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Sulfur Speciation and Stable Isotope Trends of Water-Soluble Sulfates in Mine Tailings Profiles

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Sulfur speciation and the sources of water-soluble sulfate in three oxidizing sulfidic mine tailings impoundments were investigated by selective dissolution and stable isotopes. The studied tailings impoundments—Piuquenes, Cauquenes, and Salvador No. 1—formed from the exploitation of the Rio Blanco/La Andina, El Teniente, and El Salvador Chilean porphyry copper deposits, which are located in Alpine, Mediterranean, and hyperarid climates, respectively. The water-soluble sulfate may originate from dissolution of primary ore sulfates (e.g., gypsum, anhydrite, jarosite) or from oxidation of sulfide minerals exposed to aerobic conditions during mining activity. With increasing aridity and decreasing pyrite content of the tailings, the sulfur speciation in the unsaturated oxidation zones showed a trend from dominantly Fe(III) oxyhydroxide fixed sulfate (e.g., jarosite and schwertmannite) in Piuquenes toward increasing presence of water-soluble sulfate at Cauquenes and Salvador No. 1. In the saturated primary zones, sulfate is predominantly present in water-soluble form (mainly as anhydrite and/or gypsum). In the unsaturated zone at Piuquenes and Cauquenes, the $\delta^{34}S_{SO4}$ values ranged from +0.5‰ to +2.0‰ and from −0.4‰ to +1.4‰ Vienna Canyon Diablo Troilite (V-CDT), respectively, indicating a major sulfate source from pyrite oxidation ($\delta^{34}S_{pyrite} =$ −1.1‰ and −0.9‰). In the saturated zone at Piuquenes and Cauquenes, the values ranged from −0.8‰ to +0.3‰ and from +2.2‰ to +3.9‰, respectively. At Cauquenes the ^{34}S enrichment in the saturated zone toward depth indicates the increasing contribution of isotopically heavy dissolved sulfate from primary anhydrite (∼+10.9‰). At El Salvador No. 1, the $\delta^{34}S_{SO4}$ average value is −0.9‰, suggesting dissolution of supergene sulfate minerals (jarosite, alunite, gypsum) with a $\delta^{34}S \sim$ −0.7‰ as the most probable sulfate source. The gradual decrease of $\delta^{18}O_{SO4}$ values from the surface to the oxidation front in the tailings impoundments at Piuquenes (from −4.5‰ to −8.6‰ Vienna Standard Mean Ocean Water, V-SMOW) and at Cauquenes (from −1.3‰ to −3.5‰) indicates the increasing importance of ferric iron as the main electron acceptor in the oxidation of pyrite. The different $\delta^{18}O_{SO4}$ values between the tailings impoundments studied here reflect the local climates.

1. Introduction

Acid and highly metal loaded effluents (acid mine drainage, AMD), resulting from the exposure of sulfide mineralization to oxidizing conditions during the mining process, are the principal environmental problems of the mining industry today. In the mine waste environment there are two potential sources of sulfate: dissolution of primary sulfates from the ore mineral assemblage (e.g., gypsum and anhydrite) and sulfide oxidation. These mineralogical transformations can be quantified by sulfur speciation, and the source of the water-soluble sulfate can be traced by sulfur and oxygen isotopes (*1−3*), as this is the mobile fraction of the total sulfate content.

Pyrite, the most abundant sulfide mineral, can be oxidized by dissolved atmospheric oxygen (eq 1) due to exposure to oxidizing conditions during mining activity. Of the resulting sulfate, 87.5% of the oxygen is derived from dissolved oxygen and 12.5% from water (*4*). When pyrite is oxidized by Fe^{3+} (eq 2), which results from (microbiological) oxidation of the liberated ferrous iron in eq 1, 100% of the oxygen is derived from water. Equations 1 and 2 are commonly used to describe the overall mass balance of sulfide oxidation. However, it has to be considered that these equations do not reflect the complexity of the associated electron-transfer mechanisms in sulfide oxidation, which may involve seven steps of electron transfer in the case of pyrite oxidation and eight steps in the case of pyrrhotite oxidation (*1*).

$$FeS_2 + {}^{7}/_{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \quad (1)$$

$$FeS_2 + 14\ Fe^{3+} + 8H_2O \rightarrow 15\ Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \quad (2)$$

The microbially mediated fractionation of oxygen isotopes during pyrite oxidation and sulfate reduction (*4−6*) and sulfur isotopes during sulfate reduction (*7−10*) makes the dual isotopic approach an appropriate tool for understanding the processes controlling the sulfur cycle in freshwater systems. In this study, the sulfur and oxygen isotopic composition of water-soluble sulfate is used to gain insight about the oxidation process in three oxidizing sulfidic mine tailings impoundments from Chilean giant porphyry copper deposits. The tailings impoundments are located in different climatic settings: an Alpine climate at the Piuquenes impoundment from Rio Blanco/La Andina mine, a Mediterranean climate at the Cauquenes impoundment from El Teniente deposit, and a hyperarid climate at the No. 1 impoundment from El Salvador deposit (Figure 1). The mineralogy and geochemistry of these tailings impoundments has been described in Dold and Fontboté (*11*).

