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Stable Hydrogen and Oxygen Isotope Composition of Waters from Mine Tailings in Different Climatic Environments

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The stable isotope composition of waters (δ^2H, δ^{18}O) can be used as a natural tracer of hydrologic processes in systems affected by acid mine drainage. We investigated the δ^2H and δ^{18}O values of pore waters from four oxidizing sulfidic mine tailings impoundments in different climatic regions of Chile (Piuquenes at La Andina with Alpine climate, Cauquenes and Carén at El Teniente with Mediterranean climate, and Talabre at the Chuquicamata deposit with hyperarid climate). No clear relationship was found between altitude and isotopic composition. The observed displacement of the tailings pore waters from the local meteoric water line toward higher δ^{18}O values (by $\sim +2‰$ δ^{18}O relative to δ^2H) is partly due to water−rock interaction processes, including hydration and O-isotope exchange with sulfates and Fe(III) oxyhydroxides produced by pyrite oxidation. In most tailings, from the saturated zone toward the surface, isotopically different zones can be distinguished. Zone I is characterized by an upward depletion of ^{2}H and ^{18}O in the pore waters from the saturated zone and the lowermost vadose zone, due to ascending diffused isotopically light water triggered by the constant loss of water vapor by evaporation at the surface. In zone II, the capillary flow of a mix of vapor and liquid water causes an evaporative isotopic enrichment in ^{2}H and ^{18}O. At the top of the tailings in dry climate a zone III between the capillary zone and the surface contains isotopically light diffused and atmospheric water vapor. In temperate climates, the upper part of the profile is affected by recent rainfall and zone III may not differ isotopically from zone II.

Introduction

During mining sulfide minerals are exposed to oxidation, releasing heavy metals and acidity. The kinetics of acid mine drainage (AMD) formation depends strongly on the hydraulic water flux, the geochemistry, mineralogy (grain size, primary mineralogy), and microbiology of the mine waste deposit, e.g., tailings impoundments and waste-rock dumps. Therefore exact knowledge of hydrodynamic and water−rock interaction processes in mine waste deposits is crucial for a reliable prediction of the present and future environmental impact of mining activities. Ghomshei and Allen (*1*) and Seal (*2*) outline the potential for tracing waters in mine waste deposits using δ^{18}O and δ^2H values. Few studies describe the stable isotope geochemistry of mine and/or mine-waste waters (*3*−*6*).

Aim of the Study. The stable isotope composition (reported as δ^2H, δ^{18}O) of water has been used effectively to examine fluid sources and mixing processes in the water cycle, and to help understand the geochemical processes associated with water−rock interaction and the sources and pathways of dissolved constituents (ions and gases) of groundwater (e.g., ref *7*). The hydrologic system in the tailings impoundment is essentially similar to that of a freshwater-lake system, and is defined by a network of water inputs and outputs. The potential water inputs into the system include the discharge of tailings slurry, surface runoff and subsurface flow from the catchment area, discharge from regional groundwaters, seepage from fractures, and direct input of precipitation (snow or rain). The outputs include recuperation of tailings water for use in the concentration plant, evaporation, groundwater recharge, and discrete seepages in dikes from the decantation pond. The stable isotope composition of water in tailings impoundments and discharges must be evaluated considering the processes controlling the isotopic composition of meteoric water in the recharge and catchment areas (e.g., temperature, continental effect, amount effect, altitude effect, water−rock interaction) (*2*, *7*). The aim of this study is to use δ^2H and ^{18}O data to trace the water sources and pathways in mine tailings impoundments at different Chilean climatic environments and to evaluate the relative importance of the geochemical processes associated with water−rock interaction and formation of AMD.

Mine Tailings Impoundments, and Climatic and Hydrologic Settings. The tailings impoundments studied—Talabre, Piuquenes, Cauquenes, and Carén—are located in different climatic settings formed from the exploitation of Chuquicamata (hyperarid climate), La Andina (Alpine), and El Teniente (Mediterranean) porphyry copper deposits, respectively (Figure 1, Table 1). The geology, mineralogy, and geochemistry of these tailings impoundments are described elsewhere (*8*−*12*).

Once the ore minerals are recovered by the flotation process, the tailings slurries containing about 50 wt % water and a variable amount of sulfide minerals (typically 1−6 wt % equivalent pyrite for porphyry copper tailings) are sent through pipelines or channels for final disposal in a natural depression or an artificial impoundment. After entering the impoundment, the tailings slurry meanders toward the decantation pond. Water from the decantation pond is discharged through the dam into a natural riverbed, or, if possible, the water is recovered and returned to the process. As long as the tailings are water-saturated, the sulfides oxidation is limited by the oxygen dissolved in water (<10 mg/L), but moisture can be lost rapidly through the recovery of the process water, compaction, and evaporation, thus initiating sulfide oxidation. Climate can be a major factor controlling the rate of this humidity loss and hence influences the formation of AMD (*8*).

