HYDROLOCAL AND GEOCHEMICAL PROCESSES OF TAILINGS IN HYPER-ARID CLIMATE TRACED BY PORE WATER CHEMISTRY AND STABLE ISTOTOPE COMPOSITION

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ABSTRACT

We present the results of a geochemical and multiple stable isotope study ($\delta^{34}S_{sulfide}$, $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, $\delta^{2}H_{water}$, $\delta^{18}O_{water}$) from the active tailings impoundment Talabre, which originates from the exploitation of the giant porphyry copper deposit Chuquicamata, Chile. The high concentrations of Na, K and Cl as well as the $\delta^{2}H$ and $\delta^{18}O$ values of the fresh tailings waters indicate a high contribution of recycled water from the tailings impoundment in the flotation processes. The $\delta^{34}S$ and $\delta^{18}O$ values show that the concentrations of SO_4 and Ca in pore water were controlled mainly by dissolution of primary gypsum/anhydrite and, with time of surface exposure, oxidation of pyrite. Heavy metals (Fe, Zn and Cu) and acidity liberated by the latter process were first detected in elevated concentrations in tailings surfaces older than four years. In deeper tailings, dissolution of chlorides and sulfates from buried former oxidation zones, reductive dissolution of their Fe oxyhydroxides, and possibly, infiltration of brine water seems to contribute to the changes of the $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values and the concentrations of Na, K, Cl, Fe and Zn. The covariations of the $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values as well as the concentrations of Na, K and Cl with depth record the relative importance of pore water evaporation, water-rock interaction and mixing of brine water, shallow groundwater and tailings waters.

INTRODUCTION

To prevent acid mine drainage(AMD) from sulfide-containing tailings the identification of the geochemical processes and element pathways in the early stages of tailing deposition are requiered. The objective of this study was to trace the first geochemical changes of low-sulfide tailings in an active impoundment in hyperarid climate by combining mineralogical and geochemical data of tailings and pore water with stable isotope analysis of dissolved sulfate ($\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$) and water ($\delta^{2}H_{water}$, $\delta^{18}O_{water}$).

The tailings origin from the exploitation of the giant porphyry copper deposit Chuquicamata (>70Mt Cu) in the Atacama desert, Chile. The ore sulfide assemblage is composed of pyrite, bornite, chalcopyrite, molybdenite, enargite and digenite with lesser amounts of covellite, djurleite/chalcocite, sphalerite, and tennantite. The gangue mineral are mainly quartz, alkali-feldspar, biotite, and minor anhydrite. After crushing and milling the ore was treated by an alkaline flotation process. The produced tailings (actually approximately 200,000 t/d with 2-3 wt.% sulfides) had a pH of 9.1-10.9 and were deposited since 1951 on the top of the salt pan Talabre (2500 m amsl) resulting in an impoundment surface of 52 km² (Fig. 1A). Once deposited, porphyry copper tailings often evolve an acidic environment due to sulfide (mainly pyrite) oxidation in combination with low neutralization potential of the gangue mineralogy, making this ore type prone to develop acid mine drainage (Dold and Fontboté, 2001).
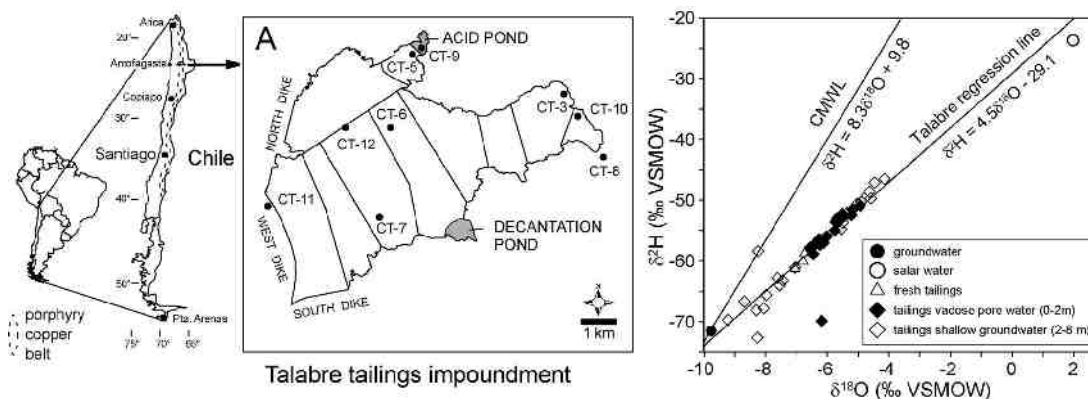
Figure 1: A. Location of sampling points at the Talabre tailings impoundment, North Chile. B. Plot of δ^2H_{water} versus $\delta^{18}O_{water}$ from the Talabre tailings impoundment. CMWL = Chile Meteoric Water Line 1990-1999 (IAEA, Vienna, Austria)