1.1. Mine Tailings Impoundments. The Piuquenes tailings (Figure 1C) contain low sulfide (1.7 wt % pyrite equiv) and low carbonate concentrations (1.4 wt % calcite equiv). The secondary mineralogy of the 35−75 cm thick oxidation zone, which was characterized by microscopy, X-ray diffraction (XRD), and differential X-ray diffraction (DXRD), is dominated by jarosite, schwertmannite, and a vermiculite-type mixed-layer mineral (*11*). The pore water of the low-pH oxidation (2.3−3.5) and neutralization (3.5−6.7) zones has up to 25 400 mg/L SO_4, 4720 mg/L Fe, 2305 mg/L Al, 1180 mg/L Cu, and 199 mg/L Zn.

At the low-sulfide (1 wt % pyrite equiv) and carbonate-depleted (0 wt % calcite equiv) Cauquenes tailings impoundment (Figure 1B), a 100−150 cm thick low-pH (pH 1.7−3) oxidation zone, with a similar secondary mineral assemblage as observed at Piuquenes (*11*), developed during the 20 years

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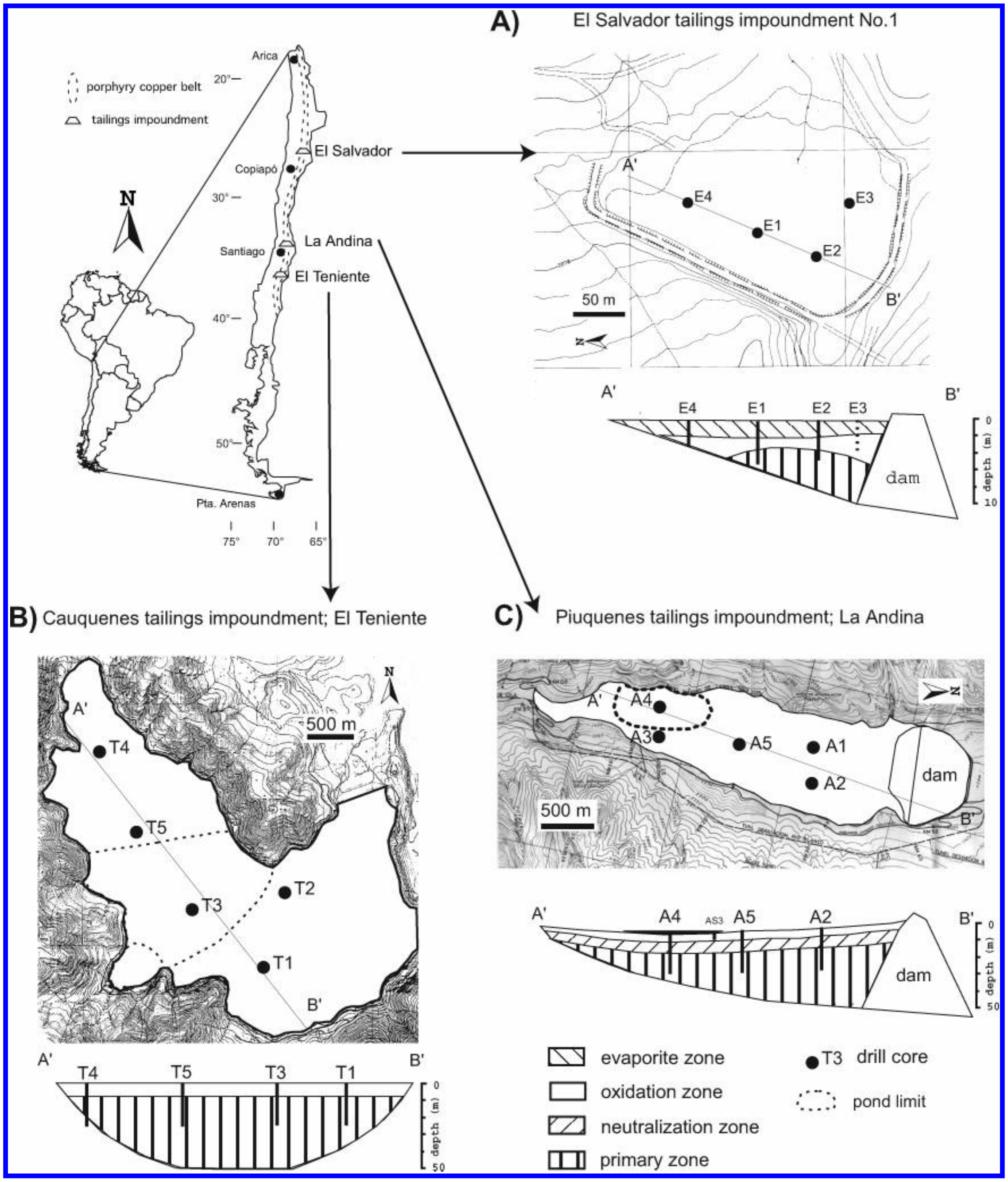

FIGURE 1. Overview of the studied tailings impoundments: (A) El Salvador No. 1, (B) Cauquenes/El Teniente, and (C) Piuquenes/La Andina, Chile. The vertical scales of the tailings profiles are exaggerated for better visibility.

after mining operations ceased (*11*). Element concentrations in the pore water from the oxidation zone are up to 21 600 mg/L SO_4, 1090 mg/L Fe, 2585 mg/L Al, 2280 mg/L Cu, and 25 mg/L Zn.

