In an attempt to further segregate extracted WDC material, suspended particles were subjected to benchtop settling in two steps. The supernatants were first placed in 2-L glass beakers. In the first step, the suspension was 13.5 cm in height and material that settled to the base of the beaker was collected after 21 hours at room temperature. Then, the remaining suspension was vigorously stirred. In the second step, the suspension was 12.3 cm in height and material that had settled to the base of the beaker after 96 hours at room temperature was separated from the remaining suspension. No consistent, substantial differences in composition were found between these fractions, likely because the plate-shaped nature of shale-derived clays prevented effective size segregation based upon settling velocity.

Iron isotopic compositions were measured for WDCs by quantitatively separating Fe from other matrix elements using an anion-exchange chromatographic method involving step-wise decreases in molar concentrations of HCl (Borrok et al., 2007). Iron isotopic analyses were conducted using a Nu Instruments HR©, double focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the U.S. Geological Survey in Denver, CO. Samples were introduced into the Ar plasma using a desolvating nebulizer system (Aridus II). ^{54}Fe, ^{56}Fe, and ^{57}Fe were measured simultaneously using pseudo-high resolution to separate the isobaric interferences of $^{40}Ar^{14}O$ on ^{54}Fe, $^{40}Ar^{16}O$ on ^{56}Fe, and $^{40}Ar^{16}OH$ on ^{57}Fe (Weyer and Schwieters, 2003). Standard-sample-standard bracketing method was used to correct for mass bias (Weyer and Schwieters, 2003). Isotopic data are reported in the conventional per mil notation relative to the Institute of Reference Materials and Measurements (IRMM)-014 reference material. The precision of the Fe isotopic analyses was determined from numerous replicates of reference materials (USGS SDO-1, n = 5, and National Institute of Standards and Technology (NIST) SRM 2709a, n = 6) and samples.

Results

The average δ^{57}Fe versus δ^{56}Fe values for all analyses of the WDCs and reference material samples were well correlated, with a slope of 0.670 and intercept of 0.003, within error of the theoretical prediction of the slope of δ^{57}Fe versus δ^{56}Fe of 0.678 (equilibrium) and 0.672 (kinetic) for mass-dependent fractionation. The δ^{56}Fe values of the WDCs ranged from 0.22 to 0.59 ‰ (Table 1). The greatest value (0.59 ‰) was substantially greater than the second greatest value (0.36 ‰) measured on any of the WDC fractions. Ultimately, no pattern emerged with regard to isotopic composition versus location along the slope where the sample was collected, or among different fractions from benchtop settling of the WDC suspensions. Therefore, the WDC data are best interpreted relative to the δ^{56}Fe values for other materials from SSHO.

		δ^{56}Fe		δ^{57}Fe	
Sample	Fraction	avg	2 σ	avg	2 σ
SRT 20-25 cm	96 hour settled	0.23	0.07	0.31	0.06
SRT 20-25 cm	96 hour suspended	0.31	0.11	0.49	0.09
SMS 20-30 cm	21 hour settled	0.35	0.10	0.59	0.06
SMS 20-30 cm	96 hour settled	0.59	0.07	0.81	0.05
SMS 20-30 cm	96 hour suspended	0.24	0.03	0.46	0.05
SMS 30-40 cm	96 hour suspended	0.22	0.12	0.35	0.05
SMS 30-40 cm	96 hour settled	0.27	0.05	0.35	0.08
SVF 40-50 cm	21 hour settled	0.29	0.06	0.43	0.07
SVF 40-50 cm	96 hour settled	0.30	0.01	0.37	0.02
SVF 40-50 cm	96 hour suspended	0.23	0.05	0.30	0.07
SVF 90-100 cm	21 hour settled	0.26	0.09	0.36	0.09
SVF 90-100 cm	96 hour settled	0.36	0.07	0.55	0.08
SVF 90-100 cm	96 hour suspended	0.35	0.01	0.53	0.06
NIST 2709A		0.23	0.07	0.33	0.08
USGS SDO-1		0.02	0.05	0.06	0.08

Table. 1. Iron isotope values of water dispersible colloid (WDC) fractions extracted from soils and then subjected to benchtop settling as indicated.

