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An analytical procedure for determination of sulphur species and isotopes in boreal acid sulphate soils and sediments

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An analytical scheme suitable for boreal acid sulphate (AS) soils and sediments was developed on the basis of existing methods. The presented procedure can be used to quantify and discriminate among acid volatile sulphide, cold chromium reducible sulphur, hot chromium reducible sulphur, elemental sulphur, sulphate sulphur, organic sulphur, total reducible sulphur and total sulphur. The sulphur fractions are recovered as either Ag_2S or $BaSO_4$ precipitates and can further be used for isotope analysis.

Overlaps between sulphur species are common during speciation, and must be minimized. Some of these overlaps are caused by poor sampling and storage, inappropriate conditions during the distillation, or natural variations in the sample (e.g. Fe^{3+} interference and grain size). The procedural impact was determined by conducting tests on both artificial and natural samples containing one or several sulphur species. The method is applied on reduced sediment from an AS soil locality (Överpurmo) and a brackish lake (Larsmo Lake) in western Finland and the results, including S-isotopes, are discussed.

Key words: sulphur species, sulphur isotopes, analytical scheme, acid sulphate soils, sediment

Introduction

Acid sulphate (AS) soils occupy large areas of the tropical and subtropical coasts of Asia, Africa, Australia, and significant areas along the boreal coastal plains of Finland and Sweden (Palko 1994, Öborn 1994, Joukainen and Yli-Halla 2003). AS soils constitute a major environmental problem due to the release of acidity and metals during oxi-

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dation of naturally occurring sulphur species (e.g. Åström 2001, Sundström et al. 2002). According to van Breemen (1973) potential AS soils commonly contain pyrite sulphur (FeS_2) between 1 and 4%, and ferrous monosulphides (FeS) comprise less than 0.01% and rarely exceed 0.6% even in reduced black muds. However, in black clays in north-eastern Sweden FeS comprises a significant amount (up to 80%) of the total sulphur (Georgala 1980). Iron sulphides are usually divided into two categories: (1) acid volatile sulphide (AVS) and (2) disulphides (FeS_2). AVS consists of amorphous FeS, mackinawite ($FeS_{0.94}$), greigite (Fe_3S_4) (Morse et al. 1987), dissolved sulphide (Morse and Rickard 2004), and amorphous monosulphides of other metals (e.g. zinc, cadmium or lead) (Lasorsa and Casas 1996, Morse and Luther 1999), while disulphides include pyrite (cubic FeS_2) and marcasite (orthorhombic FeS_2) (Rice et al. 1993). Elemental sulphur (S^0) generally occurs in small quantities (usually < 2% of total sulphur) in reduced marine muds and may be produced by oxidation of FeS, FeS_2 and H_2S (van Breemen 1973, Poulton et al. 2004). Organic sulphur is generally the most abundant sulphur species in normal soils, but in pyrite-bearing sediments and AS soils it is usually quantitatively insignificant (van Breemen 1973). For example, Georgala (1980) estimated that organic sulphur constituted less than 0.03 wt% in black clays from north-eastern Sweden. Sulphate is usually not present in large quantities in reduced sediment, but in AS soils, a large number of sulphate minerals can be found in association with oxidation of mainly pyritic material. Most of these sulphate compounds are water soluble and only persist in the absence of leaching (van Breemen 1973).

Different forms of sulphur have previously been separated and quantified by various techniques (e.g. Zhabina and Volkov 1978, Nriagu and Soon 1985, Canfield et al. 1986, Tuttle et al. 1986, Hall et al. 1988, Fossing and Jørgensen 1989, Bates et al. 1993, Rice et al. 1993, Duan et al. 1997, Sullivan et al. 2000, Kallmeyer et al. 2004). At present, most of the sulphur speciation methods are based on the sequential extraction scheme that Zhabina and Volkov introduced in 1978, where iron monosulphides are digested in HCl and iron disulphides are reduced by Cr^{2+} in an acidic solution. Elemental sulphur is commonly determined by dissolution with an organic solvent, followed by a Cr-reduction. The evolved H_2S can be determined gravimetrically as Ag_2S, ZnS or CdS (e.g. Zhabina and Volkov 1978, Tuttle et al. 1986, Di Toro et al. 1990, Bates et al. 1993), by EDTA titration (Newton et al. 1995), iodometrically, spectrophotometrically, polarographically, or by ICP-MS (Zhabina and Volkov 1978, Allen and Parkes 1995). Determination of reduced sulphur is performed under anoxic conditions, which can be obtained by using N_2, CO_2 or Ar (Zhabina and Volkov 1978, Hall et al. 1988). Sulphate is usually precipitated as $BaSO_4$ after separation of AVS (e.g. Nriagu and Soon 1985, Tuttle et al. 1986, Hall et al. 1988, Rice et al. 1993) or after removal of chromium reducible sulphur (Bates et al. 1993). Organic sulphur is commonly converted to sulphate by oxidation with Eschka's mixture and subsequently precipitated as $BaSO_4$ (e.g. Tuttle et al. 1986, Bates et al. 1993, Rice et al. 1993).