The Talabre tailings impoundment is separated into several basins with tailings surfaces exposed different time frames to weathering which offers a giant field laboratory to study the initial stages of sulfides alteration and geochemical changes in tailings after deposition. The first changes in this system were reported by Dold et al. (2005) for the first 3 years. In this abstract we present a detailed analysis of 5 years of oxidation.

The climate at Talabre is hyperarid with an average precipitation of 6.0 mm/year, an average evaporation rate of 4346 mm/year, and average monthly temperatures of 18.0°C (Ferreyra et al., 1997).

METHODS

Field methods. At Talabre, sediment samples were taken to a depth of up to 7 m by percussion soil sampling technique. Water samples were taken in the vadose zone by coring of the uppermost 2 m and extraction of pore water by displacement with epoxidized soybean oil. In the water-saturated zone, water was sampled up to 8 m depth from piezometer nests. Water samples were filtered using 0.2 μm cellulose acetate filter. Suprapure HNO_3 was added to cation subsamples. Sampling was undertaken two times within 6 months to evaluate changes of the local geochemical conditions. For comparison, samples of untreated ore rocks and recently produced tailings were taken in the mine and at the tailings discharge point.

Water pH, Eh and electrical conductivity were measured immediately in the field using a flow cell to prevent geochemical changes of water in contact with air. Alkalinity was determined by titration. The pH, grain size, color and texture of the tailings samples were determined in the field.

Stable isotope analyses. A total of 57 water samples were submitted to stable isotope analyses. The hydrogen isotope composition (δ^2H_{water}, ‰ VSMOW) was measured with a Thermo-Fischer H/Device coupled to a Delta S isotope ratio mass spectrometer (IRMS). The oxygen isotope composition ($\delta^{18}O_{water}$, ‰ VSMOW) was measured with a Thermo-Fischer Gas Bench II connected to a Delta Plus XL IRMS. Water-soluble sulfate was precipitated as $BaSO_4$ by addition of a saturated $BaCl_2$ solution and separated by filtering, as described by Dold and Spangenberg (2005). Sulfur isotope analyses ($\delta^{34}S$, ‰ VCDT) were performed by use of an on-line elemental analyzer coupled through a continuous helium flow interface (Thermo-Fischer ConFlow III) to a Delta S IRMS. The oxygen isotopic composition of the $BaSO_4$ ($\delta^{18}O_{sulfate}$, ‰ VSMOW) was measured with a high-temperature conversion elemental analyzer (Thermo-Fischer TC/EA) coupled to a Delta Plus XL IRMS.

Water analysis. Concentrations of trace elements in water samples were analyzed by inductively coupled plasma mass spectroscopy (Perkin-Elmer ELAN 6100 DRC), mayor cations and anions by ion chromatography (Dionex DX120).

Solid (tailings) analysis. Tailings samples were dried below 30°C and analyzed by ore microscopy, X-ray diffraction and X-ray fluorescence analysis. In this abstract we present the stable isotope and

geochemical data of pore water. The complete geochemical and mineralogical data set will be presented elsewhere.

