

Isotopic fractionation of sulfur during formation of basaluminite, alunite, and natroalunite

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Abstract

The extent of fractionation of sulfur (S) isotopes during precipitation of basaluminite and alunite in supersaturated $\text{Al}_2(\text{SO}_4)_3$ solutions was determined in a laboratory synthesis experiment. An acid 0.05 M $\text{Al}_2(\text{SO}_4)_3$ solution was partly neutralized with $\text{Ca}(\text{OH})_2$, NaOH, and KOH to a molar OH/Al ratio of 2.0. Subsequent aging of the precipitates for 15 weeks at temperatures of 20 and 50 °C resulted in the formation of poorly crystalline basaluminite [$\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$], of mixtures of basaluminite with crystalline natroalunite [$\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$] or alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$], and of pure crystalline alunite. No significant isotopic fractionation of S was observed during the precipitation of poorly crystalline basaluminite ($\Delta\delta^{34}\text{S}_{\text{basaluminite-solution}} = +0.04 \pm 0.34\text{‰}$). In contrast, the formation of alunite and natroalunite was accompanied by small but significant isotopic fractionation that favored the incorporation of the heavier isotope, ^{34}S , in the minerals. Sulfur-isotope fractionation ($\Delta\delta^{34}\text{S}_{\text{mineral-solution}}$) was $+0.84 \pm 0.34\text{‰}$ for alunite, and $+1.72 \pm 0.34\text{‰}$ for natroalunite. The extent of S-isotope fractionation was found to be dependent on (i) the chemical composition and (ii) the crystal structure of the synthesized minerals, and seems to be related to the physico-chemical properties of the involved ions (charge, radius, mass), the energy balance of the reaction, and the reaction rate. The results indicate that S-isotope mass balances in aerated acid soils are not significantly confounded by S isotopic fractionation effects associated with the formation of Al hydroxysulfates.

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1. Introduction

Stable-isotope techniques have been used successfully to elucidate the cycling of sulfur (S) in terrestrial and aquatic ecosystems (e.g., Krouse and Grinenko, 1991; Ohmoto and Goldhaber, 1997; Seal et al., 2000).

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The origin of S in the environment commonly can be identified if different S sources have distinct isotopic compositions (e.g., Krouse et al., 1984). Whereas source identification in anaerobic environments can be compromised by significant S isotopic fractionation that occurs during bacterial (dissimilatory) sulfate reduction (e.g., Harrison and Thode, 1957), isotopic effects during S transformation processes under aerated conditions are widely believed to be small (e.g., Krouse and Grinenko, 1991). Hence, S contributions can be quantified in situations in which two or more known sources of S have markedly different isotopic compositions (e.g., Krouse, 1977; Krouse and Case, 1983). Based on this principle, researchers have also applied isotopically distinct S-bearing compounds to forest soils and agricultural ecosystems so that the turnover of the applied S in the biosphere, pedosphere, and hydrosphere can be monitored by using a mass- and isotope-balance approach (Giesemann et al., 1995; Mörth and Torssander, 1995; Mayer et al., 1995, 2001; Zhang et al., 1998).

A prerequisite for an accurate quantitative assessment of the fate of isotopically distinct S from two or more sources is that isotopic fractionation during S transformations must be either negligible or known precisely. In terrestrial and aquatic ecosystems, the predominant biological processes of S transformation under aerated conditions include (i) immobilization of the S by transforming inorganic (mainly SO_4^{2-}) into organic S, and (ii) mineralization processes that involve the conversion of organic S-bearing compounds into inorganic SO_4^{2-} . Major physico-chemical transformation processes are SO_4^{2-} sorption on clay minerals and Fe or Al oxyhydroxides, and the precipitation and dissolution of sulfate minerals, such as gypsum, jarosite, and Al (hydroxy) sulfates.

In most biological transformation processes under aerated conditions, isotopic fractionation of S is <5‰ (Kaplan and Rittenberg, 1964; Chukhrov et al., 1980; Chae and Krouse, 1986; Schoenau and Bettany, 1989). Adsorption and desorption of SO_4^{2-} do not involve significant S isotopic fractionation (Van Stempvoort et al., 1990). Sulfur-isotope fractionation during precipitation of gypsum has been reported to be <2‰ and favors the incorporation of the heavier isotope ^{34}S in the mineral (Thode and Monster, 1965; Holser et al., 1979; Szaran et al., 1998). No information seems to be available on the extent of S-isotope fractionation

associated with the precipitation of Al-hydroxysulfate minerals, such as basaluminite [$\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$], natroalunite [$\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$], or alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$]. These minerals can represent a significant pool for S in hydrothermal systems, in the sediments associated with acidic lakes in former open-pit mines, in acid-sulfate soils, and in forest soils that have been affected by high S input from atmospheric sources (Van Breemen, 1973; Nordstrom, 1982; Khanna et al., 1987; Courchesne and Hendershot, 1990; Böttcher, 1992). To assess correctly, by stable-isotope techniques, the turnover of S in these environments, knowledge about the isotopic fractionation of S associated with the formation of Al-hydroxysulfate minerals is essential. The objective of this study was to determine the extent of such fractionation during the formation of some Al-hydroxysulfate minerals in supersaturated Al-sulfate solutions in laboratory experiments.