A complete analytical scheme for the separation and quantification of sulphur species present in a sample has not yet been developed despite several efforts. In order to determine which distillation technique is most suitable it is of importance to understand how various treatments affect the sample. There are often overlaps between different sulphur phases due to: (1) oxidation of AVS to S^0 during sampling/storage; (2) oxidation of H_2S to S^0 during the distillation process; (3) the analytical conditions and treatments used; and (4) the grain size and crystallinity of the sulphide minerals.

The aim of this study was to develop an analytical scheme suitable for the determination of sulphur species and isotopes in boreal potential and actual AS soils and shallow coastal sediments. The development of such a scheme is important because knowledge of sulphur speciation and behaviour in these materials is inadequate to understand and model how: (1) acidity is formed in and leached from AS soils; (2) marine sediments brought above the sea level by postglacial isostatic rebound (up to 9 mm per year) are turned into highly problematic AS soils; (3) the cold climatic

conditions affects neutralisation and formation of acidity in soils and waters; and (4) thick sediment layers uplifted above sea level are ultimately preserved black, and thus monosulphide-rich and highly reactive, when exposed to atmospheric oxygen. Finally, the intent to study the isotopic composition of each sulphur species in the samples puts additional constraints on the scheme. Firstly, distillation must be optimised in regard to the quantity and separation of species and secondly, sulphur must be extracted from each species in a form suitable for the later analysis of sulphur isotopes.

Material and methods

Natural samples

Reduced sediment from an AS soil locality (Överpurmo) and a brackish lake (Larsmo Lake) in western Finland were collected. The sediments are fine-grained and homogeneous with a clayey texture and black colour. The Överpurmo sediment, located 40 meters above the present sea level (due to isostatic land uplift), was deposited in a shallow coastal environment about 4000 years ago. Fresh samples were stored (within two hours after sampling) in a freezer in order to minimize oxidation. In the laboratory, the samples were thawed in a nitrogen-filled glove bag and any visibly oxidized surface material was removed, keeping only the un-oxidized core of the sample for subsequent analysis. Any shell fragments found in the sediments were removed before further analysis.

Artificial samples

Mixtures of finely ground sulphur minerals (pyrite and elemental sulphur) and chemical reagents ($Na_2S{\cdot}9H_2O$ and Na_2SO_4) were prepared in order to test the analytical scheme. The sulphur concentration in pyrite (FeS_2), elemental sulphur (S^0) and sodium sulphate (Na_2SO_4) was calculated based on the molecular formula. The range of the Na_2S concentration in $Na_2S{\cdot}9H_2O$ is 32–38% and the sulphur concentration was determined to be 13.2 ± 0.003% by dissolving a known amount of $Na_2S{\cdot}9H_2O$ in deionized water (18.2 MΩ) and precipitating the sulphide as Ag_2S (assuming 100% recovery).

Sulphur speciation method – general approach

The distillation apparatus (Fig. 1a) used for extraction of the sulphur species consists of a heating plate (with magnetic stirrer), a 500 ml reaction flask (with injection ports for reagents and nitrogen) attached to a condenser, a 250 ml buffer vessel (containing 200 ml of 0.05 M potassium hydrogen phthalate, pH 4) used for preventing formation of AgCl in the sulphide traps and a pair of 50 ml sulphide traps (containing 15 ml of 0.1 M $AgNO_3$), of which the latter is used as a safety trap only. The glassware is connected by rubber tubing.

A Cr^{2+} containing solution was prepared by percolating 1 M $CrCl_3{\cdot}6H_2O$ in 0.5 M HCl through a Jones reductor (Fig. 1b), constructed as described by Skoog and West (1976). In this process, Cr^{3+} is reduced to Cr^{2+} which can be verified by a colour change from dark green (Cr^{3+}) to bright blue (Cr^{2+}). The solution was collected in sealed plastic syringes, where it was stable for several days.

A frozen sample was thawed in a nitrogen-filled glove bag, homogenised and divided into subsamples. One of the subsamples was dried at 105°C for determination of the dry weight, while the other subsamples were used for sulphur speciation. Approximately 3 g of wet subsample was weighed (to the nearest tenth of a milligram) into the reaction flask, and 10 ml of ethanol was added to facilitate reflux condensation during distillation (Fossing and Jørgensen 1989). The distillation apparatus was flushed for 10 minutes with pure (99.5%) nitrogen gas before inserting reagents for H_2S emanation, and nitrogen flowed continuously (approximately 5 bubbles per second in the buffer vessel) throughout the distillation process. Liber-

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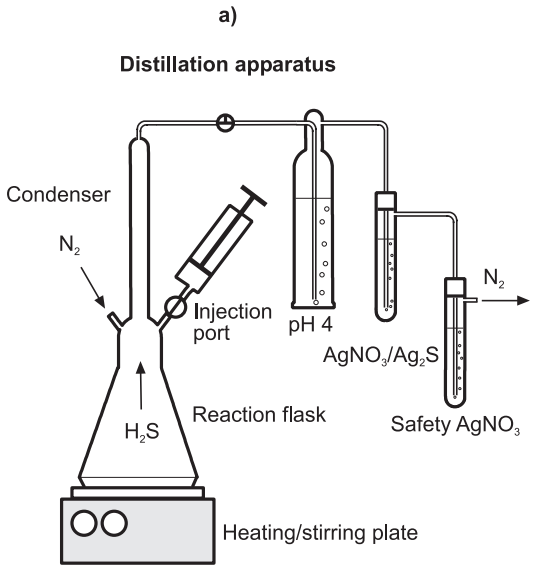