The Piuquenes/La Andina impoundment (Figure 1A) is located 50 km northwest of Santiago, central Chilean Andes, at an altitude of 2150 m above mean sea level (amsl) with Alpine climate. The water used for ore flotation (concentration plant at 3000 m amsl) comes from different sources: 40−60% of the total used water is recovered from the flotation process, 10% is from the mine drainages, and the remaining

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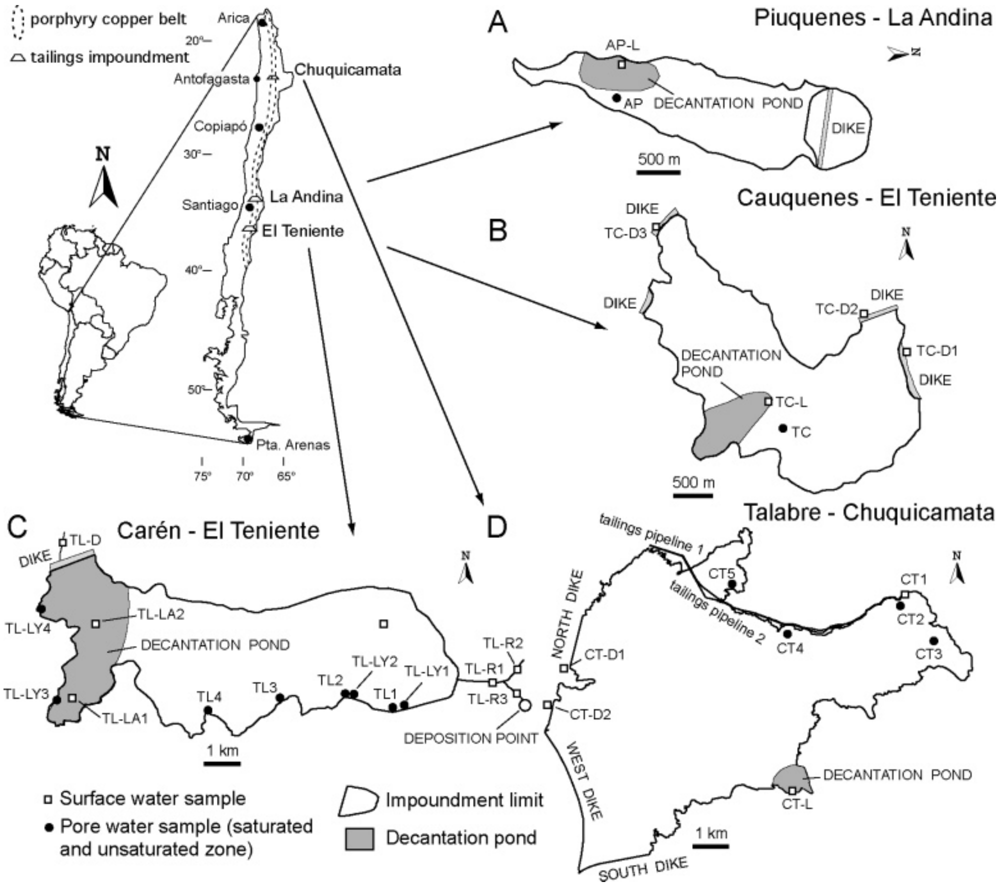

FIGURE 1. Overview of the sampling locations in the studied tailings impoundments: (A) Piuquenes/La Andina, (B) Cauquenes/El Teniente, (C) Carén/El Teniente, and (D) Talabre/Chuquicamata.

TABLE 1. Characteristics and Average Water Isotopic Composition of Studied Tailings Impoundments

impoundment	surface area	py equiv./ ca equiv.[a] (wt %)	operation time	climate precip./ evap.[b] (mm/y)	altitude (m amsl) conc. plant/ impound	$\delta^{18}O$ [c] (‰, VSMOW)	$\delta^{2}H$ [c] (‰, VSMOW)
Piuquenes	0.84 km^2	1.7/1.4	1970−1980	Alpine 700/70	3000/2150	P: −14.9 to −12.3 (−13.2 ± 0.9, $n = 14$) S: −6.3	P: −111.8 to −100.7 (−107.8 ± 3.2, $n = 14$) S: −66.2
Cauquenes	6.4 km^2	<1/0	1936−1975	Mediterranean 540/na	1910/725	P: −11.7 to −6.5 (−8.5 ± 1.7, $n = 16$) S: −10.1 to −4.9 (−8.4 ± 2.4, $n = 4$)	P: −84.6 to −55.0 (−67.7 ± 10.4, $n = 16$) S: −77.7 to −42.2 (−66.1 ± 16.2, $n = 4$)
Carén	22 km^2	1−3/0	1986−present	Mediterranean 410/na	1900/230	P: −10.6 to −5.9 (−8.4 ± 1.4, $n = 10$) S: −10.8 to −7.2 (−8.7 ± 1.6, $n = 6$)	P: −79.7 to −45.7 (−62.8 ± 10.5, $n = 10$) S: −79.0 to −60.2 (−66.4 ± 8.2, $n = 6$)
Talabre	48 km^2	1.9/0	1952−present	Hyperarid 3.2/3270	3120/2350	P: −7.6 to −3.8 (−6.9 ± 0.8, $n = 33$) S: −5.6 to −4.6 (−4.9 ± 0.6, $n = 3$)	P: −64.6 to −43.0 (−60.1 ± 4.2, $n = 33$) S: −56.8 to −44.5 (−50.7 ± 6.2, $n = 3$)

[a] py equiv. represents total sulfides concentration calculated as wt% pyrite equivalent; ca equiv. represents total carbonate concentration calculated as wt% calcite equivalent (*9*–*13*). [b] Average annual precipitation and evaporation rate. [c] Range, average, and standard deviation (1 SD) values of the isotopic composition of pore waters from the unsaturated and saturated zone (P) and waters from the decantation and other surface waters (S), n = number of analyzed samples [d] na = data not available.