2. Material and methods

2.1. Synthesis of Al-hydroxysulfate minerals

The Al-hydroxysulfate minerals were synthesized according to the procedure of Adams and Rawajfih (1977). The synthesis was conducted exactly as described in detail by Prietzel and Hirsch (1998). Solutions of 0.05 M $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (Fluka; reagent grade) were partly neutralized by rapid titration (titration time ca. 0.5 h) with dilute $\text{Ca}(\text{OH})_2$ (sample 1), NaOH (samples 2 and 4), and KOH (samples 3 and 5) to a molar OH/Al ratio of 2.0. The resulting precipitates were aged in their mother solutions for 15 weeks at temperatures of 20 °C (samples 1, 2, and 3) and 50 °C (samples 4 and 5). The aged precipitates were repeatedly rinsed with deionized water and methanol, filtered, dried in a desiccator, and finely ground with a mortar and pestle. All samples were stored in a desiccator at 20 °C prior to chemical and isotopic analyses.

2.2. Mineralogical and chemical analysis of the synthesized precipitates

To identify the chemical composition of the synthesized precipitates, mineralogical and chemical

methods were used. All precipitates were analyzed by powder X-ray diffraction (Philips PW 1820; CoK α radiation). The Al, Na, Ca, K, and S contents of the precipitates were determined in triplicate by digestion of 20-mg samples in 50 ml 6 M HNO₃ (reagent grade) and subsequent element-content analysis by ICP–OES (Perkin-Elmer Optima 3000). Sulfur contents were additionally determined using a LECO SC-444 analyzer.

2.3. Sulfur-isotope analysis

For determination of ³⁴S/³²S ratios of the Al-sulfate reagent and all precipitates, 5 mg of each sample were mixed with 50 mg V₂O₅ and 50 mg SiO₂ and heated to 1000 °C under vacuum to generate SO₂ (Yanagisawa and Sakai, 1983; Ueda and Krouse, 1986). After cryogenic purification of the SO₂ gas, its ³⁴S/³²S ratio was determined by mass spectrometry. Sulfur-isotope analyses were performed in triplicate. Additionally, 50 mg of the Al-sulfate reagent and of each mineral sample were completely dissolved in NaOH, and BaCl₂ solution was added to precipitate BaSO₄. The BaSO₄ was washed, filtered, and dried, and isotopic analyses of S were performed as described above. Results from the S-isotope measurements on the BaSO₄ agreed, within the uncertainty of the method, with those obtained by direct thermal decomposition of the Al-hydroxysulfate minerals.

All isotopic ratios are reported on the usual $\delta^{34}\text{S}$ scale in parts per thousand deviation from the sulfur isotope ratio of the V-CDT standard as established by the International Atomic Energy Agency, Vienna. The reproducibility of gas preparation and mass spectrometric measurement was ± 0.2 ‰. The uncertainty of the reported S-isotope fractionation effects between sulfate in solution and in the minerals was assessed by applying standard methods of error propagation to the analytical precision of the respective isotopic measurements as follows:

$$\text{S.D.}(\Delta\delta^{34}\text{S}_{\text{mineral-solution}}) = \left([\text{S.D.}(\delta^{34}\text{S}_{\text{mineral}})]^2 + [\text{S.D.}(\delta^{34}\text{S}_{\text{solution}})]^2 \right)^{1/2} \quad (1)$$

where S.D. is the standard deviation of triplicate $\delta^{34}\text{S}$ determinations on solution sulfate and mineral sulfate, respectively.

3. Results

3.1. Mineralogical and chemical composition of the precipitates

The XRD spectra show that sample 1 (Fig. 1a) and sample 2 (Fig. 1b) consisted almost exclusively of poorly crystalline basaluminite. Sample 3 (Fig. 1c) was a mixture of poorly crystalline basaluminite with some alunite. Sample 4 (Fig. 1d) was a mixture of alunite with small amounts of poorly crystalline basaluminite. Sample 5 (Fig. 1e) consisted exclusively of alunite. The XRD spectra indicated that all precipitates consisted of, at most, two different minerals whose ideal formulas are known (basaluminite, alunite, or natroalunite). The presence of amorphous Al(OH)₃, which would not show up in the XRD spectra, can be excluded because the pH values in the supernatants of all samples except sample 4 (pH 5.2) were lower than 4.3. This pH is too low to allow the precipitation of Al(OH)₃. Consequently, the mixing ratios of the minerals in the precipitates were calculated by comparing the chemical compositions of the precipitates with those of the ideal formulas of the pure minerals. The mineral mixing ratios for the various precipitates were calculated with an iterative procedure. The mixing ratio with the minimal sum of differences between the theoretical and the measured contents of Al, S, and other cations (Na⁺, K⁺, and Ca²⁺, respectively) for the various precipitates was identified, and accepted to represent the mineral assemblage of the sample. According to the uncertainties of the contents of different elements in the various samples (usually <10%; Table 1), the uncertainties of the calculated mixing ratios were estimated to be better than $\pm 20\%$.