Fig. 1. A sketch of the equipment used in the speciation experiments: (a) the distillation apparatus, and (b) the Jones reductor for preparation of $CrCl_2$ solution.

ated H_2S from reduced sulphur was transported, through the buffer solution into the sulphide trap and precipitated as Ag_2S. After each reaction step was complete, the trap was replaced and distillation of another species started by addition of the appropriate reagent to the reaction flask. Deoxygenating all solutions with nitrogen before analysis minimized oxidation of H_2S during reaction. The remaining slurry in the reaction flask was filtered, and the filtrate and residue were analysed for sulphate and organic sulphur, respectively.

Precipitated Ag_2S was filtered and washed with deionized water (18.2 MΩ) on preweighed Whatman (No 42) filter papers. After drying at 105°C for two hours, the precipitate was cooled in a desiccator for 30 minutes. $BaSO_4$ was filtered on S&S blue ribbon 589[3] filter papers and transferred to a preweighed porcelain crucible and slowly ignited (2 hours) to 800°C, leaving only $BaSO_4$. The crucible was left to cool in a desiccator for 30 minutes. Weight percents (wt%) of sulphur were calculated from the weights of Ag_2S or $BaSO_4$. The detection limit for S was estimated to be 0.01 wt% in a 1 g sample (dry weight).

Sequential extraction procedure

An analytical scheme (Fig. 2) was devised for distinguishing AVS, cold chromium reducible sulphur (CCrS), hot chromium reducible sulphur (HCrS), elemental sulphur (ES), sulphate sulphur (SO_4^{2-}), organic sulphur (OrgS), total reducible sulphur (TRS) and total sulphur (TotS).

For determination of ES, a wet subsample was placed in a 15 ml centrifuge tube together with 8 ml dichloromethane (CH_2Cl_2). After 24 hours, the tube was centrifuged and the supernatant (containing dissolved ES) was transferred to a reaction flask for evaporation. Solid ES in the reaction flask was subsequently heated in 50 ml of 6 M HCl and 50 ml of 1 M $CrCl_2$, and the concentration of ES was determined from the precipitated Ag_2S. ES is thought to mainly consist of S^0, but some forms of organic sulphur (e.g. organic polysulphides) may also dissolve in the organic solvent (Mossmann et al. 1991). The residue in the centrifuge tube was transferred to a reaction flask for further analyses.

The residue, or a fresh subsample if ES was not determined separately (Fig. 2), was weighed into

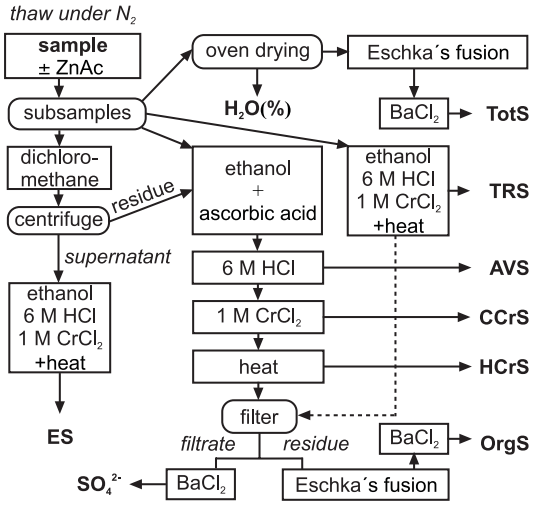

Fig. 2. Flow diagram of the analytical procedures used in this study.

the reaction flask, and 50 ml of 6 M HCl was added for the determination of AVS. The distillation was completed after approximately two hours. According to previous studies (e.g. Morse et al. 1987) AVS is believed to comprise mainly iron monosulphides and some greigite. Different treatments and chemicals are known to affect AVS recovery, and additional experiments were performed: (1) by addition of ascorbic acid (AA); (2) by heating to boiling point; (3) by addition of 5 g $SnCl_2$; and (4) by addition of 15 ml 20% (w/v) zinc acetate (ZnAc).

After removal of AVS, 50 ml of 1 M $CrCl_2$ was added, and 4–5 hours later any CCrS, consisting of "less mature" pyrite (Duan et al. 1997) and possibly some greigite and organic polysulphides (Canfield et al. 1998), had been extracted. Thereafter the reaction flask was heated to boiling point for 1–2 hours until HCrS distillation was complete. HCrS comprises "more mature" pyrite, i.e. possibly larger grains that may be coated with cements and overgrowths (Rice et al. 1993), and ES that has not been removed prior to this stage (Duan et al. 1997). The remaining content in the reaction flask was filtered, and the filtrate was used for determination of dissolved SO_4^{2-} and the residue for OrgS.