RESULTS

Hydrogeology. The δ^2H-$\delta^{18}O$ covariations of tailings waters showed an evaporative trend compared to the Chile Meteoric Water Line (Fig. 1B). The isotopic composition of water entering the tailings impoundment displayed already this evaporative trend with values between –61.2‰ to –58.8‰ δ^2H and –7.0‰ to –6.7‰ $\delta^{18}O$. Water used in the flotation, sources partly from the local El Loa River, partly from water recycled from the discharged tailings. In near-surface pore waters, an ongoing evaporative trend was observed (values between –69.9‰ to –53.0‰ δ^2H and –6.4‰ to –5.7‰ $\delta^{18}O$, Fig. 2), as found in other porphyry copper tailings impoundments (Smuda et al, in review, Spangenberg et al., 2007). A positive shift of the $\delta^{18}O$ and δ^2H values in the pore waters of the deep vadose zone was attributed to partial evaporation and capillarity-driven upward diffusion and vapor-transport of water during residence in the upper meter of the tailings section (Fig. 2 A).
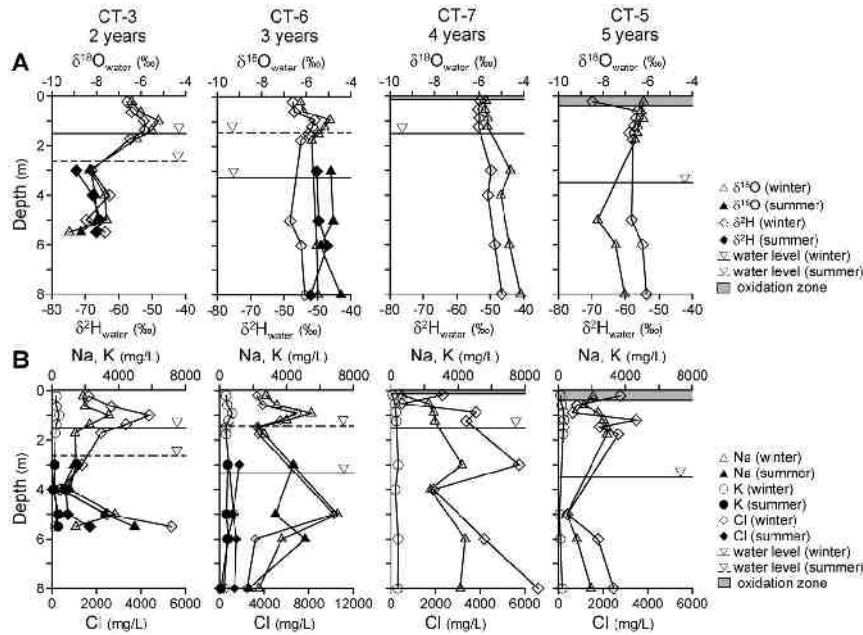

Figure 2: Water data ((A) δ^2H_{water}, $\delta^{18}O_{water}$, (B) concentrations of Na, K and Cl) from shallow groundwater taken by piezometer and pore water extracted from the vadose zone.

This is better seen in the 2 and 3 years old tailings (CT-3, CT-6) profiles, in which three isotopic zones can be distinguished. These zones were first described in Spangenberg et al. (2007). The *zone I* (saturated zone, samples from 176 cm to 800 cm depth) is in stagnant systems defined by an upward depletion in ^{18}O and ^2H ($\delta^{18}O$ = –5.5‰ to –5.8‰ and δ^2H = –53.7‰ to –55.9‰). In this zone, upwards flux (upward diffusion and vapor-transport) from the water table of isotopically lighter water is triggered by evaporative loss of water vapor at the surface. This signature can be overprinted in zones with subsurface water flow due to mixing. Follows *zone II* defined by an evaporative enrichment of the pore waters from the vadose zone by +0.8‰ in $\delta^{18}O$ and +4.1‰ in δ^2H relative to the values of the uppermost pore water sample of the zone I. The evaporation resulted in the enrichment of Na (up to 5483 mg/L; CT-6), K (742 mg/L) and Cl (6892 mg/L; Fig. 2B). The uppermost *zone III* is defined in the uppermost 100 cm of the vadose zone by an opposite isotopic shift of similar order, with depletion of the pore water in ^{18}O of 1.3‰ and in ^2H of –6.5‰. This isotopically light humidity resulted from the mixing of ascending water vapor and diffused atmospheric water vapor by near-surface advection movement. Due to the high temperature difference between day and night (up to 30°C), water vapor in the uppermost tailings can precipitate during the night, the

subsequent capillary rise transported freshly dissolved salts towards the surface, depleting the uppermost tailings in dissolved salts (e.g., CT-6, 0-18cm: 2779 mg/L Na, 375 mg/L K, 3329 mg/L Cl) and forming a surficial crust of highly soluble chlorides and sulfates.

