

Article

## **Comparing Schwertmannite and Hydrobasaluminite Dissolution in Ammonium Oxalate (pH 3.0): Implications for Metal Speciation Studies by Sequential Extraction**

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Abstract: The "poorly crystalline iron oxy-hydroxides" are one of the most reactive and environmentally important fractions in soils and sediments due to the association of many toxic elements associated with these minerals. The metal content of this fraction in sequential extraction procedures is usually evaluated by dissolution in ammonium oxalate ( $[NH_4]_2C_2O_4\cdot H_2O$ ) at pH 3.0 and 25 °C. Such chemical treatment, however, may also dissolve other mineral phases of comparable reactivity, which can lead to wrong interpretations of mineral carriers for specific metals. In this study, we compare the dissolution kinetics of schwertmannite and hydrobasaluminite, two minerals of comparable crystallinity and reactivity that play a major role in the mobility of many trace metals in waters and sediments affected by acid mine drainage (AMD). We first synthesized these two minerals in the laboratory by partial neutralization of two different metal-rich mine waters, and then we applied the standard protocol of ammonium oxalate dissolution to different specimens; the solutions were periodically sampled at intervals of 2, 5, 10, 15, 30 and 60 min to compare (i) the kinetics of mineral dissolution, and (ii) the metals released during dissolution of these two minerals. The results indicate a very similar kinetics of mineral dissolution, though hydrobasaluminite exhibited a faster rate. Some toxic elements such as As, Cr or V were clearly bonded to schwertmannite, while many others such as Cu, Zn, Si, Co, Ni and Y were clearly linked to hydrobasaluminite. These results suggest that studies linking the mobility of many elements with the Fe cycle in AMD-affected soils and sediments could be inaccurate, since these elements could actually be associated with Al minerals of poor crystallinity. The step of ammonium oxalate dissolution in sequential extraction studies should be best described with a more general term such as "low-crystallinity oxy-hydroxides".

**Keywords:** acid mine drainage; aluminum; ammonium oxalate; metal speciation; mine wastes; sequential extraction

## 1. Introduction

Traditionally, studies addressing the distribution of metals in different fractions of mine wastes (e.g., tailings) and AMD-affected soils and sediments have used the technique of sequential extraction, which considers consecutive extractions of metals by exposing the solids to dissolution in reagents of increasing chemical reactivity [1–12]. This technique has proved especially helpful when combined with Differential X-Ray Diffraction (DXRD) [4,5]. The mobility and bioavailability of toxic elements and heavy metals in these soils strongly depend on their speciation and distribution in different



mineralogical fractions with variable reactivity [13]. The "poorly crystalline iron oxy-hydroxides" is often considered one of the most reactive and, at the same time, most environmentally important fractions due to the presence of many toxic elements associated with iron minerals such as schwertmannite or ferrihydrite [1–5]. The metal content of this fraction in sequential extraction procedures is usually evaluated by dissolution in 0.2 M ammonium oxalate ( $[NH_4]_2C_2O_4\cdot H_2O$ ) at pH 3.0 and 25 °C during 1 h and only sporadic shaking (Table 1) [1–5]. Such chemical treatment, however, can dissolve other mineral phases of comparable crystallinity and reactivity which also play an important role in the mobility of metals in these environments. A clear example is that of hydrobasaluminite, a poorly crystalline (nearly amorphous) Al oxy-hydroxysulfate which is also typical in AMD environments [14–22]. Although these two minerals are formed at different pH conditions (schwertmannite at pH 2.5–3.5 and hydrobasaluminite at pH 4.0–5.5), they can coexist in soils and sediments of streams, lakes and reservoirs affected by AMD [5,9,10,12]. These two minerals also show comparable (low) crystallinity and (high) surface reactivity, which make them efficient sorbents of trace metals [16–18]. As a result, of this physical co-occurrence and chemical/crystallographical similarity, doubts exist about the extent at which the presence of hydrobasaluminite can affect the results of sequential extraction studies, which often attribute the presence of metals leached in this step to retention by schwertmannite and other related Fe(III) oxy-hydroxides such as ferrihydrite. Some studies have reported a substantial Al release in this step, suggesting partial dissolution of some Al phase in the ammonium oxalate medium [6,9,12]. Several studies [23,24] did consider a fraction of "amorphous Al/Fe oxides/oxy-hydroxides" resulting from ammonium oxalate extraction, though many other studies on mine wastes and AMD-impacted soils still considered a "poorly ordered Fe oxy-hydroxides" fraction as a result of ammonium oxalate dissolution at room temperature [4–11]. This can lead to some confusion about the actual carriers of toxic elements (e.g., As, Cr, Pb, Cd) and valuable metals (e.g., Cu, Zn, Si, Co, Ni, Y, REE) in these soils and sediments.