The El Salvador No. 1 tailings are low-sulfide (6.2 wt % pyrite equiv) and carbonate-depleted (0 wt % calcite equiv). Due to the hyperarid climate at El Salvador, no water-saturated zone is present in this tailings impoundment. The tailings show abundant blue, yellow, white and brown efflorescent salts at the top, forming a 0.3−1.5 m thick evaporation zone (Figure 1A) with paste-pH between 2 and 3.53. An oxidation zone with orange-brown horizons (paste-pH 1.9−2.8) is present at lower levels of the tailings, followed by a dark gray primary zone (*11*). Sequential extraction studies (*11*) of the water-soluble fraction have shown an increase in the concentration of mobile elements toward the surface of the tailings (up to Cu 5.04 wt %, Al 3.09 wt %, Mg 1.5 wt %, Ca 0.93 wt %, Na 0.25 wt %, Fe 0.22 wt %, and Mn 539 mg/kg).

1.2. Isotopic Composition of the Ore Minerals. The sulfur isotopic composition of the primary pyrite ($\delta^{34}S_{pyrite}$) in the deposits El Teniente (from which the Cauquenes tailings originate) and Rio Blanco/La Andina (from which the Piuquenes tailings originate) average −0.9‰ ± 0.9‰ and −1.1‰ ± 0.3‰ Vienna Canyon Diablo Troilite (V-CDT), respectively (Table 1). The sulfur and oxygen isotopic ratios of anhydrite ($\delta^{34}S_{anhydrite}$ and $\delta^{18}O_{anhydrite}$) in the primary ore assemblage of El Teniente and Rio Blanco/La Andina average +10.9‰ ± 1.4‰ and +11.9‰ ± 0.6‰ V-CDT, and +7.5‰ ± 0.7‰ and +6.7‰ ± 2.1‰ Vienna Standard Mean Ocean Water (V-SMOW), respectively (*12*). For the El Salvador deposit, the average of the $\delta^{34}S$ values for the hypogene sulfates (anhydrite, gypsum) is +10.7‰; for the supergene sulfates (jarosite, alunite and gypsum), −0.7‰; and for the

TABLE 1: δ^{34}S and δ^{18}O Values[a] of Samples Taken from the Mine Tailings Described in This Study Compared to Those of the Corresponding Ore Deposits[b]

primary ore	Rio Blanco/La Andina	El Teniente	El Salvador
Sulfides			
δ^{34}S pyrite	−1.1 ± 0.3 (−1.6 to −0.7; n = 6)[c]	−0.9 ± 0.9 (−2.8 to +1.6; n = 14)[c]	−2.3 (−10.1 to −0.3; n = 23)[d]
δ^{34}S sulfides			−3.0 (−10.1 to −0.3; n = 37)[d]
Sulfates			
δ^{34}S anhydrite	+11.9 ± 0.6 (+10.6 to +13.4; n = 14)[c]	+10.9 ± 1.4 (+8.6 to +15.5; n = 31)[c]	
δ^{34}S anhydrite and gypsum			+10.7 (+7.3 to −17.0; n = 18)[d]
δ^{34}S supergene jt, al, gy[e]			−0.7 (−4.6 to +3.6; n = 6)[d]; −2.1[f]
δ^{18}O anhydrite	+6.7 ± 2.1 (+5.0 to +8.5; n = 12)[c]	+7.5 ± 0.7 (+6.8 to +10.6; n = 29)[c]	

water-soluble sulfate in tailings	Piuquenes/Andina	Cauquenes/Teniente	El Salvador No. 1
Unsaturated Zone			
δ^{34}S sulfate	+0.5 to +2.0	−0.4 to +1.4	+0.3 to −1.8
δ^{18}O sulfate	−4.5 to −10.0	−1.3 to −4.7	+2.7 to −3.0
Saturated Zone			
δ^{34}S sulfate	−0.8 to +0.3	+2.2 to +3.9	no saturated zone
δ^{18}O sulfate	−5.8 to +4.5	−1.1 to +4.5	

[a] Values represent ‰ V-CDT or V-SMOW, respectively. [b] Average value ± standard deviation (range, n = no. of samples) is shown. [c] Isotopic data of ore minerals from Kusakabe et al. (*12*). [d] Isotopic data of ore minerals from Field and Gustafson (*13*). [e] Abbreviations: Jt = jarosite, al = alunite, gy = gypsum. [f] Isotopic data of ore minerals from Watanabe and Hedenquist (*14*).

hypogene sulfides (pyrite, chalcopyrite, chalcocite, bornite), −3.0‰ (*13*). Watanabe and Hedenquist (*14*) reported δ^{34}S = −2.1‰, δ^{18}O = 5.4‰, and δD = −96‰ for a single jarosite sample.