Discussion

The δ^{56}Fe values of the extracted WDCs span a range (0.22 to 0.59 ‰) that just intersects the lower end of the ~0.8 ± 0.3‰ value predicted for losses of micron-sized particles by mass balance by Yesavage et al (2012). The overlap hinges, however, on the single, heaviest value from a WDC sample. The bulk of WDC values, though generally heavier than soil, overlap with values for parent material. Although the WDC δ^{56}Fe values fail to fully reconcile Fe mass balance at SSHO, they may point towards such reconciliation.

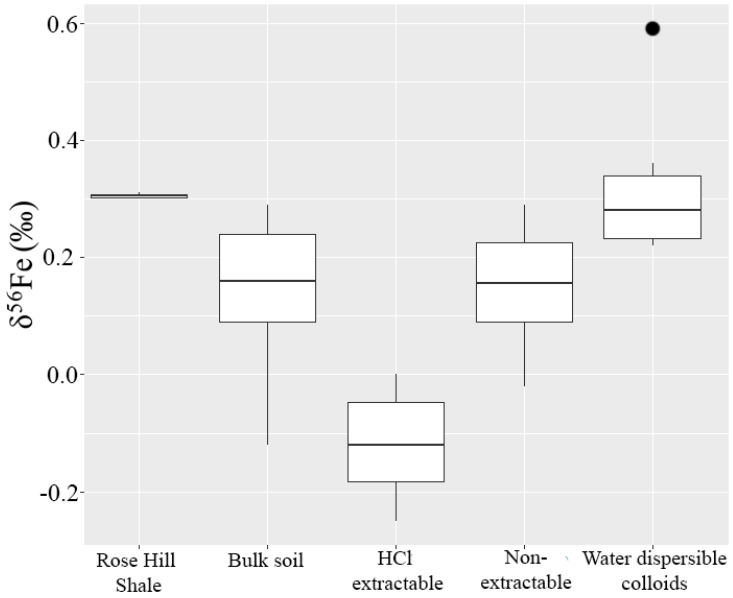

Fig. 2. Box plot of δ^{56}Fe values from parent shale, various soil components (bulk, 0.5 NHCl extractable, calculated non-extractable). All data from Yesavage et al. (2012). Compared to these are the δ^{56}Fe values of WDCs from Table 1. The outlier value of 0.59 ‰ is shown as a black circle.

Micron-sized and smaller mineral particles moving through the soil matrix at SSHO are likely a mixture of materials. Some may be secondary phases, but more may be inherited essentially unaltered from shale. Shale contains an abundance of clay-sized minerals that simply require physical disaggregation to become mobile.

Thus, some of the Fe in WDCs may be unfractionated by chemical weathering processes and the WDC $\delta^{56}Fe$ values may reflect a mixture of unfractionated, shale-mineral Fe and fractionated, chemical weathering-influenced Fe. Thus, to satisfy mass balance, the weathering-influenced Fe would be highly fractionated.

Rivers can have mild to extreme Fe isotopic enrichment in the transported colloidal to dissolved fractions (e.g., Ilina et al., 2013), and experimental studies have found isotopic depletion in Fe (oxyhydr)oxides precipitated from $Fe(III)_{aq}$ (Skulan et al., 2002). Oxidation of Fe(II) and isotopically depleted, poorly crystalline Fe in soil at SSHO are evidence of chemical transformations that should fractionate Fe isotopes. Some amount of that fractionated Fe may become associated with WDCs. Secondary nanoparticles of Fe attached to clay minerals have been found on other WDCs (Jiang et al., 2014). Attachment of fractionated, nanoparticulate Fe to clay minerals may explain why the WDC extractions here failed to isolate an isotopically heavier pool of Fe. Therefore WDCs may be a mix of fractionated and unfractionated Fe. Such mixing would account for both the complex relationship between soil $\delta^{56}Fe$ and Fe losses (Fig. 1) and the substantial variation in, and lighter than expected, $\delta^{56}Fe$ values of the WDCs (Table 1).

Acknowledgements

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