Major Elements (mg/L)											
Water sample	Κ	Na	Mg	Ca	$SO_4$	SiO <sub>2</sub>	Fe	Mn	Cu	Zn	Al
HER	1.4	48	666	530	5900	66	342	158	21	130	76
ZP	0.6	37	756	552	14,712	150	3901	317	184	182	876
Trace Elements (µg/L)											
Water sample	As	Be	Ni	Cd	Со	Cr	Pb	Se	Tl	U	V
HER	44	37	2494	186	3379	34	26	58	10	20	2
ZP	5688	23	3994	355	4126	156	408	167	12	118	177

**Table 1.** Major and trace element concentration in mine waters selected to synthesize the schwertmannite and hydrobasaluminite samples used in this study. HER—Herrerías mine; ZP—La Zarza mine.

In this study, we compare the dissolution kinetics of schwertmannite and hydrobasaluminite in ammonium oxalate medium at pH 3.0. Our objective was two-fold: firstly, to discern if both minerals show a comparable dissolution kinetics; and secondly, to investigate which specific trace elements are preferentially bound to each of these minerals. The implications of our study are relevant because they could reveal specific metal-mineral associations and dissipate doubts about metal transport and storage in AMD-affected soils and sediments. The relevance of our results can also expand to other environments where amorphous Al-Fe phases play an important role in metal mobility, such as naturally contaminated rocks, aquifers and soils [23–28].

#### 2. Materials and Methods

#### 2.1. Sample Preparation and Characterization

#### 2.1.1. Sampling and Chemical Analyses of Waters

Two samples of acidic mine water (2 L each) were collected in two distinct abandoned and flooded mines (Herrerías and La Zarza, both in the Iberian Pyrite Belt mining district, Huelva, SW Spain). The samples were transported to the laboratory and chemically analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) in an Agilent 7500ce (Agilent Technologies Inc., Santa Clara, CA, USA) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in a Varian Vista-MPX (Agilent Technologies Inc., Santa Clara, CA, USA). These waters were selected, among many other mine waters in the area, to provide a wide range of dissolved sulfate and metal concentrations (Table 1). Both waters were very acidic (pH 2.2) and contained abundant dissolved iron and aluminum (342–3901 mg/L Fe, 76–876 mg/L Al; Table 1), which a priori ensured the precipitation of abundant schwertmannite and hydrobasaluminite precipitate during titration. These waters also exhibited extremely high concentrations of other elements with potential economic interest (e.g., 21–184 mg/L Cu, 130–182 mg/L Zn, 3379–4126 µg/L Co, 2494–3994 µg/L Ni) or with well-known toxicity (e.g., 44–5688 µg/L As, 26–408 µg/L Pb, 34–156 µg/L Cr, 20–118 µg/L U) (Table 1).

#### 2.1.2. Synthesis and Characterization of Mineral Precipitates

The schwertmannite and hydrobasaluminite samples used for the dissolution experiments were obtained in the laboratory following the method described in [18] and detailed in the Appendix A. Four solid samples were obtained from the sampled mine waters: two schwertmannites (Sch 1, Sch 2) and two hydrobasaluminites (Hyb 1, Hyb 2). A small portion of these samples was removed and used for mineralogical identification by X-ray Diffraction (XRD) in a Xpert Pro MPD equipment from PANalytical (Malvern Panalytical Ltd., Almelo, The Netherlands) (CuK $\alpha$ , 45 kV, 40 mA), chemical analyses by ICP-MS and/or ICP-AES (after previous digestion) and microscopic examination by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) in a JEOL JSM-7000 microscope (JEOL Ltd., Tokyo, Japan) (20 kV). Selected samples were also studied under transmission electron microscopy (TEM) using a Philips CM200 (Malvern Panalytical Ltd., Almelo, The Netherlands). The diffractometric analyses provided the typical schwertmannite pattern with eight broad reflections which is diagnostic of this mineral [2,5,15–18] and those of hydrobasaluminite were also consistent with the known poorly ordered structure of this very low-crystallinity solid, showing two main broad shoulders (hump peaks) at positions around 9.6 and 4.5 Å (Supplemental Figures S1–S4).

As a result, of the parent mine waters having high metal concentrations, the synthetic schwertmannite and hydrobasaluminite samples obtained by titration were also notably enriched in different trace metals (Table 2). The two schwertmannite specimens contained a significant aluminum content (0.40–2.86%), in accordance with the high concentration of this metal in both parent solutions. Neither mineralogical identification by XRD nor microscopic inspection by SEM-EDS could identify mineral phases other than schwertmannite, so that this metal is supposed to have been incorporated into schwertmannite by coprecipitation. Very high contents of Al (ranging from 8 to 17 mol %) have been found in natural schwertmannites formed in these mine waters, as a result of intense adsorption and coprecipitation with Fe(III) at ambient conditions [29]. The synthetic schwertmannites also contained significant Si (0.7 wt %–1.1 wt %) and detectable amounts of arsenic (Table 2). The calculated [Fe/S] molar ratios for these schwertmannites (3.0–3.9) are rather low in comparison to the theoretical value based on the ideal stoichiometry ([Fe/S] = 8) [2], but they are still in the same order than those found in previous studies [29]. These low [Fe/S] ratios result from the combination of (1) the aforementioned presence of trace elements in the mineral phase (either by adsorption or substitution for Fe(III)), and (2) an excess of surface-adsorbed sulfate on particle surfaces [5,18].