In the tailings profiles at the central part of the tailings impoundment (CT-6 and CT-7) the δ^2H_{water} and $\delta^{18}O_{water}$ values increased below the vadose zone locally. Waters of this zone had locally very high concentrations of Na, K, and Cl (up to 7040 mg/L, 832 mg/L, 10281 mg/L, respectively; CT-6). Local brine water (CT-10) was the isotopically heaviest water found at the tailings impoundment (-23.7‰ δ^2H, 2.0‰ $\delta^{18}O$). Therefore, this isotopic shift can be explained by infiltration of brine water. A second explanation is a longer residence time of the deeper tailings water with an isotopic shift due to water-rock interaction, and dissolution of efflorescent salts from buried oxidation zones as source of Na, K and Cl.

Deeper tailings water at the eastern border of the impoundment (CT-3) was generally isotopically lighter than the other tailings waters including fresh tailings water. They plot towards the values of local groundwater (-71.5‰ δ^2H, 9.8‰ $\delta^{18}O$; Fig 2) taken at a local drilling (CT-8). The concentrations of Na , K and Cl decreased also strongly (1085 mg/L, 161 mg/L, 378 mg/L, respectively; CT-3 4m). This observation pointed to a mixing zone at CT-3 of groundwater and tailings water. The high variability in the depth of the water table and in deep water geochemistry at the different sampling sites between the two sampling campaigns seemed to result partly from local climate conditions, e.g. ongoing decrease of water table due to evaporation at CT-3. In contrast, the observed changes in the central part of the impoundment (CT-6 and Ct-7) resulted from changes in the deposition zone, which influences strongly the saturation and, most probably, the flow regime in the sedimented tailings (e.g. at CT-6, where new tailings were discharged between the sampling campaigns).

Origin of dissolved sulfate. Primary sulfate and sulfide mineral samples from Chuquicamata mine had $\delta^{34}S_{sulfate}$-values of 2.1‰ to 16.9‰, $\delta^{34}S_{sulfide}$-values of -5.4‰ to 2.6‰ and $\delta^{18}O_{sulfate}$-values of 7.5 to 11.6‰. Water-soluble sulfates in tailings entering the impoundment (CT-12) had $\delta^{34}S_{sulfate}$-values of 4.2 - 5.7‰ and $\delta^{18}O_{sulfate}$-values of 6.9 - 7.5‰. The $\delta^{34}S$-$\delta^{18}O$ covariations of dissolved sulfate from the freshly produced tailings are close to the field of primary sulfates due to the dissolution of primary anhydrite and gypsum. The $\delta^{34}S$ - $\delta^{18}O$ values of pore waters from sedimented tailings plot between the fields of $\delta^{34}S_{primary\ sulfide}$, $\delta^{18}O_{tailings\ water}$, and the $\delta^{34}S$ - $\delta^{18}O$ field of primary sulfate (Fig. 3).