2. Experimental Section

2.1. Sampling and Sample Preparation. Two hundred two samples were obtained from 14 cores at the three tailings impoundments by percussion soil sampling technique during the 1996 field campaign (*11*). Samples were numbered, as an example, A2/080, where A stands for Rio Blanco/La Andina (T for Teniente, E for El Salvador), 2 for drill core number, and 080 for the sample depth in centimeters below the surface. The pH measurements were obtained as paste-pH according to mine environment neutral drainage program (MEND) (*15*) by use of a WTW pH-meter. Samples were oven-dried at less than 30 °C and stored in air-sealed standard polyethylene bottles (PET) until analysis. From 38 tailings samples, the water-soluble sulfate fractions were obtained by mixing a 5 g tailings aliquot with 300 mL deionized water during 1 h. The solution was filtered and the dissolved sulfate was precipitated by addition of a saturated $BaCl_2$ solution. The $BaSO_4$ was separated from the solution by filtering through a 0.45 μm NH_4-acetate filter, and air-dried. These $BaSO_4$ samples were used for sulfur and oxygen isotope analyses.

2.2. Sulfur Speciation. The sulfide- and sulfate-sulfur speciation and the concentrations of water-soluble sulfate in the tailings samples (Figure 2) were obtained by the procedure described in Dold (*16*). The water-soluble fraction of the sulfates was separated by shaking a 1.0 g tailings sample in 50 mL of deionized H_2O for 1 h at room temperature. The total sulfate fraction (S_{SO4}) was obtained by treating the tailings samples in 0.2 M ammonium oxalate at pH 3.0 at 80 °C for 2 h. This dissolves all water-soluble sulfates as well as the complete Fe(III) oxides and sulfate fraction, including higher ordered ferrihydrite (6-line), goethite, primary and secondary jarosite, natrojarosite, and primary hematite. Sulfur concentrations were measured in the leachates by inductively coupled plasma−atomic emission spectroscopy (ICP-AES). The total sulfur concentrations (S_{total}) were measured using a Leco device. The sulfide−sulfur ($S_{sulfide}$) concentrations were calculated as the difference $S_{total} - S_{SO4}$.

2.3. Sulfur Isotope Analysis. The sulfur isotope analyses were performed by use of an on-line elemental analyzer (Carlo Erba 1108) coupled through a continuous helium flow interface to a Thermo Finnigan (Bremen, Germany) Delta S isotope ratio mass spectrometer (EA/IRMS) system, according to the technique described by Giesemann et al. (*17*). The 1−2 mg $BaSO_4$ samples obtained above were wrapped in tin capsules and completely oxidized to SO_2 under a flow of helium and oxygen by flash combustion at 1030 °C in an oxidation−reduction quartz tube packed with oxidizing (WO_3) and reducing (elemental Cu) agents. A helium stream carried the gases produced during the combustion through a water trap (anhydrous $MgClO_4$) and a chromatographic Teflon column, for separation of SO_2, which then enters the isotope ratio mass spectrometer. Reference SO_2 gas was injected as pulses of pure SO_2 gas, which is calibrated against the NBS-123 zinc sulfide (δ^{34}S value of +17.1‰) international standard. The stable isotope composition of sulfur is reported in δ notation as the per million (‰) deviations of the isotope ratio relative to known standards:

$$\delta = [(R_{\mathrm{sample}} - R_{\mathrm{standard}})/R_{\mathrm{standard}}] \times 1000$$

where R is the ratio of the heavy to light isotopes (^{34}S/^{32}S). For sulfur, the standard is V-CDT. The reproducibility of EA/IRMS, assessed by replicate analyses of laboratory standard materials (synthetic barium sulfate, +12.5‰ δ^{34}S; natural pyrite, −7.0‰ δ^{34}S) and tailings $BaSO_4$ samples, was better than ±0.2‰ (1 SD). The accuracy of the δ^{34}S analyses was checked periodically by analyses of the international reference materials IAEA S1 and S2 silver sulfide (−0.3‰ and +21.7‰ δ^{34}S) and NBS-123.

2.4. Oxygen Isotope Analysis. The oxygen isotopic composition of the $BaSO_4$ from section 2.1 was measured with a Thermo Finnigan high-temperature conversion el-

