Isotopic variations of Fe and Zn in Finnish acid sulfate soils

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Abstract
The use of a Neptune high-resolution MC-ICP-MS (Thermo Fisher Scientific) in this study has enabled high precision measurements of Fe and Zn isotopic ratios in Finnish acid sulfate soils in one near shore area (Vassor) and one inland area (Rintala).

Introduction
The development of precise instrumentation such as high resolution MC-ICP-MS and improved analytical methods has made it possible to obtain reliable analyses of Fe and Zn isotopes in a range of biological and geological samples (Malinovsky 2004). These stable isotopes have a wide range of applications and can for instance be used to fingerprint sources of Fe and Zn or to evaluate the biogeochemical reactions that impact their transport (Fernandez and Borrok 2009). Unlike Zn, Fe is a redox sensitive element and is fractionated by many biological and abiotic processes in soils and sediments, such as changes in redox state, complexation with soil organic matter, bacterial interactions, and during precipitation reactions and surface adsorptions (Borrok *et al*. 2009 and references therein). Non-redox fractionation of Zn isotopes have been measured during adsorption on oxides and hydroxides (e.g. Pokrovsky *et al*. 2005; Juillot *et al*. 2008) and complexation with organic matter (Jouvin *et al*. 2009).

In this study we focus on the isotopic variations of Fe and Zn in Finnish acid sulfate (AS) soils. Typical for Finnish AS soils is the abundance of metastable iron sulfide (approximate composition of $FeS_{1.1}$; up to c. 0.9% of the dry weight) and pyrite (FeS_2; commonly 1-2% of the dry weight) in the unoxidised parent material (Boman *et al*. 2008; 2010). Another characteristic feature for these soils is extensive leaching of acidity (H_2SO_4) and many potentially harmful elements, such as Zn and retention of Fe (Åström 1998). In Finland, which have the largest AS soil occurrences in Europe (Andriesse and van Mensvoort 2006), these soils cover an area of at least 43,000-130,000 ha (Yli-Halla *et al*. 1999). The total global area underlain by corresponding soils is estimated to c. 17 million ha (Andriesse and van Mensvoort 2006).

The use of a Neptune high-resolution MC-ICP-MS (Thermo Fisher Scientific) in this study has enabled high precision measurements of Fe and Zn isotopic ratios in Finnish AS soil materials. A better knowledge of the isotopic variations of Fe and Zn in these materials provides new insight into the mechanisms controlling the mobility of these metals.

Methods
Study areas and sampling
The study sites are located on typical Finnish AS soil areas in western Finland (Figure 1) and have been characterised by previous studies (e.g. Boman *et al*. 2008; 2010). One area, Vassor (63°9.484′N, 22°0.549′E), is located close to the present shore line and one area, Rintala (62°46.017′N, 22°36.822′E), is located some 100 km inland (Figure 1). One vertical core (300 cm) was collected from each site consisting of (1) the upper cultivated plough layer (0-40 cm), (2) the acidic horizon (pH <4), (3) the transition zone (pH >4.0 to 7.0) and (4) the sulfidic parent material (pH >7.0) (Boman *et al*. 2008; 2010). During sampling, the cores were sectioned into 5 cm (Vassor) and 10 cm (Rintala) increments. From these increments, using previous data in Boman *et al*. (2008; 2010) on sulfur speciation and isotopes and occurrence of *aqua regia* extractable Fe and Zn, a total of 29 samples (14 from Rintala and 15 from Vassor) were chosen for study.
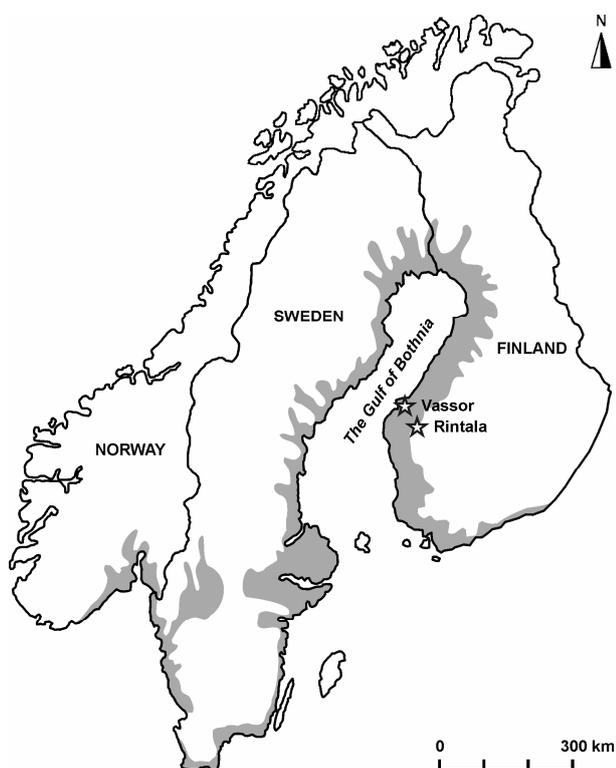
Figure 1. Location of the study areas. The shaded area indicates the maximum extent of the former Litorina Sea and the area where AS soils can be expected.