Sample	Locality	Fe	S	Si	Al	Cu	Zn	As	Cr	[Fe/S]	
		wt %	wt %	wt %	wt %	ppm	ppm	ppm	ppm		
Sch 1	Herrerías	41.25	6.10	0.25	0.40	46	1862	8	3	3.9	
Sch 2	La Zarza	32.70	6.50	0.46	2.86	1805	387	25	29	3.0	
Sample	Locality	Al	S	Si	Fe	Cu	Zn	Со	Ni	[A1/S]	
		wt %	wt %	wt %	wt %	wt %	wt %	ppm	ppm	[11,0]	
Hyb 1	Herrerías	10.80	5.05	1.61	0.12	3.7	15.2	1662	1821	2.6	
Hyb 2	La Zarza	11.52	5.80	2.17	0.25	7.1	0.8	160	209	2.4	

**Table 2.** Chemical composition (ICP-MS, ICP-AES) of schwertmannites (Sch 1, Sch 2) and hydrobasaluminites (Hyb 1, Hyb 2) obtained by neutralization of acidic mine water from Herrerías and La Zarza (Table 1) and later used for the dissolution experiments in ammonium oxalate solution.

The hydrobasaluminite precipitates also deviated from the ideal stoichiometric composition by their high concentrations of Si (1.61 wt %–2.17 wt %), Cu (3.7 wt %–7.1 wt %) and Zn (0.8 wt %–15.2 wt % in Hyb 1) (Table 2). The high Si contents are a common feature of natural hydrobasaluminites formed in mine waters [20], which are also known for their high sorptive capacity and affinity for trace metals such as Cu or Zn [16–20]. The Cu content was especially important in the Hyb 2 sample obtained from La Zarza mine water (Table 2) and provoked a striking blueish color in this compound (Supplemental material, Figures S5 and S6). As with the aforementioned schwertmannite samples, the lower Al content with respect to theoretical values (10.80 wt %-11.52 wt % in the samples vs. 16.75% of ideal hydrobasaluminite), which mostly results from the high content of adsorbed trace elements, and a sulfur content of 5.05 wt %–5.80 wt % which is also slightly higher than the ideal composition (ca. 5% S) result in [Al/S] ratios of 2.4–2.6 which are significantly below the ideal value of 4 expected for stoichiometric hydrobasaluminite [20–22]. The [Al/S] ratios are, however, very similar to those found in Cu-, Si- or Fe-rich natural hydrobasaluminites analyzed in previous studies [20]. Apart from hydrobasaluminite, no other mineral phase could be detected by XRD. However, in the particular case of Hyb 1 sample, microscopic examination by SEM revealed the presence of sparse, tiny crystals (sub-micron sized) of an unknown, Zn-rich mineral phase containing S, O and Al. The presence of this enigmatic, more crystalline solid can partly explain the high Zn concentration measured in this sample (Table 2). Most Zn hydroxides and hydroxysulfates require higher pH conditions (usually above pH 6.0) to precipitate [30], so we currently ignore the exact nature of this mineral phase. In any case, its presence even in small percentage is worth noting since it may affect the interpretation of some experimental results, as discussed below.

Microscopic examination by SEM revealed a sub-micron to nanometric size (diameters of 100–400 nm) and pseudo-spherical morphology with sub-rounded borders for the particles of both minerals. The rounded morphology of the synthetic schwertmannite particles contrasts with the characteristic hedge-hog (sea urchin) morphology exhibited by natural schwertmannite found in these systems and elsewhere [2,5,18,31] (Supplementary Figure S1). However, this morphology has also been observed by the authors in natural schwertmannite (Supplementary Figure S1), being apparently related with the fast kinetics of Fe(III) precipitation [32]. Synthetic hydrobasaluminite particles obtained in this study were morphologically similar to the natural ones found in these environments (Supplementary Figure S3), showing usually globular, pseudo-spherical geometry, though generally showed smaller particle size (50–200 nm).