The filtrate was treated with 10 ml of 30% H_2O_2 at 60ºC in order to oxidize any organic matter in the solution. The next day the volume was reduced to 200 ml, and excess (10 ml) 10% $BaCl_2$ was added dropwise, while stirring, and the solution was left overnight at 60°C before filtering and weighing the precipitated $BaSO_4$. The SO_4^{2-} may occur in the form of acid soluble sulphate (e.g. jarosite: $KFe_3(SO_4)_2(OH)_6$), water soluble sulphate (e.g. gypsum: $CaSO_4$) or as adsorbed sulphate (Begheijn et al. 1978).

The residue was washed with deionized water and dried at 105°C. Approximately 1 g of dry residue was mixed with 3 g of Eschka's mixture and placed in a porcelain crucible with an additional layer of Eschka´s mixture on top. The crucible was heated at 800°C for two hours, in order to oxidize sulphur to sulphate. The fusion residue was then transferred to a 500 ml Erlenmeyer flask and dissolved in 200 ml deionized water. After simmering for 30 minutes, the solution was filtered and the pH was adjusted to less than 4 (prevents formation of iron oxides). Excess (10 ml) 10% $BaCl_2$ was added dropwise, while stirring, to the filtrate (< 200 ml), and the solution was left overnight at 60°C before filtering and quantifying the precipitated $BaSO_4$. The OrgS fraction extracted consists of non Cr-reducible organic sulphur, and possibly $BaSO_4$. The Eschka's fusion can also be used to determine the total amount of sulphur in the sample (Fig. 2).

Total reduced sulphur, comprising AVS, CCrS, HCrS and ES, was determined on a separate subsample. After adding 50 ml of 6 M HCl and 50 ml of 1 M $CrCl_2$ to the sample, the solution was boiled for 1–2 hours for complete distillation of TRS. The remaining slurry in the reaction flask can further be analysed for SO_4^{2-} and OrgS.

Isotopic measurements

The quantities of recovered Ag_2S or $BaSO_4$ precipitates varied depending on the sample size, sulphur concentration and proportion of sulphur spe-

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cies, and analysis of the isotopic composition of sulphur was not always possible. However, when sufficient material was available, standard methods were used to prepare the samples for analysis. About 40 mg of Ag_2S (corresponding to approximately 5 mg of sulphur) was converted to SO_2 by reaction with 200 mg cuprous oxide (Cu_2O), according to the procedure by Robinson and Kusakabe (1975). The $BaSO_4$ samples were prepared following the procedures outlined by Yanagisawa and Sakai (1983), where about 10 mg of $BaSO_4$ was mixed with 200 mg (1:20) of a 1:1 V_2O_5:SiO_2 mixture. The sample mixtures were placed in small quartz-glass capsules, which were introduced into an evacuated preparation line. For both sample types, the temperature was slowly raised from 300°C to 950°C during 15 minutes to ensure complete combustion. A spiral of metallic copper was placed at the mouth of the furnace in order to convert SO_3 to SO_2. Gas yields from combustion were monitored by a pressure gauge on a volume calibrated part of the vacuum line and samples with SO_2-yields < 95% were discarded. To obtain a pure SO_2 sample, H_2O(g), CO_2(g) and uncompressible gases were removed by distillation under high vacuum.

The SO_2 was introduced into a modified VG Micromass 602 that is run by in-house software (originally developed at the Museum of Natural History in Stockholm, Sweden). The measured $^{34}S/^{32}S$ ratios are reported as $\delta^{34}S$ values, i.e. the parts per mil deviation of the sample relative to the $^{34}S/^{32}S$ ratio in the Canyon Diablo Troilite (CDT). The precision was estimated to approximately ±0.3‰, and measurements on standard materials NBS-127 $BaSO_4$ ($\delta^{34}S$ 20.3 CDT) and Göttingen CdS ($\delta^{34}S$ -20.8 CDT) gave $\delta^{34}S$ values of 20.34 and –21.1, respectively.

Results and discussion

Recovery of sulphur from pure phases and artificial mixtures

In order to test the distillation technique several sulphur compounds were analysed individually and in mixtures. AVS is represented by $Na_2S{\cdot}9H_2O$ (hereafter referred to as Na_2S), and CCrS, HCrS and SO_4^{2-} is represented by natural pyrite (FeS_2), elemental sulphur (S^0) and sodium sulphate (Na_2SO_4), respectively. The mixtures (M1-M5) were: M1 = Na_2S + FeS_2 + S^0 + Na_2SO_4; M2 = Na_2S + FeS_2 + S^0; M3 = Na_2S + FeS_2; M4 = Na_2S + Na_2SO_4; and M5 = FeS_2 + Na_2SO_4. The samples were analysed without addition of ascorbic acid and ethanol and the results are presented in Fig. 3.