30−50% is supplied by a water catchment system of stream water and rainwater (watershed area at 3000−4200 m amsl).

At El Teniente, located in the proximity of the Rancagua, central Chile with Mediterranean climate, the ore is treated after crushing and milling subsequently by acid (pH 4.5) or alkaline (pH 10.5) flotation processes. The origin of the water used for ore concentration is 59% from the flotation process and 41% from the catchment plant water from streams in the area (watershed at 1900−3800 m amsl). The tailings were deposited between 1936 and 1975 in Cauquenes impoundment (Figure 1B), at an altitude of 725 m. The Carén impoundment (Figure 1C) is now the active deposition facility of the El Teniente mine. The tailings slurry (1−3 wt % pyrite equivalent, pH 10.7) is sent from the flotation plant Colón, at 1900 m amsl, via an 87 km long channel to the Carén tailings impoundment at 220 m amsl (*12*).

The Talabre/Chuquicamata tailings impoundment is located 2300 m amsl in the Atacama Desert, 240 km NE of

Antofagasta, northern Chile (Figure 1D). The climate in this region is hyperarid (*13*). The origin of water used for ore processing by a pH 10.9 flotation circuit is roughly 60% from the CODELCO water abstraction plant in Loa basin (3120 m amsl) and 40% from the recovery of clear water from the decantation pond of Talabre.

Experimental Section

Sampling and Field Measurements. Sampling at the tailings impoundments was performed during the spring (October–November) of 2002. A total of 96 samples of water from the unsaturated (vadose) and saturated zones and surface water were collected for stable isotope analyses (Figure 1A–D). At Carén (Figure 1C) only a few samples were collected from the vadose zone due to nearly complete water saturation of the impoundment. Samples from the first 2 m were collected by 8 cm diameter thin-walled aluminum cases for pore water extraction. The cores were kept at −20 °C until pore water extraction. Pore water samples from the vadose zone were obtained by replacement with epoxidized soybean oil (Paraplex) using a modified method after Patterson et al. (*14*). Water samples from the saturated zone (>2 m depth) were obtained using drive-point piezometer nests (Solinst) with individual piezometers at different depths. Further water surface samples were taken at the tailings discharge point, decantation pond, and at the water discharge point near the dikes. At Talabre (Figure 1D), five sampling sites (CT1, CT2, CT3, CT4, and CT5) were selected, according to the tailings age (October 2002 active discharge point, recent discharge locality, 3 months, 1 year, and 3 years, respectively). All water samples were filtered (0.2 μm, regenerated cellulose) and stored at +4 °C in the darkness prior to analysis. Pore water pH (WTW pH-meter 323, Sentix 81) and Eh (WTW 330i, Sentix ORP) were measured immediately after pore water extraction. Paste-pH was measured with a special electrode (Sentix RP) inserted directly into the moist tailings. At Carén, water samples from the saturated zone were obtained at 4 sites (TL-LY1 to LY4, Figure 1C) with lysimeters (Soilmoisture Equipment Corp., CA).

Hydrogen and Oxygen Isotope Analyses. The stable hydrogen isotope analyses were performed by the dual inlet method using H_2 gas produced by reduction of water on a hot (840 °C) chromium reactor of a Thermo Finnigan H/Device connected to a Delta S isotope ratio mass spectrometer (IRMS). Oxygen isotope analyses were performed by the continuous He flow method using CO_2 equilibrated in a Thermo Finnigan GasBench connected to a Delta Plus XL IRMS. The stable hydrogen and oxygen isotope ratios are reported in the delta (δ) notation as the per mil (‰) deviation relative to the Vienna Standard Mean Ocean Water (VSMOW). The standardization of the δ^2H and δ^{18}O values relative to the international VSMOW scale was done by calibration of the reference gases and working standards with IAEA VSMOW, VGISP, and VSLAP standards. The calibration and assessment of the reproducibility of the isotopic analyses were done by replicate analyses of four working water standards prepared in the Stable Isotopes Laboratory of the University of Lausanne, as distilled tap water, two mixes of bottled mineral water, and Mediterranean ocean water (UNIL-INH, working values δ^2H = −114.0‰, δ^{18}O = −17.0‰; LIPE, working values δ^2H = −54.8‰, δ^{18}O = −8.5‰; SCH, working values δ^2H = −123.7‰, δ^{18}O = −17.7‰; MOW, working values δ^2H = 3.4‰, δ^{18}O = 0.4‰). All water samples were analyzed in duplicate. The δ^2H values reproduce to 0.3‰ and the δ^{18}O to 0.1‰.