The results of the calculations, summarized in Table 1, suggest that sample 1 consisted of 95% basaluminite, and the Ca content of 0.4 wt.% indicates that approximately 5% of the precipitate must have been co-precipitated CaSO₄·2H₂O. Apparently, Ca had not been removed completely by the washing procedure, a phenomenon which is commonly observed during the preparation of basaluminite by the method utilized (Adams and Rawajfih, 1977; Prietzel and Hirsch, 1998). Sample 2 consisted of 90% basaluminite. A Na content of 0.6 wt.% indicated

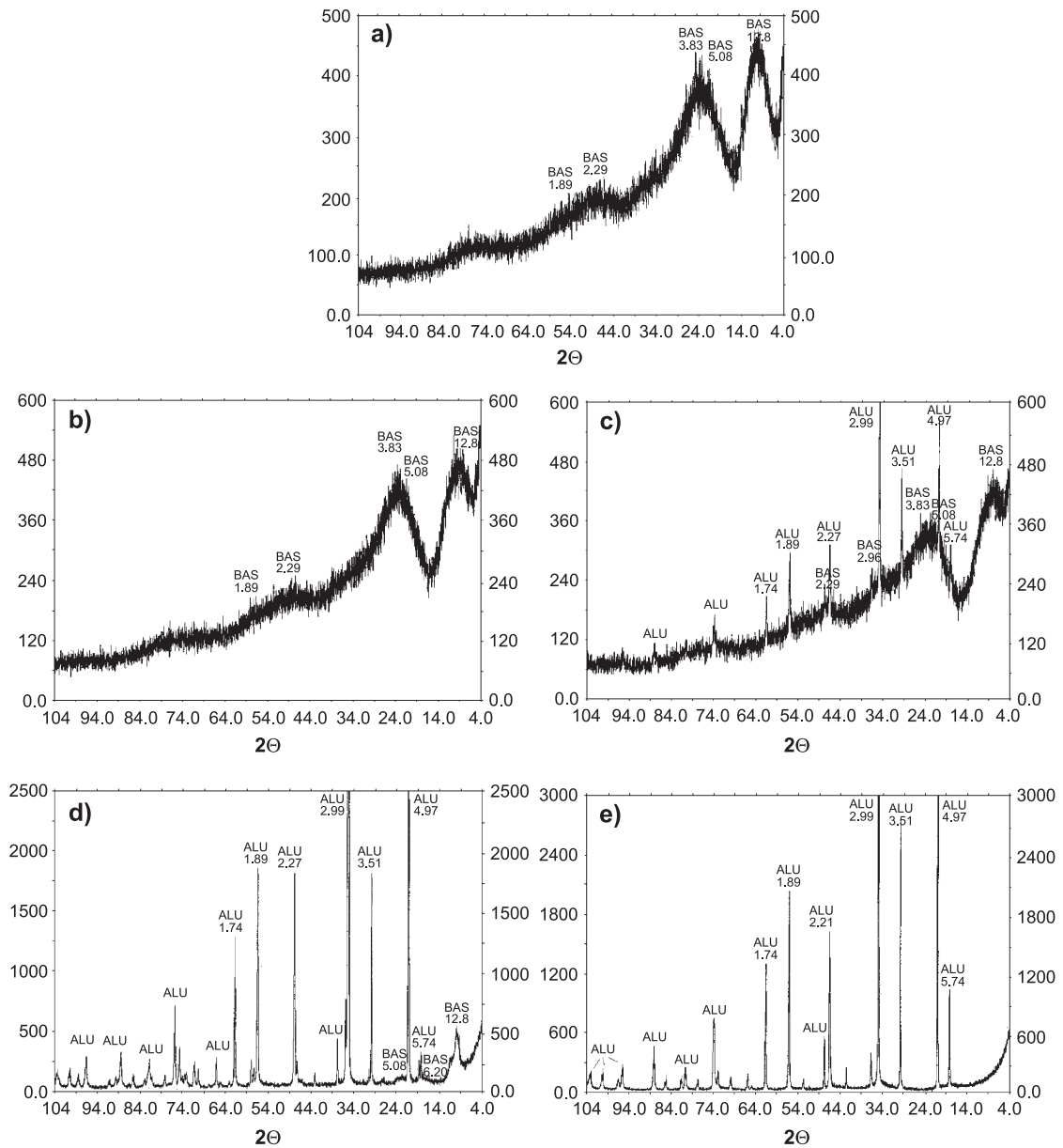


Fig. 1. XRD diagrams of the synthesized precipitates. (a) sample 1 (aged at 20 °C): basaluminite [BAS] plus traces of gypsum; (b) sample 2 (aged at 20 °C): mixture of 90% basaluminite [BAS] and 10% natroalunite; (c) sample 3 (aged at 20 °C): mixture of 70% basaluminite [BAS] and 30% alunite [ALU]; (d) sample 4 (aged at 50 °C): mixture of 75% natroalunite [ALU] and 25% basaluminite [BAS]; (e) sample 5 (aged at 50 °C): pure alunite [ALU]. Values denoted at peak tops represent typical interplanar (d) values in 10^{-10} m.

the presence of 10% natroalunite. According to XRD and chemical data, sample 3 consisted of 70% poorly crystalline basaluminite and of 30% alunite. Sample 4 contained 75% natroalunite and 25% basaluminite, and sample 5 consisted of pure alunite.