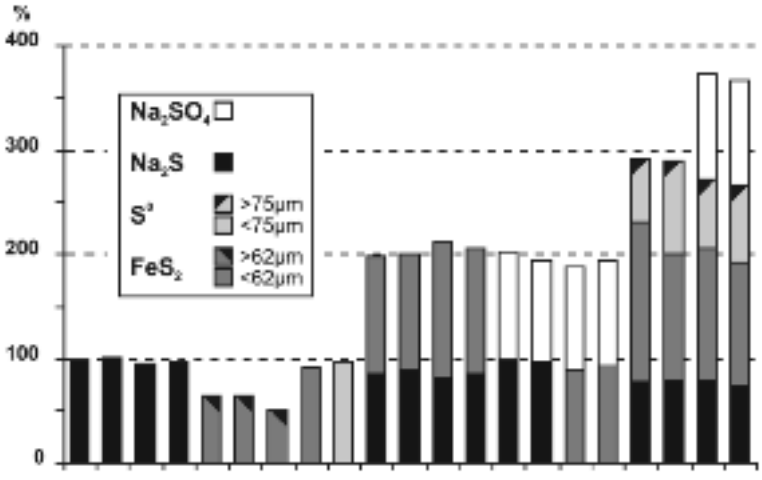

Fig. 3. Summed recoveries (%) of sulphur species, separated individually and from mixtures (including different grain sizes). Ideally, each compound will show a (theoretical) recovery of 100%, and the sum of e.g. four species equals 400%. Deviations from 100% for an individual compound indicate cross-contamination between sulphur pools, or loss of sulphur.

The recoveries for two different grain sizes of FeS_2 (< 62µm and > 62µm) and S^0 (< 75µm and > 75µm) show significant differences. For fine grained FeS_2 the recovery was 90.4% but only 59.4 ± 6.4% (1 SD) for the coarser fraction. For S^0 the results were similar, i.e. 96.2% and 71.9 ± 11.0%, respectively. However, grain sizes above 62 µm for pyrite and elemental sulphur are extremely rare in natural sediments and AS soils, except for sites close to e.g. ore deposits.

The Na_2SO_4 was completely recovered (100.1 ± 1.1%) from the mixtures (M1, M4 and M5), and apparently did not affect the recovery of other species. The Na_2S was completely recovered when separated individually (98.4 ± 2.2%) and with sulphate (96.4% and 99.9%), but when separated in mixture with FeS_2 (M3) only 85.4 ± 2.9% was recovered, while the recovery of FeS_2 was 118.5 ± 7.7%. However, the sum of Na_2S + FeS_2 in M3 (203.9 ± 5.5%) shows that a fraction of Na_2S was recovered in the FeS_2 pool, explained by partial oxidation of Na_2S to elemental sulphur, subsequently extracted with the cold Cr-reduction. Similar results have been reported by Fossing and Jørgensen (1989).

In M1 and M2, the recovery of FeS_2 was even larger (130.5 ± 14.2%), and it is likely that some of the "additional FeS_2" comes from original S^0, and consequently that a small fraction of S^0 (presumably very fine grained) was reduced by the cold Cr-reduction. The sum of recoveries for M1 (369.7 ± 2.3%) and M2 (290.0 ± 1.0%) were slightly below the expected 400% and 300%, respectively, and can be attributed to the large grain size of unreacted S^0. In all experiments with coarser fractions of S^0 (> 75µm), the dissolution of S^0 was incomplete even after 18 hours of distillation, compared to complete distillation after 4 hours using the finer fraction.

Sulphur species in sediments

When comparing the sum of reduced sulphur species (AVS, ES, CCrS and HCrS) with TRS in the potential AS soil and lake sediment (Table 1), there is an indication that little, or none, of the H_2S developed from the individual distillation steps is lost during the process. It has previously been shown that Cr^{2+} does not reduce any significant quantities of sulphate or organic sulphur in sediments (e.g. Zhabina and Volkov 1978, Howarth and Jørgensen 1984, Canfield et al. 1986), and no excess CCrS or HCrS is expected from the SO_4^{2-} pool. For sulphur species in the Överpurmo and Larsmo sediment CCrS comprised the largest pool (except for the Larsmo sample treated with ZnAc, where AVS was the largest pool), followed by AVS, HCrS, ES, and minor amounts of SO_4^{2-} (< 0.01 wt%) and OrgS (< 0.1 wt%). The concentration of TotS is somewhat lower than the combined sum of the separated sulphur species.