Results and Discussion

Isotopic Signature of Waters and Pore Waters from the Tailings. The isotope data from the tailings impoundments studied are summarized in Table 1 (complete data set in Table A, Supporting Information). At Piuquenes, the δ^{18}O values of the pore waters (unsaturated and saturated zone) ranged from −14.9 to −12.3‰ and δ^2H values ranged from −111.8 to −100.8‰. At Cauquenes, the δ^{18}O values ranged from −11.7 to −6.5‰ and δ^2H values ranged from −84.6 to −55.0‰. The decantation pond had the isotopically heaviest water (δ^{18}O = −4.9, δ^2H = −42.3‰). The Carén pore waters had an isotopic composition (δ^{18}O = −10.6 to −5.9‰, δ^2H = −79.7 to −45.7‰) similar to those of Cauquenes. The pore waters from Talabre were the isotopically heaviest (δ^{18}O = −7.6 to −3.8 ‰, δ^2H = −64.6 to −43.0‰). The samples plot in the δ^{18}O–δ^2H diagram (Figure 2A) close or slightly displaced to the right of the global meteoric water line (GMWL, $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$) (*15*) and a local Chilean meteoric water line (CMWL, $\delta^2\text{H} = 8.3\delta^{18}\text{O} + 9.8$). The CMWL was determined from isotope data on precipitation in stations at different altitudes (Coyhaique, 45°21′0″, Puerto Mont, 41°28′12″, Punta Arenas, 53°00″, and Santiago, 3327′0″) from 1993 and 1994, available from the database of the International Atomic Energy Agency/World Meteorological Organization (*16*). The CMWL is very similar to the local meteoric water line for Northern Chile ($\delta^2\text{H} = 7.8\delta^{18}\text{O} + 9.7$), as determined by Aravena et al. (*17*), based on the isotope data for 1984 and 1986 precipitation. The samples are grouped in δ^{18}O–δ^2H clusters, with the isotopically light end defined by the water at Piuquenes (Alpine climate) and the heavier end defined by the water at Talabre (hyperarid climate) (Figure 2A). The pore waters of Piuquenes and Talabre (both with concentration plants at ~3000 m amsl and impoundments at ~2200 m amsl), and Cauquenes and Carén (concentration plants at ~1900 m amsl, impoundments at 230–750 m amsl) tailings do not show a clear isotopic gradient with the altitude from the concentration plant and the impoundment (Table 1). The isotopic compositions of the pore waters differed depending on climatic environment (e.g., arid, humid, warm, cold) and local isotopic exchange processes, such as evaporation and water–rock interaction, including iron-oxide hydrolysis, silicate, sulfates and Fe(III) oxyhydroxides hydration, and O-isotope exchange with mineral phases (Figure 2B; see below).

Evaporation, Exchange, Mixing, and Capillarity Driven Flow in Tailings. The main δ^2H vs δ^{18}O covariations observed in the tailings waters appear to be related to temperature effects and evaporation processes (meteoric water in the recharge and catchment areas), condensation, and rain intensities. The relative importance of these processes and isotopic exchange is better seen in the δ^{18}O–δ^2H diagrams for the individual impoundments (Figure 2C–F). There was a strong positive correlation between δ^2H and δ^{18}O values for Cauquenes ($r^2 = 0.962$, $n = 20$), Carén ($r^2 = 0.899$, $n = 20$), and Talabre ($r^2 = 0.956$, $n = 42$), and no correlation for Piuquenes ($r^2 = 0.085$, $n = 14$) (see below). Separation of the water samples from the meteoric water line is caused by isotopic fractionation during phase separation and geochemical processes (Figure 2B) (*2*, *7*). Removal of water by evaporation causes enrichment in ^{2}H and ^{18}O in the residual water, thereby producing a positive trend from the starting composition, and a shift of the slope of the δ^{18}O–δ^2H line to less than 8 (Figure 2B) (*7*, *18*). At Piuquenes, Cauquenes, and Talabre, the isotopically heaviest waters were from the decantation ponds. At Carén impoundment, this evaporative isotopic enrichment is overprinted by mixing of the isotopically light initial tailings waters originated at the high altitude concentration plant (~1900 m amsl) with isotopically heavier meteoric water in the catchment area of the impoundment (~230 m amsl) (Table 1). In general, the pore waters of the saturated zone and the decantation pond define an evaporation line with slope between 6.7 for the Mediterranean climate at Carén, and 4.9 for the highly evaporative