#### 2.2. Experimental Setup

Half a liter (0.5 L) of NH<sub>4</sub>-oxalate solution 0.2 M was prepared with reagent-grade ammonium oxalate (Merck) and ultra-pure, MilliQ water. The pH of this solution was adjusted to pH 3.0 with oxalic acid, following the method described in [1–7]. Then, 25 mL of this solution was poured into different glass vials, which were subsequently placed in an automatic stirring unit (Supplemental material,

Figure S6). Exact amounts of 200 mg (dry weight) of schwertmannite and hydrobasaluminite mineral powder (Sch 1, Sch 2, Hyb 1 and Hyb 2) were added to their corresponding vials with the ammonium oxalate solution. This solid-to-solution ratio accounted for schwertmannite and hydrobasaluminite concentrations of  $5 \times 10^{-3}$  M and  $10^{-2}$  M, respectively, in the resulting suspensions. This concentration is notably higher than the one originally proposed by previous authors ( $3 \times 10^{-4}$  M) [5–7] and could potentially introduce some variation in the experimental results (e.g., as regards to dissolution rate) with respect to the standard conditions. We selected this concentration to ensure that most trace

elements of interest (e.g., Co, Ni, As, V, Cr, Ce, Be, Sc, Y) were well above the detection limit of the analytical technique used in the resulting final solution (see below). As discussed in a later section, this mineral density of the suspensions apparently did not cause a significant change in the dissolution behavior or reaction rate with respect to previous studies. Following the standard method originally proposed by Dold [4,5] and which is commonly applied

in most sequential extraction studies of mine wastes and AMD-related soils and sediments [6–12], the dissolution experiments were conducted for 1 h at nearly constant room temperature (22–23 °C) in the dark and with a low stirring rate to ensure gentle agitation during the experiments. During this period, consecutive sub-samples of solution (2 mL each) were directly pipetted from the vials at 2, 5, 10, 30, 45 and 60 min of reaction time. These solution samples were immediately filtered through 0.2 µm nitrocellulose membrane filters (Millipore), diluted in 8 mL of ultra-pure, deionized MilliQ water (to fulfil the minimum volume of 10 mL required for the spectrometric analyses) and directly analyzed for metal concentrations. An additional sample of the initial ammonium oxalate solution had been previously taken and used as blank. The rest of the solution was left in the vials for several hours to observe their stability. Three of them remained highly transparent during this time, with no sign of subsequent mineral precipitation. However, one of the solutions (solution with hydrobasaluminite sample Hyb 1) presented a slight turbidity and, after some time, a very small quantity of a whitish, very fine-grained precipitate could be observed in the vial bottom. Because of the tiny amount of this solid, it was not possible to obtain enough solid to study its composition by XRD or SEM. The pH was occasionally measured during the experiments and corrected when necessary by adding a few drops of oxalic acid to maintain the solution at pH 3.0.

#### 2.3. Analytical Methods

The chemical analyses for element concentrations in the different solution samples were conducted by ICP-AES in a Varian Vista-MPX instrument. Although a long list of elements was analyzed in all the solutions (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Sr, Ti, Tl, V, W, Y, Zn), only a few of them with geochemical interest and/or environmental relevance (including anion-forming elements such as S and Si, major metals such as Fe, Al, Cu and Zn, or trace elements such as As, Be, Cr, Co, Ni, Ce, Sc and Y) will be discussed here. The rest of elements were either not significant for the discussion on element mobility (e.g., Na, K, Ca, Mg, Mn) or showed below-detection concentrations in all cases (e.g., Ag, Bi, Ba, Ca, La, Li, Mo, Ni, P, Pb, Rb, Sb, Se, Sr, Ti, Ta, W). Detection limits were usually 1 mg/L for major metals (except for Cu and Zn, 0.1 mg/L) and between 0.01 and 0.1 mg/L for most trace elements excluding Se (0.2 mg/L), Sb (0.25 mg/L) and P (1 mg/L).

#### 3. Results

#### 3.1. Composition of Final Oxalate Solutions

The chemical composition of the oxalate solutions after 60 min of reaction time is displayed in Table 3. As expected, the solutions were dominated by either Fe and S in the case of schwertmannite solutions, or Al and S in the case of hydrobasaluminite. The solutions also showed an important concentration of other elements such as Si, Cu and Zn, and significant amounts of trace elements such as As, Co, Ni, Ce or Y (Table 3), in accordance with the high metal content detected in their

respective dissolving mineral phases (Table 2). Not so important, though still measurable, were the concentrations of other elements such as Be, Cr, Sc or V in some of the samples.

Major Metals (mg/L) Trace Elements (µg/L) Sample S Si Fe A1 Cu Zn Be Ce Cr Co Ni Sc V Y As Sch 1 460 30 2500 240 15 4.5 <100 60 <100 195 140 < 100<10 <25 <10 Sch 2 575 85 2570 440 30 4.5 7580 <10 < 100125 160 < 100<10 230 70 Hyb 1 425 265 <1 790 285 425 <100 265 980 <25 5355 7765 110 <25 3525 Hyb 2 575 405 <1 890 535 65 < 1001051010 <25 1085 2780 115 <25 2890