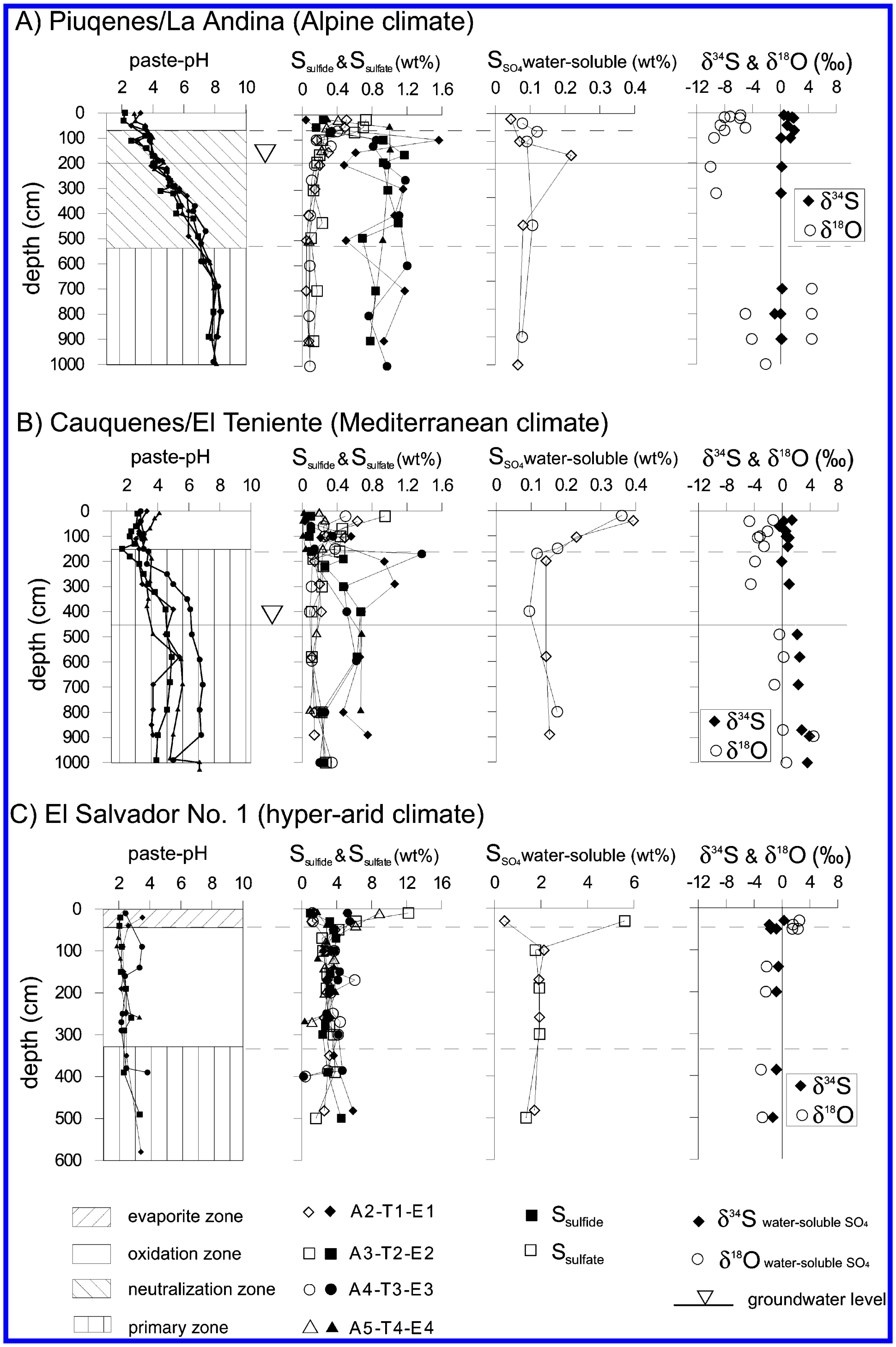

FIGURE 2. Paste-pH, sulfur speciation of $S_{sulfide}$ and $S_{sulfate}$, water-soluble $S_{sulfate}$, and isotopic data of the water-soluble sulfates ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) for samples taken from the three studied tailings impoundments. Note the difference in scale of the sulfur speciation data between Piuquenes/La Andina, Cauquenes/El Teniente, and El Salvador No.1.

emental analyzer (TC/EA) coupled to a Delta Plus XL isotope ratio mass spectrometer. Samples of 0.1−0.2 mg were wrapped in silver capsules and completely reduced in the TC/EA, in which oxygen is converted to CO under a flow of helium at 1470 °C in a glassy carbon reactor with an outer tube of aluminum oxide. A helium stream carried the gases produced during the combustion through a chromatographic column, for separation of CO, which then enters the isotope ratio mass spectrometer. Reference CO gas was injected as pulses of pure standard gas. The oxygen isotope ratios (δ^{18}O) are reported relative to V-SMOW. The reproducibility of the TC/EA/IRMS measurements, assessed by replicate analyses of the laboratory barium sulfate standards (UNIL, +14.0‰; UVA, +12.4‰) was better than ±0.3‰ (1 SD). The accuracy of the TC/EA/IRMS δ^{18}O analyses was checked periodically by analyses of international reference barium sulfates NBS-127 (+9.3‰) and IAEA SO-5 (+13.0‰) and SO-6 (−10.8‰).