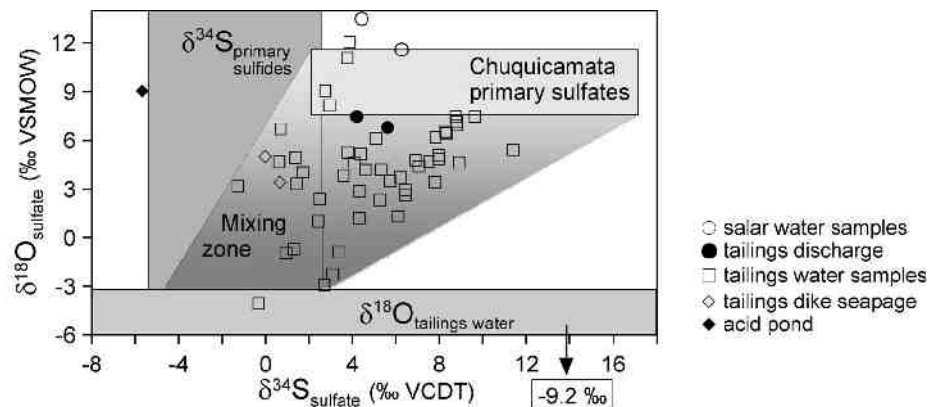Figure 3. Plot of $\delta^{34}S_{sulfate}$ versus $\delta^{18}O_{sulfate}$. The vertical band represents the $\delta^{34}S$ range of primary sulfides. The horizontal band represents the $\delta^{18}O$ range of tailings waters. The light gray box represents the $\delta^{34}S$-$\delta^{18}O$ values of primary sulfates. The diagonal band represent the mixing between dissolved sulfate from primary anhydrite and gypsum, and sulfate from oxidation of sulfides.

This can be explained by the increasing contribution of sulfate from oxidizing primary sulfides to the dissolved sulfate in tailings pore water.

Sulfide oxidation and heavy metal liberation. At CT-3 (2 years), which represents the youngest sampled tailings, the pyrite grains do not show signs of oxidation, the pH is still above neutral at the surface (pH~8, Fig. 4A).
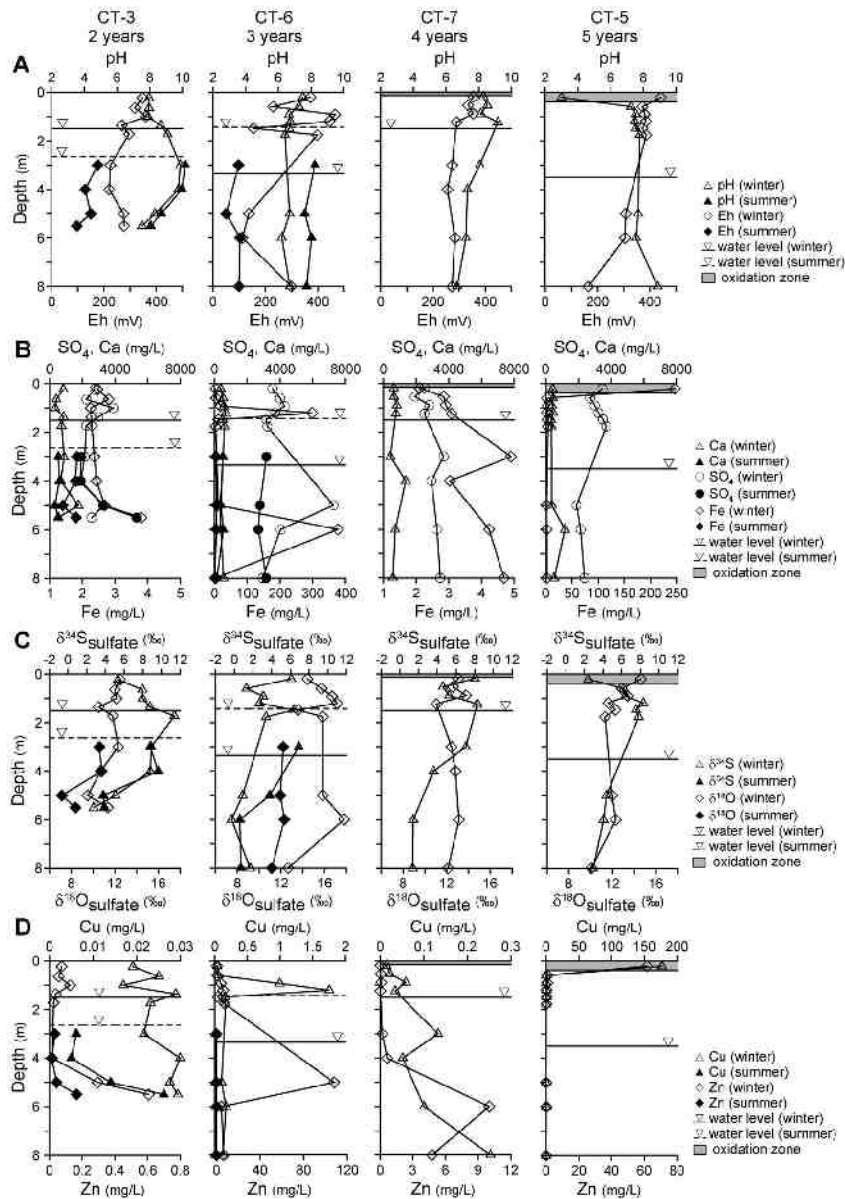