Analyses
The dried ($50^{o}C$) samples were analysed for $^{56}Fe/^{54}Fe$ and $^{66}Zn/^{64}Zn$ ratios by high-resolution MC-ICP-MS using a Neptune (Thermo Fisher Scientific). The measured $^{56}Fe/^{54}Fe$ and $^{66}Zn/^{64}Zn$ ratios are reported as $\delta^{56}Fe$ and $\delta^{66}Zn$ values, respectively, in parts per mil deviation of the sample relative to the corresponding isotopic ratios of IRMM-014 and IRMM-3702 standards, respectively. The total concentrations of Fe and Zn were analysed by ICP-SFMS (Element2, Thermo Fisher Scientific) after digestion of about 2 g of dried material in $HCl:HNO_3:HF$ (3:1:1).

Results and discussion
Iron and Zn
The total concentrations of Fe (percentage of dry weight) and Zn (mg/kg of dry weight) are presented in Figure 2. Generally, Fe is mostly retained in Finnish AS soils due to precipitation of various ferric minerals e.g. oxyhydroxides [e.g. $Fe(OH)_3$ and $FeOOH$] and jarosite [$KFe_3(SO_4)(OH)_6$] (e.g. Palko 1994; Åström 1998). The decrease of Fe in the upper meter at Rintala (Figure 2) is therefore most likely explained by heterogeneities of parent material (Österholm and Åström 2002).

In the sulfidic parent material at Rintala and Vassor, up to c. 28% of Fe, calculated from sulfur speciation data in Boman *et al*. (2008; 2010) and total Fe in this study (Figure 2), is associated with iron sulfides, while the rest is most likely associated with silicates (cf. Åström and Björklund 1997). In the acidic horizon and upwards, the corresponding iron sulfide associated Fe content is <1% (Boman *et al*. 2008; 2010), indicating the mobility of this metal within the soil column. The carrying phases of Zn in the studied materials are not fully known, but according to Åström and Björklund (1997), trace elements such as Zn in similar AS soil materials are largely associated with aluminosilicates.

The decrease of Zn in the acidic horizon at both locations (partial decrease at Rintala) as well as the concentration peak of this element in the transition zones (slightly elevated at Vassor) (Figure 2) is typical for Finnish AS soils (e.g. Åström 1998). Above c. 100 cm at Rintala, the Zn concentration was, however, increasing (Figure 2), which may be explained by heterogeneities of parent material (Österholm and Åström 2002). The reason for the increase of Zn (and other elements) in the transition zone is not fully understood but Åström (1998) suggested that it may be due to (1) downward migration of elements (Zn in this case) released in the acidic horizon followed by (2) reprecipitation/adsorption of the element in the transition zone.
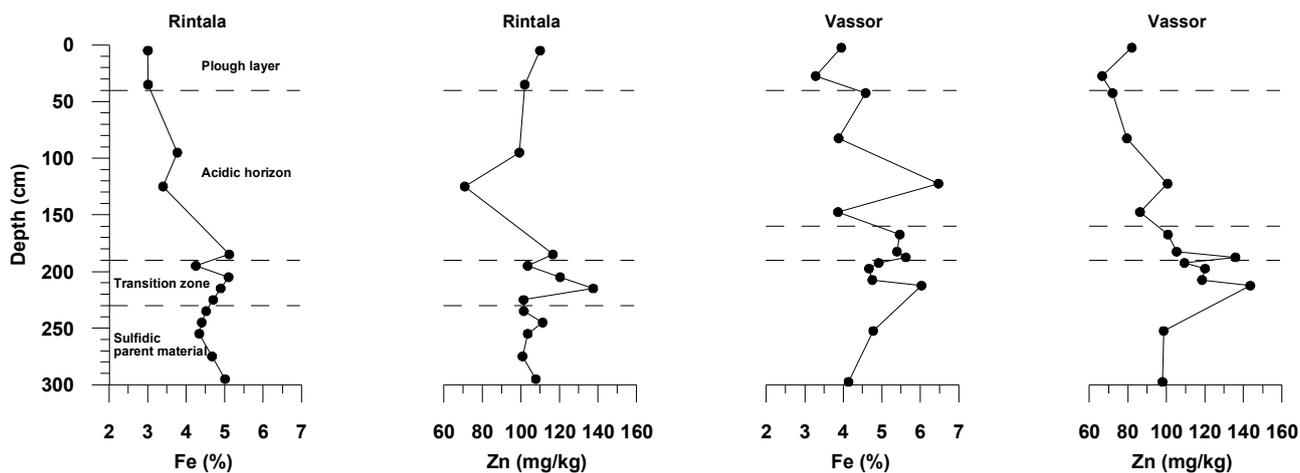
Figure 2. Total concentrations of Fe (percentage of dry weight) and Zn (mg/kg of dry weight) at Rintala and Vassor.