3.2. Sulfur-isotope ratios of the precipitates and the solution

The $\text{Al}_2(\text{SO}_4)_3$ reagent used for preparation of the mother solution had a $\delta^{34}\text{S}$ value of $-0.05 \pm 0.27\text{‰}$.

Table 1
Mineralogical and chemical composition and $\delta^{34}\text{S}$ values (‰) of the synthesized Al-hydroxysulfate precipitates^a

| Sample number | Minerals (mol%) | Stoichiometric formula | | Chemical composition, wt.% | | | | | | |
|----------------------------------|--------------------|---|--------|----------------------------|----------|-------|---------|-------|-----------------------------|---|
| | | | | S | Al | Na | K | Ca | $\delta^{34}\text{S}$ value | $\Delta\delta^{34}\text{S}$, mineral–solution |
| 1 Ca(OH) ₂ 20°C | Basalum. (95%) | Al ₄ (OH) ₁₀ SO ₄ · 4H ₂ O | Meas. | 9.3±1.1 | 21.7±2.4 | 0±0 | 0.1±0 | 0.4±0 | −0.01±0.20 | +0.04±0.34 |
| | Gypsum (5%) | CaSO ₄ · 2H ₂ O | Theor. | 7.1 | 22.8 | 0 | 0 | 0.4 | | |
| 2 NaOH 20°C | Basalum. (90%) | 0.90Al ₄ (OH) ₁₀ SO ₄ · 4H ₂ O | Meas. | 9.1±0.7 | 20.7±0.8 | 0.6±0 | 0±0 | 0±0 | +0.27±0.35 | +0.32±0.44 |
| | Natroalunite (10%) | 0.10NaAl ₃ (SO ₄) ₂ (OH) ₆ | Theor. | 7.8 | 23.0 | 0.6 | 0 | 0 | | |
| 3 KOH 20 °C | Basalum. (70%) | 0.70 Al ₄ (OH) ₁₀ SO ₄ · 4H ₂ O | Meas. | 9.5±0.2 | 22.7±0.4 | 0±0 | 2.7±0.2 | 0±0 | +0.25±0.35 | +0.30±0.44 |
| | Alunite (30%) | 0.30 KAl ₃ (SO ₄) ₂ (OH) ₆ | Theor. | 9.5 | 22.2 | 0 | 2.8 | 0 | | |
| 4 NaOH 50°C | Natroalunite (75%) | 0.75 NaAl ₃ (SO ₄) ₂ (OH) ₆ | Meas. | 14.0±0.7 | 21.1±1.2 | 4.1±0 | 0±0 | 0±0 | +1.24±0.20 | +1.29±0.34 |
| | Basalum. (25%) | 0.25 Al ₄ (OH) ₁₀ SO ₄ · 4H ₂ O | Theor. | 13.8 | 21.1 | 4.4 | 0 | 0 | | |
| 5 KOH 50°C | Alunite | KAl ₃ (SO ₄) ₂ (OH) ₆ | Meas. | 14.8±2.7 | 19.1±0.4 | 0±0 | 8.3±0.4 | 0±0 | +0.79±0.21 | +0.84±0.34 |
| | | | Theor. | 15.5 | 19.6 | 0 | 9.4 | 0 | | |

^a Arithmetic mean value±standard deviation of triplicate measurements. The $\delta^{34}\text{S}$ value of the Al₂(SO₄)₃ solution was −0.05‰. Weight percentage values of S, Al, Na, K, and Ca have been quantified to calculate the mixing ratio of the hydroxy sulfate minerals identified by XRD in the precipitates. Meas.: Measured contents of S, Al, Na, K, and Ca in the precipitates; Theor.: theoretical contents of the respective elements in a mixture of ideal minerals with the mixing ratio stated in column 2.

The $\delta^{34}\text{S}$ values of the Al-hydroxysulfate minerals (Table 1) varied between -0.01 and $+1.24\text{‰}$, indicating a preferential precipitation of the heavier isotope ^{34}S in most minerals. For the basaluminite-dominated sample 1, the difference between the $\delta^{34}\text{S}$ values of the solution and the mineral ($\Delta\delta^{34}\text{S}_{\text{basaluminite-solution}}$) was $+0.04\pm 0.34\text{‰}$, indicating no isotopic fractionation of S during the precipitation of basaluminite. Hence, a $\Delta\delta^{34}\text{S}_{\text{basaluminite-solution}}$ value of 0‰ was used for the following calculations.