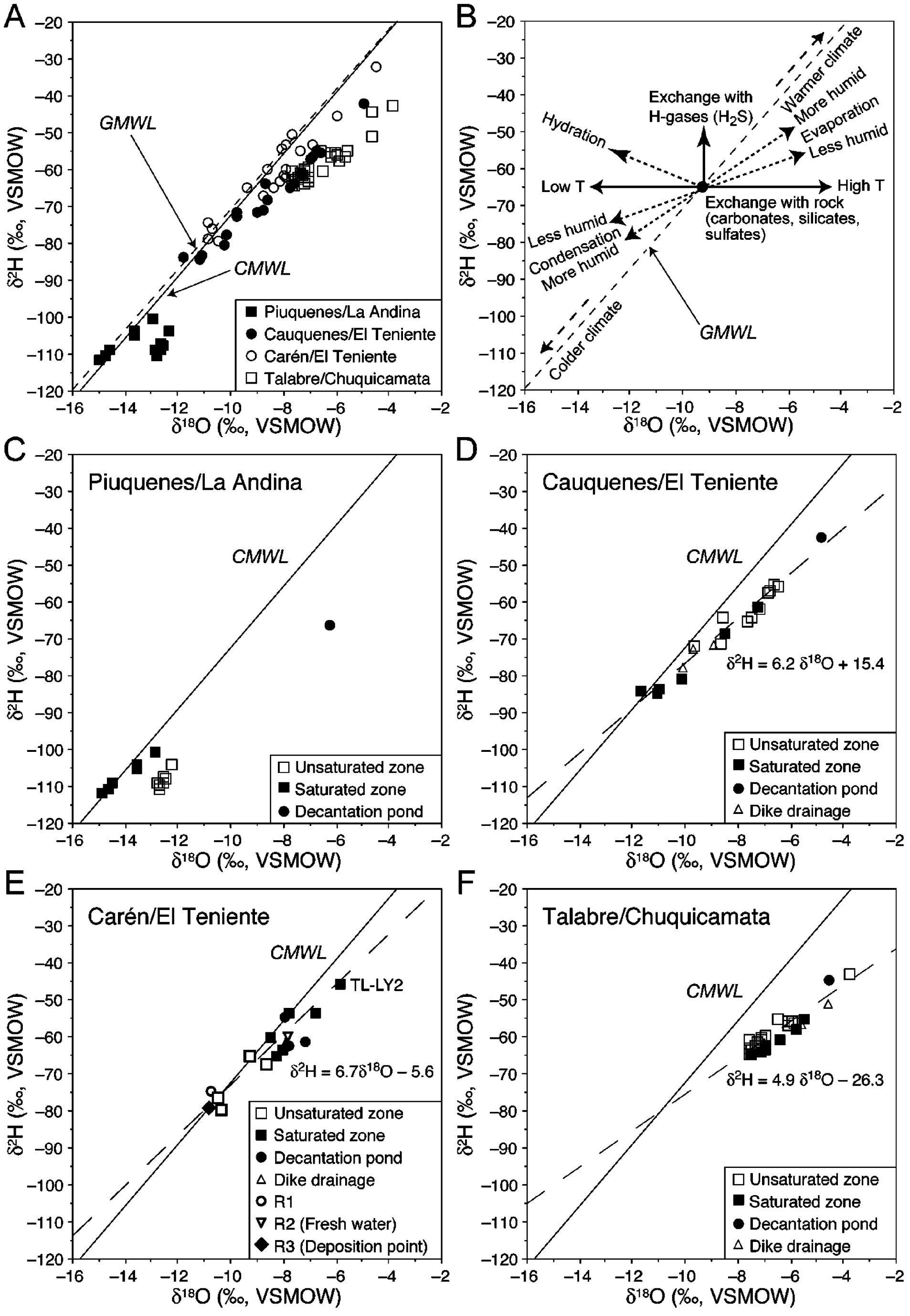

FIGURE 2. (A) Plot of δ^2H versus δ^{18}O for waters from the studied tailings impoundments: Piuquenes/La Andina (Alpine climate), Cauquenes/El Teniente, Carén/El Teniente (Mediterranean climate) and Talabre/Chuquicamata (hyperarid climate). GMWL = Global Meteoric Water Line after Rozanski et al. (*15*). CMWL = Chilean Meteoric Water Line from 1993 to 1994 IAEA/WMO data (*16*). (B) Schematic plot of δ^2H and δ^{18}O variations due to physical and chemical processes determining displacement of the isotopic composition of waters from the GMWL. Plots of δ^2H versus δ^{18}O for waters from: (C) Piuquenes/La Andina, (D) Cauquenes/El Teniente, (E) Carén/El Teniente, and (F) Talabre/Chuquicamata. Regression lines for the different tailings impoundments are also presented.

hyperarid climate at Talabre. Evaporation slopes generally vary between 4 and 7 for 0 to >95% relative humidity (h) (*18*). The slopes of 6.2 and 6.7 determined at Cauquenes and Carén require an h > 90%, which is too high for a Mediterranean climate. The slope of the δ^{18}O−δ^2H line determined for Talabre pore water (4.9) was similar to the slope of 4.3 determined by Leybourne and Cameron (*19*) for groundwater from the Spence porphyry-cooper, which is located just south of the Chuquicamata mine in the Atacama Desert, northern Chile. These slopes appear also to be too high (h ~60%) for a hyperarid climate. However, high relative humidity in the pore gas near the vadose−groundwater interface and also in the air near the tailings surface of water-saturated systems (e.g., Carén impoundment) is very likely. Steeper slopes than expected may result from a mixing of evaporated and evolved water, both chemically and isotopically, with meteoric water of variable isotopic composition (e.g., ref *18*). A positive displacement of the δ^2H values due to H-isotope exchange with H-bearing volatile phases would also increase the slope of the δ^{18}O−δ^2H line (*18*).