**Table 3.** Element concentrations measured in the ammonium oxalate solution at the end of the dissolution experiments.

Based on the metal concentrations obtained in the final oxalate solutions (Table 3), the amount of sample used in the experiments (200 mg) and the iron and/or aluminum content of the different samples (Table 2), we calculated the mass percent of mineral precipitate theoretically dissolved during the experiments. The theoretical amounts of schwertmannite and hydrobasaluminite dissolved during the dissolution experiments are 75% in the case of the sample Sch 1, 96% for Sch 2, 87% for Hyb 1, and 92% for Hyb 2. These mass balance calculations do not take into consideration the mass of particulate matter removed in the different sub-samples of 2 mL, which could have been significant in the first 2–10 min of reaction time when mineral dissolution was still not complete. We have estimated the amount of particulate iron and aluminum removed in these sampling stages based on the dissolved iron or aluminum concentrations obtained in the 2 mL solutions, the original iron or aluminum content, and the decreasing volume of water in the vials. These estimations suggest, for example, that in sample Sch 1 we could have removed by repeated pipetting around 10–15% of the iron initially contained in the sample as particulate matter. Thus, the method followed in our experiments would have never allowed to obtain a 100% recovery of the mineral precipitates because a small part was removed from the suspension, especially in the first 2 samplings (2 and 5 min). After the third one (10 min, 30 min, 45 min, and 60 min), the mineral dissolution was almost complete (transparent solutions with no evident turbidity). Deviation of the resulting estimates of dissolution rates from 100% are thus relatively small (4–25% for schwertmannite, 8–13% for hydrobasaluminite) and can be ascribed to the experimental approach used, in addition to some other minor sources of error such as the analytical uncertainty of the spectrometric analyses. Despite this limitation, which precludes a total dissolution of the mineral sample, the experimental data and visual observations show that virtually all the amount of mineral precipitate remaining in the oxalate solutions had been dissolved after 1 h of reaction.

#### 3.2. Kinetics of Schwertmannite and Hydrobasaluminite Dissolution

As deduced from Figure 1, the kinetics of the dissolution reactions was, as expected, very similar in both minerals, being in the order of  $5 \times 10^{-5}$  to  $5 \times 10^{-6}$  mol·L<sup>-1</sup>·s<sup>-1</sup>. The dissolution rate was not linear and, for both minerals, the dissolution curves show a first, exponential phase where all elements (Fe or Al, in addition to S and Si) are quickly released to the oxalate medium, followed by a second phase with a plateau that suggests nearly total dissolution of the mineral samples (Figure 1A). In the case of schwertmannite, the plateaus start at around 30 min reaction time, whereas the dissolution of hydrobasaluminite was still faster, and the plateau suggesting virtually complete dissolution started at around 10 min (Figure 1B).

According to previous studies [3,5], the first segment of the curves may correspond to a first order equation defining surface-controlled dissolution, whereas the second part is usually considered to indicate the instant at which the spherical geometry of schwertmannite and hydrobasaluminite collapses, and dissolution of the mineral remnants is controlled by the remaining surface area.



**Figure 1.** Progressive release of iron (Fe (**A**)), aluminum (Al (**B**)), sulfur (S (**C**,**D**)), and silicon (Si (**E**,**F**)) during dissolution of schwertmannite (left column) and hydrobasaluminite (right column) in ammonium oxalate solution at pH 3.0.

The evolution of the [Fe/S] molar ratio in the ammonium oxalate solution during the dissolution experiments with schwertmannite samples shows a first value of 2.0–2.8 after 2 min reaction time, followed by a subsequent gradual increase towards values around 2.6–3.1 (Figure 2A). The latter values are only slightly lower than those measured in the original dissolving precipitates (Table 2), suggesting a very high extent of mineral dissolution in both experiments, in agreement with the mass balance calculations provided in the previous section. As already observed by previous researchers [2,5], the gradual increase of the [Fe/S] ratio likely indicates a preferential release of the more labile, surface-adsorbed sulfate (SO<sub>4</sub><sup>2–</sup>) with respect to more strongly bonded Fe(III) at the beginning of the



experiments. The trends defined by the experimental points in the Fe vs. S binary plot also show a good correlation ( $R^2 = 0.97-0.98$ ) and slopes matching [Fe/S] values of 2.6–3.0 (Figure 2B).

**Figure 2.** Temporal evolution of the Fe/S molar ratio (**A**) and Al/S molar ratio (**C**) during dissolution of schwertmannite (Sch) and hydrobasaluminite (Hyb), respectively, in ammonium oxalate solution at pH 3.0. The respective plots of Fe vs. S (**B**) and Al vs. S (**D**) are also indicated for these experiments.

The experiments with hydrobasaluminite also resulted in [Al/S] ratios of 2.1–2.3 (Figure 2C) which are rather similar to those measured in the original dissolving precipitates (Table 2). In both experiments, this ratio reached its maximum value soon after the beginning of the dissolution at only 2–5 min of reaction time (Figure 2C). However, while this ratio remained nearly constant during the rest of the dissolution time in the sample Hyb 1, in the case of sample Hyb 2, the [Al/S] ratio experienced a slight decrease at 30 min reaction time (to a value of 1.6) and then increased again to [Al/S] = 1.9 (Figure 2C). The reasons for this apparent variability are not clear. The evolution of Al with respect to S in the Hyb 2 experiment indicates an important increase of S concentration at nearly constant Al in the time interval comprised between 10 min and 30 min reaction time (Figure 2D). This observation excludes the possibility of Al precipitation in the course of the experiment, which is consistent with the pH of the solution (3.0, far below the first hydrolysis point of Al(III) [14,15]), and with previous studies [21]. On the other hand, the shift in S content in the Hyb 2 solution suggests a late detachment of structurally incorporated SO<sub>4</sub><sup>2–</sup> anions from the lattice of this hydrobasaluminite sample [22,33].