The formation of pure alunite (sample 5) was associated with a $\Delta\delta^{34}\text{S}_{\text{alunite-solution}}$ value of $+0.84\pm 0.34\text{‰}$. For sample 3 (70% basaluminite, 30% alunite), a $\Delta\delta^{34}\text{S}$ value of $+0.30\pm 0.44\text{‰}$ was observed, which is close to the theoretically expected $\Delta\delta^{34}\text{S}$ value of $+0.25\pm 0.34\text{‰}$ calculated according to Eq. (2):

$$\Delta\delta^{34}\text{S}_{\text{sample 3}} = 0.7 \cdot \Delta\delta^{34}\text{S}_{\text{basaluminite-solution}} + 0.3 \cdot \Delta\delta^{34}\text{S}_{\text{alunite-solution}} = +0.28\text{‰} \quad (2)$$

with $\Delta\delta^{34}\text{S}_{\text{basaluminite-solution}} = 0\text{‰}$ and $\Delta\delta^{34}\text{S}_{\text{alunite-solution}} = +0.84\text{‰}$.

The largest difference between the $\delta^{34}\text{S}$ values of the mineral and the solution ($\Delta\delta^{34}\text{S}_{\text{mineral-solution}} = +1.29\pm 0.34\text{‰}$) was observed for sample 4, which consisted of 75% natroalunite and 25% basaluminite. Because $\Delta\delta^{34}\text{S}_{\text{basaluminite-solution}}$ was 0‰ , the theoretical $\Delta\delta^{34}\text{S}$ value of pure natroalunite was calculated according to Eq. (3) and was found to be $+1.72\pm 0.34\text{‰}$:

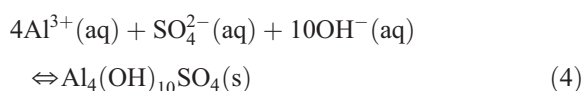
$$\Delta\delta^{34}\text{S}_{\text{natroalunite}} = (\Delta\delta^{34}\text{S}_{\text{sample 4}}) / 0.75 = 1.72\text{‰} \quad (3)$$

Consequently, the extent of S-isotope fractionation during the formation of natroalunite in supersaturated $\text{Al}_2(\text{SO}_4)_3$ solution appears to be approximately twice as large ($\Delta\delta^{34}\text{S}_{\text{natroalunite-solution}} = +1.72\pm 0.34\text{‰}$) than that associated with the formation of alunite ($\Delta\delta^{34}\text{S}_{\text{alunite-solution}} = +0.84\pm 0.34\text{‰}$). The analytically determined $\Delta\delta^{34}\text{S}$ value of $0.32\pm 0.44\text{‰}$ for sample 2 agreed well, within the uncertainty of the method, with the theoretically expected $\Delta\delta^{34}\text{S}$ value for this precipitate consisting of 90% basaluminite and 10% natroalunite ($\Delta\delta^{34}\text{S}_{\text{sample 2}} = 0.1 \cdot \Delta\delta^{34}\text{S}_{\text{natroalunite-solution}} = 0.17\text{‰}$).

4. Discussion

In the following, we discuss potential reasons for the different extent of isotopic fractionation of S during the formation of the investigated Al-hydroxysulfate minerals based on a detailed assessment of the involved reactions and their thermodynamic and kinetic characteristics.

At temperatures $<100\text{ °C}$, dropwise addition of $\text{Ca}(\text{OH})_2$, NaOH , or KOH to an $\text{Al}_2(\text{SO}_4)_3$ solution results in immediate precipitation of basaluminite (Adams and Rawajfih, 1977) according to the following overall reaction:



The solubility product K_{sp} of amorphous basaluminite at 298 K is $10^{-116.0}$ ($pK_{\text{sp}} = 116.0$; Adams and Rawajfih, 1977). Using this pK_{sp} value and the thermodynamic data of the aqueous reactants summarized in Table 2, the standard Gibbs free energy of reaction $\Delta G^\circ_{\text{r}}$ for the precipitation of amorphous or poorly crystalline basaluminite was calculated to be $-662.11\text{ kJ mol}^{-1}$. The standard Gibbs free energy of formation $\Delta G^\circ_{\text{f}}$ is $-4933.33\text{ kJ mol}^{-1}$ for amorphous and poorly crystalline basaluminite, and $-4941.88\text{ kJ mol}^{-1}$ for crystalline basaluminite (Adams and Rawajfih, 1977).