Isotopic variations of Fe and Zn

The isotopic variations of Fe are presented in Figure 3. The δ^{56}Fe value varied slightly within the profiles and between the sites. The main difference between the sites was the general occurrence of positive δ^{56}Fe values ($\pm 1\sigma$), ranging from (-0.01 ± 0.02)‰ to (0.31 ± 0.03)‰, in the parent material at Rintala compared to more negative δ^{56}Fe values ($\pm 1\sigma$), ranging from (-0.19 ± 0.01)‰ to (0.16 ± 0.01)‰, at Vassor. This is believed to reflect different depositional conditions during the formation of these sediments (cf. Malinovsky 2004), with more oxidised conditions at Rintala and more reduced conditions at Vassor. This is also indicated in the ratio between metastable iron sulfide and pyrite which is consequently much lower at Rintala (c. 10/90) compared to Vassor (c. 50/50) (Boman *et al.* 2008; 2010). Approaching the lower border of the transition zone, both sites displayed similar features with a sudden dip towards more negative δ^{56}Fe values (Figure 3). This may have several explanations but the main reason is most likely redox driven processes which have shown to produce the largest Fe isotope fractionations in nature (Johnson *et al.* 2008). The transition zone is subject to fluctuating redox conditions due to occasional changes in the groundwater level which will certainly contribute to changes (variations) in the isotopic composition. Above the transition zone at both sites, the δ^{56}Fe values ($\pm 1\sigma$) were positive and ranged from (0.01 ± 0.04)‰ to (0.17 ± 0.05)‰ at Rintala and from (0.05 ± 0.01)‰ to (0.16 ± 0.04)‰ at Vassor (Figure 3). This slight increase of δ^{56}Fe probably reflects precipitation of ferric minerals (Johnson *et al.* 2008) and possibly some loss of isotopically light Fe.
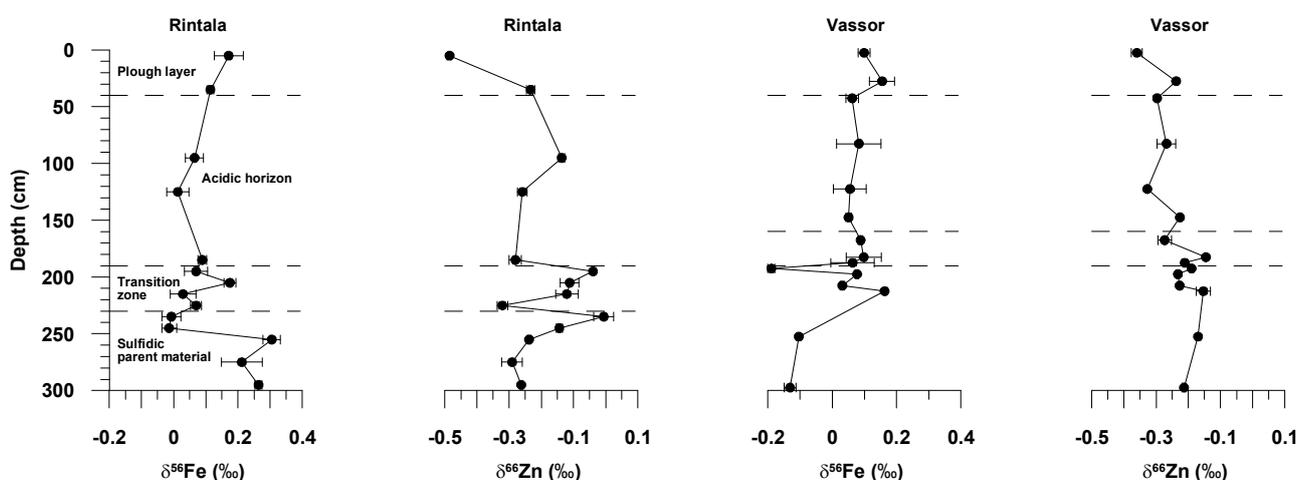

Figure 3. Isotopic variations of Fe and Zn at Rintala and Vassor (error bars are one standard deviation).

The isotopic variations of Zn are presented in Figure 3. At both sites, all measured δ^{66}Zn values ($\pm 1\sigma$) were

negative and ranged from (-0.49 ± 0.01)‰ to (-0.01 ± 0.03)‰ at Rintala and from (-0.36 ± 0.02)‰ to (-0.15 ± 0.02)‰ at Vassor. Generally, the δ^{66}Zn values were slightly decreasing upwards, implying enrichment of the heavier isotopes in the leached Zn fraction. However, we do not have any isotopic data to support this assumption. Possibly this isotopically heavy Zn has previously been adsorbed on oxides and hydroxides and is now released due to the acidic conditions (Pokrovsky *et al*. 2005).

Conclusions
This study shows that the isotopic composition of Fe and Zn varies within the soil column of Finnish AS soils. There are indications of loss of isotopically heavy Zn during oxidation of AS soils, but the possible fractionation mechanism is not known. The isotopic variations of Fe are probably related to redox processes. More detailed studies on the partitioning, together with isotopic analyses, of Fe and Zn in Finnish AS soils are needed. Speciation of Fe and Zn will significantly contribute to the understanding of the isotopic variations in these profiles.

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