#### 3.3. Release of Trace Elements Associated with Schwertmannite and Hydrobasaluminite

The progressive release of different trace elements associated with either schwertmannite or hydrobasaluminite upon mineral dissolution in ammonium oxalate are shown in Figures 3 and 4. With the exception of Al (which is present in hydrobasaluminite as a major component but also in schwertmannite as trace element by the reasons explained above), two groups of trace elements can be distinguished on the basis of their affinity for one or other mineral. A first group of trace elements are exclusively bound to either schwertmannite (e.g., As, Cr, V) or hydrobasaluminite (e.g., Be, Ce, Ni, Sc, Y) (Figure 3). A second group of trace elements were present in both dissolving minerals (Table 2) and were always therefore detected in the oxalate solution during the dissolution experiments. This second group includes some important metals such as Si (present in the solids and aqueous solutions as SiO<sub>2</sub>; Figure 1), Cu, Zn, Co and Ni (Figure 4). This dual metal-mineral association is perfectly consistent with many previous studies and with the well-known affinity of these minerals for different trace elements. Arsenic and chromium are usually associated with schwertmannite and tend to be retained in this mineral during Fe(III) precipitation from acid mine waters [34–37], while recent research has pointed to the capacity of hydrobasaluminite to sequester Si, Cu and Zn [16,19,20], as well as valuable elements such as light rare-earths (e.g., La, Ce) and yttrium [38,39].

The release of trace elements during mineral dissolution follows a similar pattern with respect to that displayed by the major metals, iron and aluminum (Figure 3). With the exception of Ni, which exhibits a slower rate of detachment, the experimental points for the rest of elements fit well with the exponential curves shown in Figure 1, suggesting that all these elements are released to the solution at the same rate than the major elements (Fe or Al, S) during mineral dissolution, regardless of their position in the mineral (e.g., adsorbed or substituted).

Among the elements associated with schwertmannite, aluminum exhibited the fastest rate of desorption in sample Sch 1, as 90% of this metal had been already released to solution after only 10 min reaction time (Figure 3A). Arsenic showed a slower release rate, though 95% of this element had been also dissolved at 30 min of dissolution time. Chromium and vanadium fall in-between, and both elements showed release rates of 80% (Cr) and 90% (V) after 30 min reaction time. Conversely, arsenic showed the fastest rate of release in sample Sch 2, as 90% of this element had already been released to the solution at only 5 min, while it took 30 min for Al to reach the same percent value of re-dissolution (Figure 3C). This observation suggests that the extent and rate of element release upon dissolution is strongly sample-dependent. Some differences in the release rate of the elements could have also resulted from a different position in the mineral lattice. Thus, aluminum is thought to be chiefly present as Al<sup>3+</sup> ions adsorbed as outer-sphere complexes on the schwertmannite surfaces [29], while arsenate, chromate and vanadate are all known for their capacity to substitute partially for sulfate anions in the schwertmannite structure [35].

Regarding the elements bound to hydrobasaluminite, Ce and Y showed the fastest rates of desorption (>90% at 10 min) in sample Hyb 1, closely followed by Sc and Be (85–90% at 10 min) (Figure 3B). The release of all these elements was even faster in sample Hyb 2 (85–92% metal recovery in only 5 min; Figure 3D). In the former case, nickel displayed the slowest release rate (50% at 10 min and 70% at 30 min), though a clear slope break in the dissolution curve was evident for this metal at 45 min, when metal recovery was almost complete (>95%). The slower rate of detachment of Ni from hydrobasaluminite as compared to the rest of the elements could be tentatively interpreted as indicative of the dissolution of another mineral phase distinct from hydrobasaluminite. The slowest rate of dissolution would indicate a slightly higher crystallinity, which is consistent with the SEM observations (Section 2.1.2).



**Figure 3.** Leaching of different elements associated with schwertmannite (Al, Cr, V, As (**A–C**)) or hydrobasaluminite (Be, Ce, Ni, Sc, Y (**B–D**)) during dissolution in ammonium oxalate (pH 3.0). Element leaching is expressed as percentage with respect to their respective contents in the final solutions (Table 3).