The formation of alunite and natroalunite at temperatures $<100\text{ °C}$ is kinetically inhibited (Nordstrom, 1982). As shown by Adams and Rawajfih (1977) and Adams and Hajek (1978), the addition of NaOH and KOH to an $\text{Al}_2(\text{SO}_4)_3$ solution will initially result in precipitation of basaluminite, and not in a direct formation of alunite. However, basaluminite is metastable in solutions with Na^+ or K^+ activities $>10^{-5}\text{ mol l}^{-1}$ (Nordstrom, 1982). It converts into natroalunite or alunite in a re-dissolution/re-precipitation process (Adams and Rawajfih, 1977; Nordstrom, 1982). This reaction is kinetically restrained and therefore proceeds very slowly at 25 °C . Even though the reaction can be accelerated by increasing the temperature to 50 °C , or by seeding the solution with alunite crystals or clay, several weeks are needed for a complete conversion of basaluminite to alunite in a K^+ -rich solution, or to natroalunite in a

Table 2

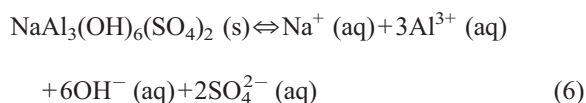
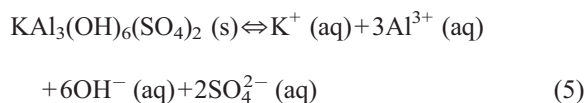
Thermodynamic properties of various aqueous species involved in the formation of Al-hydroxysulfate minerals

| Species | Standard Gibbs free energy of formation ΔG°_f [kJ mol ⁻¹] | Standard-state enthalpy of formation ΔH°_f [kJ mol ⁻¹] | Standard-state entropy S° [J K ⁻¹ mol ⁻¹] | Reference ^a |
|------------------------------------|---|--|--|------------------------|
| K ⁺ (aq) | -282.5 | -252.14 | 101.2 | a |
| Na ⁺ (aq) | -262.0 | -240.34 | 58.45 | a |
| Al ³⁺ (aq) | -488.8 | -540.9 | -342 | a |
| Al(OH) ²⁺ (aq) | -697 | -771 | -185 | b |
| OH ⁻ (aq) | -157.2 | -230.01 | -10.9 | a |
| SO ₄ ²⁻ (aq) | -744.0 | -909.3 | 18.5 | a |
| Al(OH) ₃ (s) | -1154.89 | -1293.13 | 68.44 | a |
| H ₂ O (l) | -237.14 | -285.83 | 69.95 | a |
| H ⁺ (aq) | 0 | 0 | 0 | a |

^a (a) Nordstrom and Munoz (1994); (b) Palmer and Wesolowski (1993).

Na⁺-rich solution (Adams and Rawajfih, 1977; Prietzel and Hirsch, 1998; this study).

For the conversion of basaluminite to alunite or natroalunite, the respective ΔG°_r values can be calculated from the ΔG°_f value of poorly crystalline basaluminite (-4933.33 kJ mol⁻¹), the ΔG°_f values of the involved aqueous species (Table 2), and the ΔG°_f values of alunite and natroalunite, respectively. The ΔG°_f values of alunite and natroalunite can be calculated using the pK_{sp} values of 85.4 (alunite) and 79.7 (natroalunite) (Adams and Rawajfih, 1977; Nordstrom, 1982) of their solubility equilibria shown in Eqs. (5) and (6):



The resulting ΔG°_f values are -4667.55 kJ mol⁻¹ for alunite and -4614.02 kJ mol⁻¹ for natroalunite. Consequently, the ΔG°_r values for the conversion of basaluminite into alunite and natroalunite at 25 °C are -145.08 and -112.05 kJ mol⁻¹, respectively. It is noteworthy that the ΔG°_r values were calculated for standard-state conditions (298 K, 0.1 MPa). In our experiment, three of the five samples were synthesized and aged at 20 °C (293 K) and 0.1 MPa pressure, which is close to standard-state conditions. Samples 4 and 5 were synthesized at 50 °C (323 K), which is a larger deviation from standard-state

conditions. To our knowledge, no standard enthalpy values of formation ΔH°_f and entropy values S° are available for basaluminite and natroalunite. Therefore, the effects of increased temperature on the Gibbs free energy of reaction for the formation of alunite and natroalunite at 50 °C could not be addressed.

The conversion of basaluminite into alunite in a K⁺-rich solution results in a greater reduction of free energy and proceeds considerably faster than the conversion of basaluminite into natroalunite in a Na⁺-rich solution. This difference was evident in that, after 15 weeks of mineral aging at 20 °C, the presence of natroalunite was not yet detectable by XRD (Fig. 1b), whereas significant amounts of alunite had been formed within the same time period. At 50 °C, the entire initial basaluminite had been converted to alunite after 15 weeks, whereas the conversion of basaluminite to natroalunite was still incomplete (75% conversion). Similar observations were reported by Prietzel and Hirsch (1998), who also showed that the natroalunite was much more resistant to dissolution by strong acids and bases than alunite. Prietzel and Hirsch (1998) attributed this resistance to the development, during the slow crystallization of natroalunite, of coarser grained crystallites than occur for alunite.