The recovery of AVS (Table 1) in the Överpurmo sample did not show any major differences whether using cold 6 M HCl (0.46 ± 0.04 wt%), cold 6 M HCl and addition of 5 ml of 0.1 M ascorbic acid (AA) (0.40 ± 0.04 wt%) or heating of 6 M HCl with addition of AA (0.42 ± 0.03 wt%). Pruden and Bloomfield (1968) showed that presence of Fe^{3+} in sediments could affect the determination of reduced sulphur by oxidizing H_2S to elemental sulphur in the reaction flask. To prevent this, Fe^{3+} is converted to Fe^{2+} by adding AA (Hsieh et al. 2002) or $SnCl_2$ (Pruden and Bloomfield 1968) to the sample. Hsieh and Shieh (1997) noticed that addition of AA to a freeze-dried sediment increased recovery of AVS, but not in a fresh sample of the same sediment. This was probably due to the formation of Fe^{3+} during the freeze-drying, and that the fresh sediment only contained Fe^{2+}. The reason why AA in this study did not have an effect was probably due to lack of reactive Fe^{3+} in the sediment. Amorphous FeS and mackinawite are completely dissolved in cold 6 M HCl, while decomposition of greigite may be incomplete (Cornwell and Morse 1987). This, and possible formation of elemental sulphur during breakdown of greigite (Allen and Parkes 1995) requires harsher treatments (e.g. use of heat and/or a reducing agent). Addition of $SnCl_2$ to the Överpurmo sample increased the recovery of AVS (0.74 ± 0.03 wt%) (Table 1), most likely due to the reduction of small amounts of disulphides (Cornwell and Morse 1987). Therefore AA, which is a milder reagent

Table 1. Sulphur (S) speciation in a potential acid sulphate soil (Överpurmo) and a lake sediment (Larsmo Lake). Results are in weight percent of dry weight (± 1 SD, deviation values for $\sum_{redS}$ and $\sum_{totalS}$ are the maximum calculated errors).

Treatments	AVS	CCrS	HCrS	ES(***	SO_4^{2-}	OrgS	$\sum_{redS}$	TRS	$\sum_{totalS}$	TotS
Överpurmo										
Ascorbic acid (AA) + 6 M HCl(*	0.40 ± 0.04	2.17 ± 0.06	0.09 ± 0.04	–	< 0.01	0.08 ± 0.01	2.66 ± 0.14	–	2.75 ± 0.15	2.65 ± 0.02
AA + 6 M HCl(*	0.16 ± 0.03	2.16 ± 0.05	0.10 ± 0.02	0.12 ± 0.03	< 0.01	0.07 ± 0.01	2.54 ± 0.13	–	2.62 ± 0.14	–
6 M HCl(*	0.46 ± 0.04	2.14 ± 0.01	0.05 ± 0.03	–	< 0.01	0.07 ± 0.01	2.65 ± 0.08	–	2.73 ± 0.09	–
Heat + AA + 6 M HCl(*	0.42 ± 0.03	–	–	–	–	–	–	–	–	–
Heat + SnCl2 + 6 HCl(*	0.74 ± 0.03	–	–	–	–	–	–	–	–	–
Heat + 6 M HCl + Cr^{2+}(**	–	–	–	–	–	–	–	2.67 ± 0.01	–	–
Larsmo Lake										
6 M HCl(*	0.14 ± 0.02	0.25 ± 0.01	0.03 ± 0.01	0.10 ± 0.03	< 0.01	0.05 ± 0.01	0.52 ± 0.07	–	0.58 ± 0.08	0.51
Heat + 6 M HCl + Cr^{2+}(**	–	–	–	–	–	–	–	0.51 ± 0.01	–	–
Zinc acetate + 6 M HCl(*	0.24	0.16	0.04	0.05	–	–	0.49	–	–	–

AVS = acid volatile sulphide; CCrS = cold Cr-reducible S; HCrS = hot Cr-reducible S; ES = elemental S; SO_4^{2-} = sulphate S; OrgS = organic S; $\sum_{redS}$ = sum of AVS, CCrS, HCrS, and ES; TRS = total reducible S; $\sum_{totalS}$ = sum of AVS, CCrS, HCrS, ES, SO_4^{2-}, and OrgS; and TotS = total S by Eschka's fusion.

(* The treatments were used for determination of AVS.

(** Treatments for determination of TRS.

(*** ES removed with dichloromethane prior to AVS.

– = Not measured.

but still effective in preventing Fe^{3+} interference (Hsieh et al. 2002), is proposed as the preferable reagent to use when analysing AS soil samples.

A major concern during sampling is the oxidation of AVS to elemental sulphur by atmospheric oxygen, leading to a lower AVS recovery and a higher ES recovery (or higher HCrS). Addition of ZnAc will fix dissolved sulphides and AVS (monosulphides and possibly greigite) as the more stable ZnS, which however will decompose as easily as the original reduced sulphur species during analysis (Morse et al. 1987, Duan et al. 1997). The addition of ZnAc to the Larsmo sample increased the AVS pool by approximately 42% to 0.24 wt%, while the CCrS pool decreased by approximately 36% to 0.16 wt%. This is possibly due to conversion of greigite to ZnS, which means that no S^0 is formed upon acid treatment in the analytical procedure. We therefore believe that the addition of ZnAc gives more accurate separations, and that consequently there is a risk that the CCrS pool for the Överpurmo sample is overestimated. Lasorsa and Casas (1996) noticed that addition of ZnAc may allow additional AVS to form in the sediment during storage for more than two weeks, and as a consequence, they recommended that ZnAc should not be used. We suggest, in contrast, that ZnAc could be admixed, prior to analysis, with the thawed sediment in order to prevent a proportion of greigite to end up in the CCrS pool. However, the assumed conversion of greigite to ZnS is not certain and should be verified in a separate experiment.