The graphs given in Figure 4 compare the metal releasing curves for elements present in both minerals. These graphs evidence a much higher content of Cu, Zn, Co and Ni per mass unit in hydrobasaluminite with respect to schwertmannite. In terms of metal concentration in the final oxalate solution, hydrobasaluminite dissolution released around ten times more Cu, ten times more Zn, and around six times more Co, in comparison with its schwertmannite counterpart (present in the same amount and synthesized from the same mine water) (Figure 4). Among these elements, the amount of Cu and Si released to solution during hydrobasaluminite dissolution was especially important (285–535 mg/L Cu, 265–405 mg/L Si), confirming the high sorptive capacity of this mineral phase (Table 3; Figures 1 and 4).

An exception to this behavior was observed in the case of Zn, Co and Ni released during dissolution of sample Hyb 1 (Figure 4). These elements did not follow the normal increasing curve of progressive dissolution during the experiments but, on the other hand, showed an opposite evolution with a first "flush" (due to an immediate release during hydrobasaluminite dissolution) followed by a slightly decreasing trend. This apparently anomalous behavior can only be explained by the aforementioned presence of another, more crystalline solid phase that would have not been dissolved in the oxalate solution during the experiments. This is consistent with the experimental observations.

This remaining solid phase could have partly adsorbed some Zn, Co and Ni initially released from

hydrobasaluminite. Although we could not confirm this hypothesis by SEM investigation (due to the very little amount of this solid recovered from the flasks), this seems a plausible explanation and would be coherent with the known lower solubility of more crystalline oxy-hydroxysulfates in ammonium oxalate [1,3,5].



**Figure 4.** Release of Cu (**A**), Zn (**B**), Co (**C**) and Ni (**D**) during dissolution in ammonium oxalate (pH 3.0) using either schwertmannite (Sch 1, Sch 2) or hydrobasaluminite (Hyb 1, Hyb 2).

#### 4. Discussion

# 4.1. Similarities between Schwertmannite and Hydrobasaluminite Dissolution: Implications for Trace Element Speciation Studies

Our results have several implications as regards to the current procedures of sequential extraction which are routinely applied in the study of metal speciation in soils and sediments affected by AMD. Firstly, it is evident that the recipe of 1 h dissolution in NH<sub>4</sub>-oxalate solution at 25 °C not only dissolves entirely the schwertmannite present in these sediments or wastes but can also dissolve completely other oxy-hydroxysulfates of similar crystallinity and reactivity such as hydrobasaluminite, which may also be abundant is these environments. Among many other available extractants (e.g., citrate, malonate, EDTA, sodium dithionate, etc.), ammonium oxalate is usually the preferred option and most commonly used dissolving medium in studies of iron speciation in soils and mine wastes due to its good specificity resulting from faster dissolution kinetics of poorly crystalline hydrous iron oxy-hydroxides (e.g., schwertmannite, 2 line-ferrihydrite) as compared to the more crystalline oxides (e.g., goethite, hematite) [1–12]. However, the behavior of other metal oxy-hydroxides and/or oxy-hydroxysulfates of similar (or even lower) crystallinity and comparable morphology and particle

size, such as hydrobasaluminite (or its more dehydrated counterpart, basaluminite), is very similar in this ammonium oxalate medium. The kinetics of dissolution of hydrobasaluminite is even faster than that of schwertmannite. The Al-chelating power of oxalic acid and its derived salts is well-known in medicine and in the food industry, where oxalate is recognized as an efficient Al-leaching agent [40]. Therefore, it is not possible to discriminate among these two minerals with this extraction technique using oxalate as dissolving medium, and this step of the sequential extraction should be best considered as "Low-crystallinity oxy-hydroxides", implying that it can contain both Fe and Al minerals.

An immediate consequence of this fact relates with the presence of trace metals in the poorly crystalline oxyhydroxide fraction. Leached metals during this step are traditionally considered to be present in schwertmannite as adsorbed or coprecipitated elements. However, our results clearly indicate that a big portion of these metals released to the ammonium oxalate solution can actually be associated with hydrobasaluminite if this mineral is also present at significant amounts in the studied solids. This is especially the case for Zn, Cu and Si among the major elements, and Co, Ni, Ce or Y among the trace metals (Figures 2–4). This may be especially important in studies dealing with the recovery of critical elements with potential economic value (e.g., Cu, Zn, Co, REE) from mine wastes.