The extent of S-isotope fractionation observed during formation of the different Al-hydroxysulfate minerals, the reaction kinetics of the various precipitation processes, and important mineralogical properties of the precipitates are summarized in Table 3. No significant isotopic fractionation of S was observed during the rapid formation of poorly crystalline basaluminite, a reaction which is charac-

Table 3

Extent of isotopic fractionation of S compared with mineralogical and chemical properties of the precipitates and with thermodynamic and kinetic characteristics of the respective reactions of mineral formation

| Mineral | Extent of isotopic fractionation ($\Delta\delta^{34}\text{S}_{\text{mineral-solution}}$) | Crystal structure | Resistance to acid dissolution ^a | Rate of mineral formation | Energy yield during mineral formation (ΔG°_r) |
|--------------|--|--------------------|---|---------------------------|--|
| Basaluminite | Negligible | Amorphous | Low | Very fast | -662.11 kJ mol ⁻¹ |
| Alunite | 0.84±0.34‰ | Crystalline | High | Slow | -145.08 kJ mol ⁻¹ |
| Natroalunite | 1.72±0.34‰ | Highly crystalline | Very high | Very slow | -112.05 kJ mol ⁻¹ |

^a Prietzel and Hirsch (1998).

terized by a large negative ΔG°_r value. In contrast, the slow formation of alunite (intermediate negative ΔG°_r value), and particularly the very slow formation of natroalunite (least negative ΔG°_r value), were associated with a small but significant isotopic fractionation of +0.84±0.34‰ and +1.72±0.34‰, respectively, favoring the heavier isotope ³⁴S in the minerals.

There are two types of isotopic fractionation effects, equilibrium and non-equilibrium (kinetic) effects. Equilibrium isotopic fractionation requires that chemical equilibrium between reactants and products is established and its extent may be influenced by various factors, among which are temperature, chemical composition (oxidation state, ionic charge, atomic mass, electronic configuration), and crystal structure (e.g., O'Neil, 1986; Chacko et al., 2001). One rule of thumb is that among different varieties of the same compound, the denser one is typically enriched in the heavier isotope if isotopic equilibrium is achieved (e.g., Criss, 1999). Kinetic isotope effects are usually associated with fast, incomplete, or unidirectional processes, typically resulting in a preferential enrichment of the lighter isotope in the reaction products. At low temperatures, both equilibrium and non-equilibrium isotope fractionation effects are typically larger than at high temperatures (Ohmoto and Lasaga, 1982), and kinetic isotope fractionation may become increasingly relevant compared to equilibrium isotope fractionation (Seal et al., 2000). Our experiment was a synthesis experiment and not a true isotope-reversal approach, and it is therefore difficult to differentiate conclusively between equilibrium and kinetic isotope-fractionation effects. Nevertheless, there seems to be a causal relationship between the extent of S-isotope fractionation during the formation of the various Al-

hydroxysulfate minerals and the following variables: (1) the chemical composition of the minerals, (2) their crystal structure, (3) the rate of their formation, and (4) the energy balance ΔG°_r of their formation. Whereas variables (1) and (2) may give rise to equilibrium isotope fractionation of S, variables (3) and (4) are likely to cause non-equilibrium isotope effects.

4.1. Chemical composition

The formation of natroalunite and alunite was associated with an enrichment of ³⁴S in the minerals. The isotopic effect observed for natroalunite was approximately twice as large (+1.72±0.34‰) than that observed for alunite (+0.84±0.34‰). The larger isotopic fractionation for minerals with the lower cation mass is consistent with results from studies by Thode and Monster (1965) and Kusakabe and Robinson (1977), who found a higher enrichment of ³⁴S for the formation of CaSO₄·2H₂O compared to the formation of BaSO₄. The fractionation is also consistent with the theoretical considerations of Sakai (1968), who postulated a decreasing ³⁴S enrichment for the precipitation of sulfate salts with increasing mass of the counter cation under isotope equilibrium conditions (CaSO₄>SrSO₄>BaSO₄>PbSO₄; "cation mass dependence" principle). According to Sakai (1968), the vibrational energy of the sulfur atom in sulfate is only slightly modified by the crystalline field; therefore, the isotopic composition of any sulfate mineral is expected to be only slightly different from the associated aqueous ion. The S-isotope fractionation values obtained in our study for the formation of alunite (+0.84‰) and natroalunite (+1.72‰) agree with the concept of Sakai (1968) and also match well the value reported by Thode and

Monster (1965) for the formation of gypsum at ambient temperature (+1.65‰). On the contrary, the lack of any S-isotope fractionation observed for the formation of basaluminite cannot be explained satisfactorily with the cation mass dependence concept because Al and Na have similar atom masses.

4.2. Crystal structure

The extent of isotope fractionation during the precipitation of solids in supersaturated inorganic solutions is also influenced by the crystal structure of the precipitates. Heavy isotopes are preferentially incorporated in more closely packed or better-ordered structures (e.g., Kyser, 1987; Hoefs, 1997). Thus, isotope fractionation should be larger when well-crystallized solids are formed in a slow reaction, whereas the rapid formation of amorphous solids is expected to result in negligible isotopic fractionation. This trend was observed in our experiment, wherein the highly crystalline natroalunite displayed larger isotope effects than the crystalline alunite (intermediate value), and the amorphous basaluminite showed negligible isotope fractionation for S (Table 3). The observed increase in the enrichment of ^{34}S in the precipitates (basaluminite < alunite < natroalunite) can therefore be explained by a combination of the cation mass dependence principle (alunite < natroalunite) and crystal-structure effect (basaluminite < (natro)alunite). It seems likely that the enrichment of ^{34}S is caused by equilibrium isotope effects during the re-dissolution/re-precipitation process between basaluminite and (natro)alunite.