At the Piuquenes tailings impoundment, the samples from the saturated zone of a near neutral pH plot close to the local

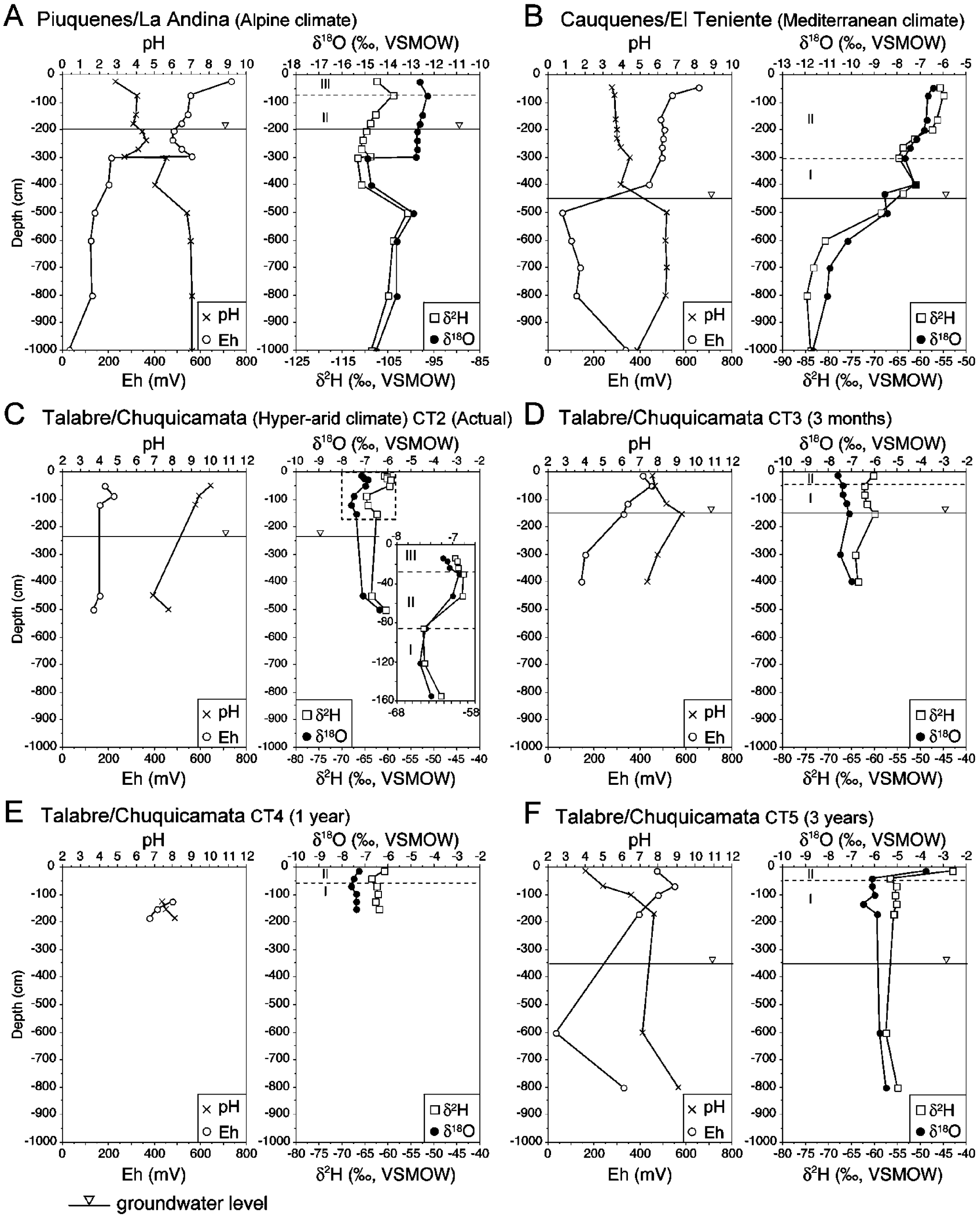

FIGURE 3. Vertical profiles of pore water pH, Eh, and isotopic composition (δ^2H and δ^{18}O) for the studied tailings impoundments. Insert in the δ^2H and ^{18}O versus depth plots for Talabre CT2 in panel C show 3 distinct isotopic zones from the saturated zone toward the surface (see text for explanation).

meteoric water line, at the region for cold (Alpine) climate (Figure 2C). The high precipitation rate (700 mm/y) and low evaporation (70 mm/y), and therefore recharging of meteoric waters in the tailings impoundment, may explain the isotopic signature in the waters from the saturated zone. Samples from the unsaturated zone were displaced from the meteoric water line by +2‰ δ^{18}O relative to δ^2H. This is better seen in the distribution of the isotopic values in the vertical profiles across the saturated and unsaturated zones (Figure 3A). The higher δ^{18}O values in the acidic (pH as low as 2.8) and oxidizing (Eh up to 700 mV) unsaturated zone (Figure 3A) suggest that these waters were affected to different degrees by evaporation and water–rock interaction processes, or were formed in a different seasonal climatic regime.

The oxidation of pyrite take place in three major steps, including oxidation of sulfide sulfur and ferrous iron by atmospheric oxygen, and hydrolysis and precipitation of ferric complexes and minerals. The net reaction is as follows:

$$FeS_2 + {}^{15}/_4\, O_2 + {}^{7}/_2 H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