3. Results and Discussion

3.1. Sulfur Speciation. The stratigraphy of the Piuquenes tailings impoundment is characterized by a low-pH oxidation zone (pH 2.3−3.5) at the top, where the average primary sulfide content of 0.85 wt % $S_{sulfide}$ of the tailings was depleted to as low as 0.04 wt % (Figure 2A). The sulfide mineral

TABLE 2: δ^{18}O and δ^{34}S Values of Samples Taken from Increasing Depths of the Three Tailings Impoundments

Piuquenes/Andina			Cauquenes/Teniente			El Salvador No.1		
sample/depth (cm)	δ^{34}S	δ^{18}O	sample/depth (cm)	δ^{34}S	δ^{18}O	sample/depth (cm)	δ^{34}S	δ^{18}O
AS3/010	+0.5	−5.7	T5/035	+1.4	−1.3	E1/030	+0.3	+2.5
AS1/015	+1.1	−7.2	T1/040	+0.2	−4.7	E1/040	−1.8	+1.6
AS4/018	+1.7	−8.0	T3/60	−0.4		E1/050	−0.8	+2.3
AS2/021	+1.9	−5.8	T4/080	+0.5	−2.1	E2/050	−1.6	+1.5
A3/050	+1.0	−8.6	T1/100	+0.6	−3.2	E4/140	−0.5	−2.2
A3/060	−	−5.0	T1/105	+1.0	−3.5	E1/200	−0.8	−2.3
A3/070	+2.0	−8.0	T2/140	+0.8	−2.6	E3/386	−0.8	−3.0
A3/100	+1.5	−9.5	T1/200	−0.1	−3.9	E2/500	−1.3	−2.8
A4/100	+0.1		T1/290	+1.0	−4.5			
A3/215	+0.2	−10.0	T1/490	+2.2	−0.4			
A3/320	+0.1	−9.2	T1/580	+2.5	+0.2			
A3/700	+0.3	+4.5	T1/690	+2.3	−1.1			
A3/800	+0.1	−5.0	T1/870	+2.8	+0.1			
A5/800	−0.8	+4.5	T3/895	+3.9	+4.5			
A3/900	+0.2	−4.1	T2/1000	+3.6	+0.6			
A2/900	+0.1	+4.5						
A4/1000		−2.1						
avg ± SD	+0.7 ± 0.8	−4.9 ± 4.9		+1.5 ± 1.3	−1.6 ± 2.4		−0.9 ± 0.6	−0.3 ± 2.3

oxidation was accompanied by the precipitation of secondary Fe(III) hydroxide sulfate minerals, mainly as jarosite and schwertmannite (*11*). Between 0.37 and 0.42 wt % of the sulfate was fixed in this mineral assemblage, and a maximum of 0.08 wt % was found to be water-soluble (e.g., gypsum), which represents 9−17% of the S_{SO4}. Lower down in the tailings, in the neutralization and primary zones (pH 3.5−8.4), 73−100% of the sulfate was found to be water-soluble (0.07−0.22 wt %).

At Cauquenes, the sulfur speciation is very similar to that at Piuquenes (Figure 2B). The average primary $S_{sulfide}$ content of 0.6 wt % was depleted in the oxidation zone to concentrations as low as 0.01 wt % (Figure 2B). S_{SO4} concentrations showed a trend of increasing values toward the tailings surface (up to 0.95 wt %). Up to 0.4 wt % of the S_{SO4} was present as water-soluble sulfate in the oxidation zone, corresponding to 47−73% of the total sulfate content. The upward trend of water-soluble sulfate is due to the higher capillary transport to the surface of the tailings in the Mediterranean climate at Cauquenes. Additionally, ferric iron concentrations in the low-iron sulfide (1 wt % pyrite equiv) system of Cauquenes are too low to fix all sulfate as secondary Fe(III) oxyhydroxide sulfate minerals (e.g., jarosite and schwertmannite). In the primary zone, 98−100% of the S_{SO4} was water-soluble (0.09−0.14 wt %).

The sulfur speciation data from samples taken at the El Salvador No. 1 tailings impoundment showed that most of the S_{SO4} (about 2.0 wt % in the oxidation and primary zone and up to 12.2 wt % in the evaporite zone) was water-soluble (Figure 2C). The water-soluble sulfate fraction ranged between 37% and 100% of the S_{total}, with an average of 69.2%. This high concentration of water-soluble sulfate suggests that there was not enough free ferric iron available to fix the sulfate, as in the low-iron sulfide system at Cauquenes. However, the El Salvador No. 1 tailings have relatively high sulfide content for a porphyry copper system (average 6.2 wt % pyrite equiv). The pyrite grains in these tailings are mainly fresh (not oxidized), and only very small amounts of secondary Fe(III) oxyhydroxides sulfates were present. As a result, the $S_{sulfide}$ concentrations range between 1.8 and 5.6 wt % and do not show depletion in the oxidation zone, in contrast to the Piuquenes and Cauquenes tailings systems. Nevertheless, the pH values at El Salvador No. 1 are around 2 throughout the tailings stratigraphy and only locally increases up to 3.5 in the primary zone (Figure 2C). This low sulfide oxidation rate was attributed by Dold and Fontboté (*11*) to the lack of microbial oxidation activity, which might result from microbial poisoning due to high Mo concentration (up to 1000 mg/kg). The same authors suggested that the source of acidity at El Salvador No.1 is predominantly primary jarosite (resulting from the supergene ore formation at the El Salvador ore deposit) and to a lesser extent sulfide oxidation.