4.3. Rate of formation

The formation of basaluminite and that of alunite at 50 °C was complete after 15 weeks, and a chemical equilibrium can be assumed among the various reactants. This is not true for the formation of alunite at 20 °C, and for the formation of natroalunite at either 20 or 50 °C, where the presence of metastable basaluminite indicated that the reaction had not been completed during the aging time of 15 weeks. The observed S-isotope fractionation during the formation of alunite at 20 °C and natroalunite at 20 and 50 °C may therefore be due to both equilibrium and non-equilibrium S-isotope effects. Unfortunately, with our

experimental design, a clear attribution of the observed S-isotope fractionation to equilibrium and non-equilibrium effects cannot be made.

4.4. Energy balance ΔG°_r of the mineral formation reaction

In a two-phase system (liquid+solid) under given physical (p , T) and chemical conditions, the chemical composition and the crystal structure of a precipitate determine the energy balance of its formation. It is also well-known that the crystal structure of a mineral will be strongly influenced by the rate of precipitation. Fast precipitation may result in amorphous precipitates, whereas highly ordered crystallinity is more likely at slow precipitation rates. Furthermore, theoretical evidence for a cause-and-effect relationship between the energy balances (ΔG°_r values) of the investigated precipitation reactions and their rates has been provided by Brezonik (1994) in his Linear Free Energy Relationships and by Stumm and Morgan (1994) with the Microscopic Reversibility Principle. Hence, it seems that variables (1) to (4) are interlinked with each other. A high release of energy during mineral precipitation (basaluminite >> alunite > natroalunite) was always associated with a high reaction rate, resulted in a poorly ordered crystal structure, and was associated with negligible isotope effects (Table 3). In contrast, low energy release during mineral formation resulted in slow reaction rates, well-ordered crystal structures, and significant isotope effects.

Higher reaction temperatures during precipitation of solids in supersaturated solutions result in lower isotope fractionation effects (e.g., Hoefs, 1997; Chacko et al., 2001; Cole and Chakraborty, 2001). Results from this study provide no conclusive relationships between the temperature during formation of alunite and natroalunite and the extent of S-isotope fractionation. The S-isotope fractionation during formation of natroalunite at 20 °C (sample 2) was slightly higher ($\Delta\delta^{34}\text{S}=0.32\pm 0.44\text{‰}$) than the theoretically expected value calculated (Eq. (1)) from the chemical and isotopic properties of sample 4 aged at 50 °C ($\Delta\delta^{34}\text{S}=0.17\pm 0.44\text{‰}$). Even though this difference is statistically insignificant due to the high uncertainty of the method, the observed tendency agrees with the general rule that isotope fractionation effects are typically larger at low temperatures than at

high temperatures (Ohmoto and Lasaga, 1982). A similar observation was made for the extent of S-isotope fractionation during the formation of alunite at 20 °C (sample 3: $\Delta\delta^{34}\text{S}=0.30\pm 0.44\text{‰}$) and at 50 °C ($\Delta\delta^{34}\text{S}=0.25\pm 0.34\text{‰}$). We conclude that the investigated range of 30 K was too small to identify significant temperature effects on S-isotope fractionation. Likewise, Szaran et al. (1998) did not observe a temperature effect on isotopic fractionation of S during the precipitation of gypsum in supersaturated solution within the range between 7 and 57 °C.

5. Conclusions

The rapid precipitation of amorphous basaluminite in a partly neutralized $\text{Al}_2(\text{SO}_4)_3$ solution is associated with no significant S-isotope fractionation. The subsequent slow crystallization of alunite in K^+ -rich solutions, and the very slow formation of highly crystalline natroalunite in Na^+ -rich solutions, are associated with a S-isotope fractionation between +0.84‰ and +1.72‰, with the heavier isotope ^{34}S being enriched in the minerals. The extent of isotopic fractionation was found to depend on the chemical composition and the crystal structure of the synthesized minerals, and seemed to be related to the mass of the involved cations, and to the energy balance and the rate of the precipitation reactions. Because we did not carry out reversed experiments, it is difficult to distinguish conclusively between equilibrium and non-equilibrium S-isotope effects. However, most of our observations seem to be consistent with equilibrium isotopic fractionation during the re-dissolution/re-precipitation process between basaluminite and (natro)alunite. This study indicates that isotopic fractionation of S during precipitation of basaluminite, alunite, and natroalunite will shift the $\delta^{34}\text{S}$ values by less than +2‰. Consequently, S-isotope mass balances in aerated acid soils are not significantly confounded by S isotopic fractionation effects associated with the formation of Al hydroxysulfates.

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