These reactions would affect both δ^{18}O and δ^2H values, and produce lower $\delta^{18}O_{water}$ values as a result of the sulfates and oxides produced, all of which are enriched in ^{18}O relative to water. Oxidation of ferrous to ferric iron by atmospheric oxygen (~ 23.5‰ δ^{18}O; *2*) produces ^{18}O-enriched water. The pore waters may be enriched in ^{18}O and ^{2}H compared to the original composition during hydration of the sulfates and ferric oxides. Further O isotope exchange between water and the produced sulfates and Fe(III) oxyhydroxides cause a shift of the ^{18}O values of the water away from the initial value (Figure 2B). Furthermore, the carbonates, metal oxyhydroxides, sulfates, and sulfides undergo dissolution at low pH, and silicates weathering (*20*), facilitating the O-isotope exchange with dissolved O-containing ions. Thus, the magnitude of the δ^{18}O shift is most likely related to the extent of isotopic exchange with the products of pyrite oxidation. The ^{18}O-enrichment due to pyrite oxidation and/or O-exchange with minerals may be superseded by an increase in the δ^{18}O and δ^{2}H values due to evaporative fractionation. The relative importance of the ^{18}O-enrichment in the pore waters due to pyrite oxidation (with minor change of the δ^{2}H values) and evaporative fractionation can be assessed by comparing the δ^{18}O and δ^{2}H variations in relatively old tailings in cold regions (Piuquenes, Alpine climate, 22 years old; Figures 2C and 3A) with tailings in temperate (Cauquenes, Mediterranean climate, 28 years old, Figures 2D and 3B) and hyperarid (Talabre CT5, 3 years old, Figures 2F and 3F) regions.

At Cauquenes, the δ^{18}O vs δ^{2}H covariations follow an evaporation and water−rock interaction trend (slope of 6.2), with the more positive values of the vadose zone becoming more negative in the saturated zone (Figure 2D). The δ^{18}O and δ^{2}H variations along the vertical profile in the >27 years old tailings at Cauquenes (Figure 3B) represent steady-state conditions with constant evaporation and flux from the water table. The isotopically heavy end in the δ^{18}O−δ^{2}H diagram is defined by the highly evaporated water in the decantation pond, and the isotopically light end is represented by the >6 m deep tailings pore waters (Figure 3B). These waters most likely represent the final isotopic signature resulting from the mixing of the isotopically light waters from the catchment area (725−1000 m amsl) and old evolved tailings (1900−3800 m amsl) waters. There is a strong negative correlation between the isotopic composition and pH values for Cauquenes pore waters, which define mixing lines ($\delta^{18}\mathrm{O} = -1.417\mathrm{pH} - 1.661$, $r^2 = 0.980$ and $\delta^{2}\mathrm{H} = -9.087\mathrm{pH} - 24.701$, $r^2 = 0.974$, $n = 11$) between end points defined by evaporated and exchanged water from the vadose zone (pH ~ 3, δ^{18}O ~ −7‰, δ^{2}H ~ −55‰) and relatively older more evolved pore-waters from the saturated zone (pH ~ 7, δ^{18}O ~ −11‰, δ^{2}H ~ −85‰) (Figure A, SI). This correlation confirms the combined effect of isotope exchange with Fe(III) oxydydroxides and sulfates produced by pyrite oxidation and released acidity that triggered hydrolysis, hydration, and dissolution, as a main factor controlling the isotopic variations in a system affected by AMD. The extent of these isotopic exchange processes influencing the water isotopic composition serves to differentiate hydrologic systems affected by mining effluents like AMD from low-temperature natural systems unaltered by human activities.

The waters of the Carén tailings impoundments have δ^{18}O and δ^{2}H values plotting along the Chilean meteoric water line or displaced by up to 2‰ to higher δ^{18}O values (Figure 2E). This can be interpreted as an evaporation and water−rock interaction trend, where the isotopically light initial water ($\delta^{18}\mathrm{O} = -10.8$‰ and $\delta^{2}\mathrm{H} = -79.0$‰) is from the discharged tailings (point TL-R1 in Figure 1C) and the isotopically heavy residual water is from the saturated zone (TL-LY2, $\delta^{18}\mathrm{O} = -5.9$‰ and $\delta^{2}\mathrm{H} = -45.7$‰). Before entering the impoundment the discharged tailings receive isotopically heavier fresh water from the river Carén ($\delta^{18}\mathrm{O} = -7.8$‰ and $\delta^{2}\mathrm{H} = -60.2$‰, point TL-R2 in Figure 1C) draining the eastern part of the catchment area of the impoundment (<230 m amsl). When the tailings arrive at the nearly water-saturated impoundment (the upper surface was briefly exposed to oxidation by atmospheric O_2), the pH drops from 8.5 to 7.6 and Eh increases from 340 to 375 mV. The surface pore water samples from the vadose zone in sites TL1 to TL4 (open boxes in Figure 2E) fall in the δ^{18}O−δ^{2}H line between water from the discharged tailings and water from freshwater stream (river Carén). These waters have lower δ^{18}O and δ^{2}H values (~2‰ δ^{18}O and ~20‰ δ^{2}H) than the up to 80 cm deep water samples obtained with lysimeters near site TL1 (TL-LY2, Figures 1C and 2E). This isotopic shift is opposite that observed in the vertical profile from the old tailings at Cauquenes, whose signature is dominated by an evaporative trend. At Carén, the isotopically heavy pore waters originate from the mixing of catchment (230−500 m amsl) and tailings waters, and the light end has the isotopic signature of the actual inflowing tailings originated at 1900−3400 m amsl (*12*).