Figure 4: Water data ((A) pH, Eh, (B) Ca, SO_4 and Fe concentrations, (C) $\delta^{18}O_{sulfate}$, $\delta^{34}S_{sulfate}$, (C) Cu and Zn concentrations) from shallow groundwater and pore water from the vadose zone

The geochemical data of the pore water does not show noteworthy alterations (low concentration of Cu: 0.017- 0.030 mg/L; Zn: 0.013-0.61 mg/L; Fig. 4D).

After four years of exposure to oxidation (CT-7), the tailings evolved a 13 cm thick oxidation zone at the surface with a paste-pH of 4.7. After five years a 38 cm thick low-pH (pH ~3) oxidation zone developed, causing liberation and mobility of metals, e.g. Fe (247 mg/L), Cu (177 mg/L) and Zn (61.8 mg/L). The $\delta^{34}S_{sulfate}$-values of dissolved sulfate from these oxidized tailings decreased from 8.3‰ to 2.4‰. This ^{34}S-depletion was a result of the contribution of isotopically light sulfur from pyrite oxidation which increased with time of surface exposure. In deeper vadose zones, the higher $\delta^{34}S_{sulfate}$-

values indicated the dominant influence of primary sulfate dissolution on the dissolved sulfate (e.g., CT-3 0.5 - 2 m, CT-5 1 - 2 m, Fig. 4C).

Locally, Fe and Zn concentrations in pore water increased strongly below the water table, e.g. at CT-3 5 m (Fe 3.80 mg/L, Zn 0.61 mg/L), CT-6 1.2 m (Fe 298 mg/L, Cu 1.75 mg/L) and 5 m (Fe 11.16 mg/L, Zn 108 mg/L), and CT-7 6m (Fe 4.23 mg/L, Zn 10.02 mg/L), while the redox conditions at these points decreased. Davranche et al. (2000) have shown that reductive dissolution can liberate Fe and Zn from Fe oxyhydroxides. Therefore, a possible explanation for the observed increase in these metals may be the reductive dissolution of Fe hydroxides in buried old oxidation zones, as mentioned by Dold et al. (2005). This interpretation was supported by the increasing $\delta^{34}S_{sulfate}$ values (0.9 - 2.7‰ $\delta^{34}S$) due to the contribution of isotopically lighter sulfate from oxidized sulfides to the dissolved sulfate.

CONCLUSIONS

At the Talabre tailings impoundment, the variations of the $\delta^{34}S_{sulfide}$, $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, δ^2H_{water}, and $\delta^{18}O_{water}$ values and element concentrations in pore water allow to assess the relative importance of climatic influences (e.g., capillary rise), mixing of waters from different sources (e.g., groundwater, tailings water), and mineralogical changes (e.g., dissolution of primary minerals, sulfide oxidation). The dissolution of gypsum/anhydrite and the oxidation of pyrite (in oxidation zones at the surface and in former, buried oxidation zones), are the main processes controlling the $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ variations. The δ^2H and $\delta^{18}O$ values of fresh tailings water record the recycling of water in the flotation process. The enrichment in ^2H, ^{18}O, Na, K and Cl of surface-near waters is mainly due to evaporation. Water-Rock interaction in deeper tailings (including dissolution of efflorescent salts from buried former oxidation zones and reductive dissolution of Fe oxyhydroxides) and mixing of isotopically light groundwater and possibly isotopically heavy brine waters with tailings water can explain the isotopic (^2H and ^{18}O) and elemental (Na, K, Cl) changes in different zones of the tailings impoundment.

ACKNOWLEDGEMENTS

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