The HCrS pool in the Överpurmo and Larsmo samples did not show any major variations in recovery (Table 1). Since HCrS did not differ much, whether ES was removed or not, we consider that this is evidence for very little (or no) elemental sulphur in the sediments. The identified and quantified ES is probably the result of oxidation of AVS during analysis (i.e. after the addition of dichloromethane), sampling or storage.

Sulphur-isotopic compositions

Ideally, the distillation procedure recovers all of the sulphur in each species as Ag_2S or $BaSO_4$ precipitates, thus allowing for analysis of the isotopic composition of each species. However, as shown above, there are several opportunities for overlap in the extraction of different species. Determining the isotopic composition of Ag_2S and $BaSO_4$ precipitates collected in the speciation test above (mixtures M1 and M3–M5, Table 2) and comparing them to the original composition of the 'pure' compounds used tests for the effect on the isotopic composition of sulphur.

As the compounds chosen to represent the species AVS, CCrS, HCrS and SO_4^{2-} were off-the-

Table 2. Isotopic compositions ($\delta^{34}S$) and recovery (%, in brackets) of sulphur (S) containing chemical reagents (Na_2S and Na_2SO_4) and natural sulphur minerals (FeS_2 and S^0). The values for pure reagents were determined on individually prepared samples, while values for compounds are after separation from various mixtures. The analytical precision for $\delta^{34}S$ was estimated to 0.3‰.

Species	Acid volatile sulphide	Cold Cr-reducible S	Hot Cr-reducible S	Sulphate S
Compounds	Na_2S	FeS_2	S^0	Na_2SO_4
Pure reagents	0.5	9.3	1.0	7.1
$Na_2S + FeS_2 + S^0 + Na_2SO_4$	–0.4 (79.6)	6.8 (126.7)	–0.5 (65.9)	7.7 (99.7)
$Na_2S + FeS_2$	0.3 (84.7)	8.6 (113.1)	–	–
$Na_2S + FeS_2$	0.1 (89.4)	8.8 (110.4)	–	–
$Na_2S + Na_2SO_4$	–0.3 (99.9)	–	–	7.0 (101.6)
$Na_2S + Na_2SO_4$	0.3 (96.4)	–	–	7.3 (100.5)
$FeS_2 + SO_4$	–	9.8 (89.8)	–	7.1 (99.5)
$FeS_2 + SO_4$	–	9.4 (93.1)	–	7.5 (101.2)

– = Not measured.

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shelf chemical reagents and mineral sulphides (Table 2), some inhomogeneity in $\delta^{34}S$ is probable. This, together with analytical error, may to some degree encroach upon the integrity of the data and the results may be regarded as tentative only. The differences in $\delta^{34}S$ values of the compounds were significantly large to reveal isotope mixing between critical pairs, but mixing of pairs with similar $\delta^{34}S$ and mixing with more than two members is impossible to be correctly estimated. Furthermore, the $\delta^{34}S$ value is defined on a one-dimensional scale and mixing between e.g. FeS_2-Na_2S or FeS_2-S^0 in the same sample cannot in this case be discriminated. Therefore, the mixture M2 from the separation experiment above was excluded. With the exception of M1, the experiments were set up to reveal overlaps and mixing between pairs of species with significantly different $\delta^{34}S$ values.

Starting from an initial $\delta^{34}S$ value of +0.5‰ (Table 2), the extracted AVS ranges from –0.4‰ to +0.3‰, a decrease slightly larger than the estimated analytical precision (±0.3‰). With the exception of M4, the recovery of AVS and HCrS was low, and incomplete reaction may have caused fractionation of S-isotopes, and depletion of ^{34}S in the emanated H_2S is probable. The SO_4^{2-} was more or less quantitatively recovered in all experiments and, with the exception of M1 ($\delta^{34}S$ = 7.7‰), the $\delta^{34}S$ of the extracts were similar ($\delta^{34}S$ = +7.0–7.5‰) to that of the pure reagent (7.1‰). This shows that the speciation method does not cause overlap involving SO_4^{2-}. However, the $\delta^{34}S$ of CCrS varies considerably and overlap between the other species is significant.

Mixture M1 contained all species and the results varied; recoveries of AVS and HCrS were low and CCrS was high, while the recovery of SO_4^{2-} was close to 100% (Table 2). The $\delta^{34}S$ of CCrS showed a large decrease and, judging from the recoveries, the incorporated sulphur originated from AVS and HCrS. The high $\delta^{34}S$ of the SO_4^{2-} (+7.7‰) is somewhat mysterious; mass balance considerations suggest that the residual material of both AVS and HCrS should be roughly +4‰ (assuming no crossover to CCrS) and could not increase the value +7.1‰ if mixed with SO_4^{2-}. The recovery also indicates that this is not a possibility, so more probably, it must be deemed analytical. In the binary mixtures M3 and M4, the recoveries of AVS and CCrS nearly added up to the expected 200% and mass balance was preserved. The recovery of CCrS in M3 was slightly high and the decrease in $\delta^{34}S$ was significant; the only possible contaminant in M3 was AVS and the overlap during distillation clearly affected the isotopic composition of CCrS. The recovery of AVS and SO_4^{2-} was almost 100% for both species in M4, and no significant change was noted in the isotopic composition of either species (the low $\delta^{34}S$ in the first M4 AVS was probably caused by analytical error). In M5, there was no overlap between CCrS and SO_4^{2-}, but there was some loss of CCrS that perhaps was coupled with fractionation of sulphur, as seen in one measurement with $\delta^{34}S$ of +9.8‰.