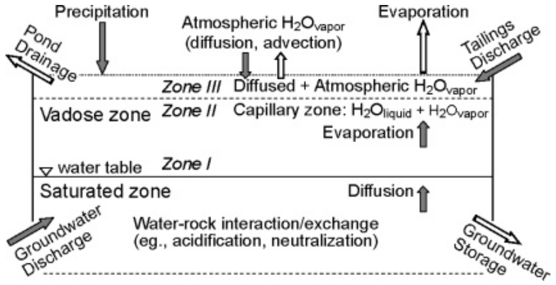

FIGURE 4. Schematic model of water flux in tailings impoundments. Solid arrows depict changes in liquid water composition due to the addition of water; open arrows depict changes due to the removal of water. The δ^{18}O and δ^{2}H variations along a profile define three zones: Zone I is defined by the upward diffusion and vapor-transport of liquid water from the water table toward the surface. Zone II is defined by an evaporation-driven capillary flow of liquid and vapor water. Zone III is the area between the capillary zone and the surface in hyperarid climates that contains isotopically light diffused and atmospheric water vapor (see text for explanation). In temperate and cold climates, the profiles are generally disturbed by rainfall events, and zone III may not differ isotopically from zone II.

The pore waters from the hyperarid climate of Talabre follow an evaporative δ^{18}O−δ^{2}H trend (slope of ~5), and are enriched in heavy isotopes (δ^{18}O ranging from −7.6 to −3.8 ‰ and δ^{2}H values ranging from −64.6 to −43.0‰) compared to those of the studied tailings from colder climates (Figure 2F). The samples from the unsaturated zone at Talabre are relatively enriched in ^{2}H compared to the saturated zone samples, showing a vertical displacement from the δ^{18}O−δ^{2}H line (Figure 2F). A ^{2}H enrichment and/or ^{18}O depletion of waters relative to the local meteoric water can be caused by processes such as gas exchange (H_2S, H_2, CH_4, CO_2) and mineral hydration, as silicates and Fe-oxyhydoxides (Figure 2B, refs *7* and *20*). The high SO_4^{2-} tailings pore-waters have generally dissolved H_2S concentrations in the order of a few mmol/L or less, and their effect on the water δ^{2}H values of water may be negligible (e.g., *7*). The positive shift in δ^{18}O and δ^{2}H values in the pore waters of the vadose zone are attributed to the partial evaporation and capillarity-driven upward diffusion and vapor-transport of water during residence in the upper meter of the tailings profile (Figure 3C−F). This is better seen in the actual tailings (CT2) profile (zoom in Figure 3C), in which three isotopic zones can be distinguished, and permitted the development of a schematic water flow model associated with the hydrologic inputs and outputs to these systems (Figure 4). *Zone I* is defined by an upward depletion in ^{18}O and ^{2}H ($\delta^{18}\mathrm{O} = -6.4$ to -7.5‰ and $\delta^{2}\mathrm{H} = -60.6$ to -64.6‰) of the pore waters from the saturated zone and the lowermost vadose zone (samples from 86 to 500 cm depth). In this zone, upward flux (diffusion and vapor-transport) of isotopically lighter water is triggered by evaporative loss of water vapor at the surface. *Zone II* is characterized by a capillary flow of a mix of vapor and liquid pore water from the vadose zone, which define an evaporative isotopic enrichment by +0.6‰ in δ^{18}O and +4.8‰ in δ^{2}H relative to the values of the uppermost pore water sample of zone I. *Zone III* is defined in the uppermost 40 cm of the vadose zone by an opposite isotopic shift of similar order, with depletion of the pore water/humidity in ^{18}O and ^{2}H to values as low as −7.6‰ in δ^{18}O and −64.6‰ in δ^{2}H. This isotopically light humidity, which could be recovered from some tailings samples immediately frozen after sampling, results from the mixing of ascending water vapor and diffused atmospheric water vapor by near-surface advection movement. A similar δ^{18}O and δ^{2}H depth profile only with zone II and III was observed in high-evaporative unaffected soil systems in southern Australia (*21*). At Piuquenes (sampling performed in spring, Figure 3A), only zones II and III can be differentiated, and the saturated zone appear to be affected by groundwater circulation/heterogeneities. In the temperate climates, the top part of the profile is affected by recent rainfall (e.g., ref *21*) and contains a mix of evaporated moisture and rainfall (e.g., profile at Cauquenes, Figure 3B) and/or recently discharged tailings waters and may not differ isotopically from zone II. Zone III is overprinted by evaporative fractionation in dryer surface tailings (e.g., Talabre profiles CT3, CT4, CT5, Figure 3D−F).

The variations of the δ^{18}O and δ^{2}H values of pore waters from four sulfidic mine tailings impoundments at different climatic regions of Chile provide insight into the fluid−fluid and fluid−sediment mixing and phase separation processes. These processes appreciably modify the isotopic composition of AMD waters, and differentiate them from unaffected fresh waters.

This study highlights the informative potential of using the stable isotopes of oxygen and hydrogen as a natural tracer in acid rock drainage and to illustrate how the ^{18}O and ^{2}H concentrations from tailings pore waters link the microscale water−rock interaction processes (e.g., chemical reactions, isotope exchange) to the macro-scale physical processes (e.g., evaporation, condensation, precipitation).

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Supporting Information Available

Table A, hydrogen and oxygen isotope composition, pH, Eh and conductivity of all the samples; Figure A, plot of δ^{2}H and δ^{18}O versus pH for waters from the Cauquenes/El Teniente impoundment. This material is available free of charge via the Internet at http://pubs.acs.org.

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