3.2. Stable Isotopes: 3.2.1. δ^{34}S. The $\delta^{34}S_{SO4}$ values from the water-soluble sulfate in the unsaturated zones of the Piuquenes and Cauquenes tailings stratigraphy (+0.5‰ to +2.0‰ and −0.4‰ to +1.4‰, respectively) differed from those of the underlying saturated primary zone (−0.8‰ to +0.3‰ and +2.2‰ to +3.9‰, respectively; Figure 2 and Tables 1 and 2).

The $\delta^{34}S_{SO4}$ values for the unsaturated oxidation zones are very similar to the range of +0.5‰ to +1.5‰ for $\delta^{34}S_{SO4}$ reported by Taylor et al. (*4*) from their pyrite oxidation experiments. They exposed pyrite under different conditions, including anaerobic/aerobic, wet/dry, sterile, and with inoculation by *Acidothiobacillus ferrooxidans*, and measured the $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values in the resulting sulfate. For their wet/dry experiment, which is the most realistic condition for the unsaturated oxidation zone of tailings studied here, they reported $\delta^{34}S_{SO4}$ values of +0.8‰ for the sterile sample and +0.5‰ for the inoculated sample. These values are similar to those found in the unsaturated oxidation zone of Piuquenes and Cauquenes tailings samples, suggesting that the $\delta^{34}S_{SO4}$ signatures resulted from pyrite oxidation. Additionally, a small contribution from primary sulfate minerals (e.g., anhydrite $\delta^{34}S_{SO4}$ +10.9‰ and +11.9‰) may explain the slightly ^{34}S-enriched sulfate in the oxidation zone of these tailings impoundments (up to +2.0‰ $\delta^{34}S_{SO4}$). Consequently, the measured $\delta^{34}S_{SO4}$ values in the oxidation zones from Piuquenes and Cauquenes are interpreted to be the result of microbial sulfide oxidation and primary sulfate dissolution.

At Piuquenes, the $\delta^{34}S_{SO4}$ values from the saturated zone formed a narrow range from −0.8‰ to +0.3‰ (Figures 2A and 3A), whereas at Cauquenes the $\delta^{34}S_{SO4}$ values increased from +2.2‰ to +3.9‰ with increasing depth of the tailings (Figures 2B and 3B). This increase at Cauquenes can be explained by two processes: (1) mixing of sulfate from pyrite oxidation (~0‰ to +2.0‰) with sulfate from anhydrite dissolution (+10.9‰), with increasing importance of anhydrite dissolution toward depth (Figures 2B and 3B); and (2) by microbial sulfate reduction, as bacteria prefer to use ^{32}S, resulting in higher $\delta^{34}S_{SO4}$ values (*18*). In general, these tailings systems are organic-carbon-poor, and at Cauquenes the acidic environment is not favorable for the growth of