The notably low recoveries and isotopic cross-contamination seen in the results are probably largely effects of grain size variation in the artificial samples prepared and attention must be given to diminution of the reagents in future experiments. However, we believe that this effect is limited to the artificial sample and that the more homogenous and finer grain size of clayey sediments results in better extraction of species (see Table 1) and less isotopic cross-contamination.

The isotopic compositions of sulphur species in the Överpurmo sediment are presented in Table 3. Duplicate samples were analysed in two parallel distillation lines and showed identical results within error, indicating the consistency of the method for extracting sulphur species for isotopic measurements from this type of sediments. The $\delta^{34}S$ values of the reduced sulphur species (AVS, CCrS and HCrS) were similar and varied only within a small range ($\delta^{34}S$ = 5.1-5.6‰) while the value of OrgS was slightly lower (4.1‰). The high $\delta^{34}S$ of the TotS (6.0‰) was intriguing, but considering that the result of the TotS method (2.65 wt%, Table 1, Överpurmo A) was less than the sum of the species (2.75 wt%) in the same sample, it seems reasonable to believe that there is some loss of sulphur in the TotS method. Heating the sample with Eschka's mixture might cause volatilization of sulphur, leaving a residue slightly enriched in ^{34}S.

Table 3. Isotopic composition ($\delta^{34}S$) of sulphur (S) species from the Överpurmo sediment. The analytical precision for $\delta^{34}S$ was estimated to 0.3‰.

Species	$\delta^{34}S$	Average $\delta^{34}S$	1 SD
Acid volatile sulphide	4.9 5.4	5.1	0.25
Cold Cr-reducible S	5.4 4.9	5.1	0.24
Hot Cr-reducible S	5.5 5.6	5.6	0.03
Organic S	4.2 4.1	4.1	0.04
Total S	6.0	–	–

– = Not measured.

The isotopic composition is used to study the relationship between sulphur species and can reflect the prevailing conditions during their formation. Reduced sulphur species (AVS, CCrS and HCrS) commonly develop in this type of sediments through dissimilatory sulphate reduction, while OrgS may form by assimilatory sulphate reduction (incorporation into marine organisms). Sulphur assimilated by living organisms constitutes 0.5–3.0% of the dry weight (Dinur et al. 1980), and according to Kaplan et al. (1963) the maximum contribution of sulphur to the sediment from marine organisms (e.g. animals and algae) would be about one percent dry weight of the organic matter. Applying this reasoning to the Överpurmo sediment, where the content of organic matter was determined to 10.6%, suggests that the sulphur (OrgS) incorporated in the organic matter would be about 0.1 wt%. This is in agreement with the actual OrgS content of 0.07 ± 0.02 wt % determined in the Överpurmo sediment, and we propose that this sulphur originates from assimilatory sulphate reduction. Since the isotopic fractionation during assimilatory sulphate reduction is small, the organic sulphur in marine organisms (and terrestrial plants) should directly reflect the $\delta^{34}S$ isotopic ratio of the sulphate available in the growth environment (Dinur et al. 1980). At present, sulphate in freshwater has a $\delta^{34}S$ of 6 ± 3‰ and 20 ± 3‰ in seawater (Dinur et al. 1980), which indicates that the OrgS in the Överpurmo sediment may have been formed under the influence of freshwater. In a closed system sulphate will be completely reduced, yielding sulphides with similar $\delta^{34}S$ as the starting sulphate (Goldhaber and Kaplan 1980). The isotopic compositions of reduced sulphur species (AVS, CCrS and HCrS) and organic sulphur (OrgS) in the sample thus further establish that the Överpurmo sediment was deposited in a freshwater environment.

Conclusions

The presented scheme provides a nearly complete analytical procedure for the separation and quantification of sulphur species present in boreal AS soils and in shallow coastal sediments. In order to optimize the analysis of sulphur species, the following must be considered: (1) separation and recovery of sulphur species is more accurate for fine-grained samples (e.g. clayey sediments) but coarser material can be analysed if the procedures are adjusted for grain size effects (e.g. longer reaction times, harsher treatments); (2) if abundant, elemental sulphur can be analysed separately in a first step using dichloromethane; (3) ascorbic acid should be added to prevent Fe^{3+} from oxidizing H_2S to S^0; and (4) addition of ZnAc improves the separation of AVS.

The Ag_2S and $BaSO_4$ precipitates from the speciation procedure can further be analysed for the isotopic composition of sulphur, thus allowing for discussion of the origin of the sulphur species. With the suggested modifications, cross-contamination between sulphur species is reduced and when combined with isotopic data, the procedure is a useful tool for future studies of sulphur-rich sediments and boreal AS soils.

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