#### 4.2. Control of pH and Ionic Charge on Metal Retention

It has been also shown that certain elements such as As, Cr and V were still clearly associated with schwertmannite and retained by this mineral during the precipitation of Fe(III) upon neutralization to pH 3.5. This agrees with many previous studies [16,34–36], being also consistent with the speciation of these elements in the acidic solutions. In contrast with the metal cations which are preferentially adsorbed onto hydrobasaluminite at pH 4.0–5.0 (e.g., present as  $Cu^{2+}$ ,  $Zn^{2+}$  or  $Co^{2+}$  in the aqueous phase), these other elements are usually present as diverse anionic species in solution (e.g., H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>,  $HCrO_4^-$ ,  $H_3V_2O_7^-$ ). These ionic complexes may form arsenate, chromate or vanadate ions that can replace for sulfate in the schwertmannite structure [35]. Since there is a net distinction in the behavior of metal cations and oxyanions during sorption as a function of pH (i.e., increasing sorption with increasing pH for metal cations vs. increasing sorption with decreasing pH for oxyanions [41]), the partition between trace elements in different mineral phases (e.g., As, Cr, V in schwertmannite formed at low pH, and Cu, Zn, Si, Co or Ni in hydrobasaluminite or any other Al oxy-hydroxide at higher pH) is consistent and should be expected under oxidizing, near-surface conditions where Fe(III) is abundant and precipitates before Al solids are available as sorbent surfaces. Under strictly anoxic conditions (e.g., deep strata of pit lakes), however, many oxyanion-forming elements (including As, Cr, V, Se, Sb and U) have been also observed to adsorb onto hydrobasaluminite [19,20].

#### 4.3. Future Research

In the case that the exact carriers of specific metals of interest need to be discerned, other extraction procedures could be rehearsed to differentiate between schwertmannite- and hydrobasaluminite-associated metals. Chelating agents applied in medical treatments of Al-related diseases (e.g., ascorbic acid, salicylic acid, cathechol, acetohydroxamic acid, etc.) are known to be efficient Fe(III) scavengers as well [42], so their use in sequential extraction studies would not provide any specificity. On the other hand, Silicic acid (Si(OH)<sub>4</sub>) is known to interact with Al<sup>3+</sup> or (Al(OH)<sub>3(s)</sub>) forming insoluble hydroxyaluminosilicates (HAS) which help reduce the Al content in human blood [43,44], so its validity to sequester poorly ordered Al minerals from sediments could be explored.

Other possible approaches to discriminate between iron and aluminum oxy-hydroxysulfates could rely on element-specific chemical properties, such as (1) the photochemical reactivity of Fe(III), or (2) the amphoteric behavior of Al(III). The latter case seems particularly interesting since several hydroxides, including NaOH and LiOH, have been proved to be very efficient extractans of basaluminite and other aluminum hydroxysulfates (e.g., alunite) in soils [45]. Dissolution in NaOH or LiOH would not affect, a priori, Fe(III) minerals such as schwertmannite, but could dissolve oxy-hydroxides

of other amphoteric elements such as Cr, Pb or Zn, so that the results concerning the presence of these elements in hydrobasaluminite or other Al oxy-hydroxides would not be reliable. In any case, further research is needed to define a method that allows discrimination between Fe(III)-bonded and Al(III)-bonded elements in mine wastes and AMD-affected soils, and future studies should explore different approaches and extracting media.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/9/1/57/s1, Figure S1: SEM pictures of natural and synthetic schwertmannite; Figure S2: XRD pattern of synthetic schwertmannite; Figure S3: SEM and TEM pictures of natural and synthetic hydrobasaluminite; Figure S4: XRD pattern of synthetic hydrobasaluminite used in the dissolution experiments; Figure S5: Sequence of pictures showing the synthesis of one of the hydrobasaluminite precipitates used for the oxalate dissolution experiments; Figure S6: Final aspect of the oxalate solutions after the end of the experiments.

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## Appendix A

#### Synthesis of Schwertmannite and Hydrobasaluminite Mineral Samples for the Dissolution Experiments

The selected mine waters were previously filtered through 0.45 µm membrane filters (Millipore) to avoid any contamination by detrital, fine-grained suspended particles in the resulting fresh precipitates of iron and aluminum oxy-hydroxysulfates. The filtered waters (1 L) were adjusted to the specific pH values by gentle, dropwise addition of NaOH 1 M with continuous stirring at room temperature (Supplemental material, Figure S5). The solution pH was continuously controlled with a previously calibrated CRISON 2001 pH meter. Based on previous studies [16,18,20], the target pH values were set in 3.5 for schwertmannite synthesis and 5.0 for hydrobasaluminite synthesis. The addition NaOH soon provoked the precipitation of either Fe(III) or Al from the solutions, resulting in brownish orange (schwertmannite) or whitish (hydrobasaluminite) colloidal suspensions. The precipitation of both minerals releases protons and tends to decrease the pH of the initial solutions [15,18], so that these waters were strongly buffered at pH values around 2.5-2.8 in the case of schwertmannite and at values of 4.0–4.5 in the case of hydrobasaluminite. When the target pH values were attained, the colloidal suspensions were vacuum-filtered through 0.45 µm (Supplemental material, Figure S5), washed three times with ultra-pure deionized water (MilliQ), and dried at room temperature during 24 h. The solid samples were subsequently homogenized and slightly powdered in an agate mortar mill. A small portion was removed for mineral identification (XRD, SEM-EDS, TEM, ICP-MS, ICP-AES) and another portion of 200 mg (dry weight) was used for the dissolution experiments. The samples were vacuum-packed in air-tight plastic bags during the time elapsed between mineral synthesis and dissolution experiments, which was lower than 48 h.

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