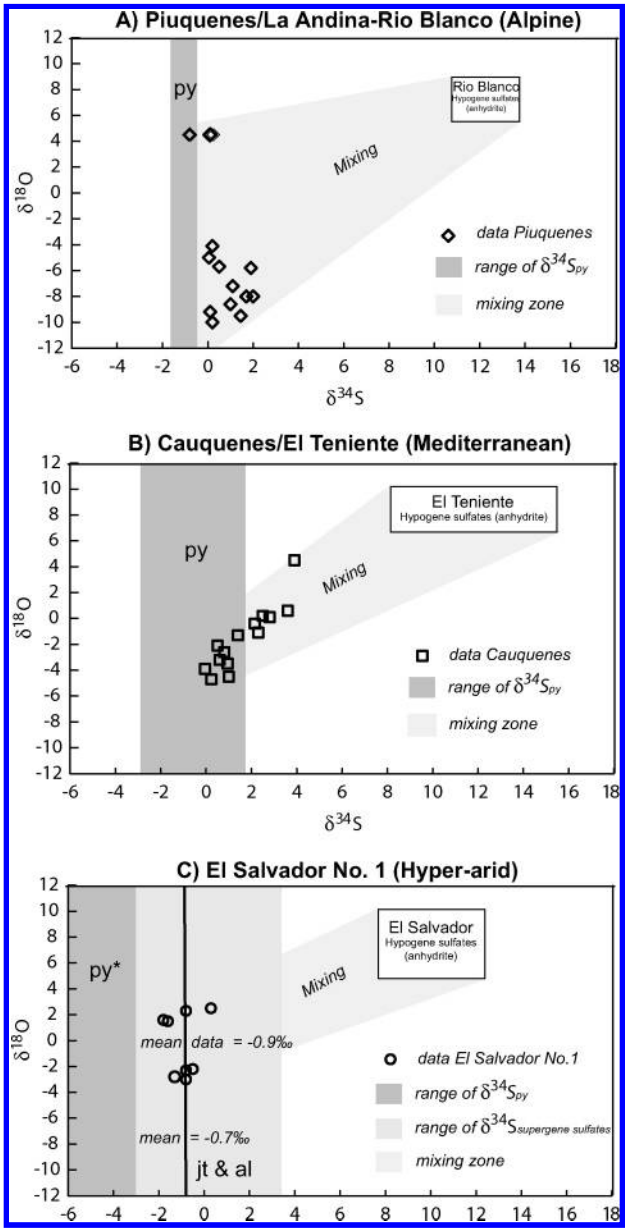

FIGURE 3. Scatter plot of $\delta^{34}S$ versus $\delta^{18}O$. The vertical bands represent the range of pyrite $\delta^{34}S$ values from *Field and Gustafson (*13*) and "Kusakabe et al. (*12*) and additionally the supergene sulfates in case of El Salvador. Py* at El Salvador is corrected after Field and Gustafson (*13*). The hypogene boxes are the values for hypogene sulfate (anhydrite and gypsum). The "mixing" zones were drawn to span the range of hypogene sulfates and the data obtained in this study. The vertical line in panel C represents the mean of −0.7‰ of the supergene jt and al at El Salvador, data from *Field and Gustafson (*13*). Abbreviations: py = pyrite, jt = jarosite, al = alunite.

sulfate-reducing bacteria (SRB). At Piuquenes, however, SRB were detected below the oxidation zone (*19*), but no ^{34}S enrichment was measured. Thus, the higher $\delta^{34}S_{SO4}$ values toward the primary zone at Cauquenes can be mainly attributed to an enhanced sulfate contribution from anhydrite dissolution. At Piuquenes this trend is not observed, as in the primary sulfate assemblage anhydrite and gypsum are only present as minor trace minerals.

At El Salvador the $\delta^{34}S_{SO4}$ values averaged −0.9‰ (Figure 3C), suggesting that the sulfate may have originated from the dissolution of supergene sulfate minerals [mean −0.7‰ of the data from Field and Gustafson (*13*); −2.1‰ for jarosite from Watanabe and Hedenquist (*14*)]. This is in line with the interpretation of Dold and Fontboté (*11*) that the main source of acidity and sulfate in this tailings impoundment is supergene jarosite and not sulfide oxidation.

3.2.2. δ^{18}O. Two trends of the $\delta^{18}O_{SO4}$ data can be observed: (1) a shift of the average from lighter values at Piuquenes/Andina (−4.9‰ ± 4.9‰, Alpine climate), toward heavier signatures at Cauquenes/Teniente (−1.6‰ ± 2.4‰, Mediterranean climate) and at El Salvador No. 1 (−0.3‰ ± 2.3‰, hyperarid climate; Table 2). This trend has to be seen as a result of the climatic differences of the three studied sites, as the preferential loss of ^{16}O during evaporation led to isotopically heavier residual water in more arid climates, therefore, more of the heavier water can be expected at El Salvador.

(2) The $\delta^{18}O_{SO4}$ values showed a decreasing trend from the top of the tailings to the base of the unsaturated zone from −5.0‰ to −10.0‰ at Piuquenes and from −1.3‰ to −4.7‰ at Cauquenes (Figure 2). This decrease of $\delta^{18}O_{SO4}$ values, which occurs mainly from the surface to the oxidation front (35−70 cm depth) of the unsaturated zone at Piuquenes and Cauquenes (100−150 cm depth), indicates that isotopically light oxygen from H_2O is incorporated in the sulfate. This suggests an increasing importance of ferric iron as main electron acceptor in the pyrite oxidation at the oxidation front (eq 2). At the surface, higher evaporation and increasing activity of atmospheric oxygen ($\delta^{18}O$ = +23.5‰) in the oxidation process (eq 1) leads to heavier signatures. The values of the lower part of the unsaturated zone, which are similar to those at the oxidation front (Table 2), might originate from down-washed sulfate from the oxidation front. In the saturated primary zone the $\delta^{18}O_{SO4}$ values at Piuquenes ranged between −5.0‰ and +4.5‰, and at Cauquenes, between −0.4‰ and +4.5‰, reflecting the $\delta^{18}O$ variations of the primary sulfate mineralogy (i.e., anhydrite and gypsum).

At El Salvador No. 1, samples from the uppermost oxidation zone at the interface with the evaporite zone exhibited $\delta^{18}O_{SO4}$ values of +1.5‰ to +2.5‰ (Figure 2C and Table 2), resulting most likely from strong evaporation. The $\delta^{18}O_{SO4}$ values of −2.2‰ to −3.0‰ in samples from the underlying material suggest that water-soluble sulfate was derived from the primary jarosite as suggested by the $\delta^{34}S_{SO4}$ data.

We have shown in this study that O and S stable isotopes help in discerning the source of sulfur in water-soluble sulfates, such that microbial oxidation of sulfides can be distinguished from dissolution of primary sulfates (e.g., anhydrite). $\delta^{34}S_{SO4}$ data obtained with samples from El Salvador suggest dissolution of primary jarosite as the main sulfate source, rather than pyrite oxidation. $\delta^{18}O$ data suggest oxidation via atmospheric oxygen at the surface of the tailings impoundments, with increasing importance of Fe^{3+} as oxidant toward the oxidation front. The variation of the $\delta^{18}O_{SO4}$ values record the climatic effect of evaporation, resulting in isotopically heavier water, showing a trend from lower values at Piuquenes (Alpine climate) to higher at Cauquenes (Mediterranean climate) and El Salvador (hyperarid climate).

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