



## GEOCHEMICAL AND ISOTOPIC CHANGES IN THE ACTIVE TAILINGS IMPOUNDMENT CARÉN FROM THE PORPHYRY COPPER DEPOSIT EL TENIENTE, CHILE

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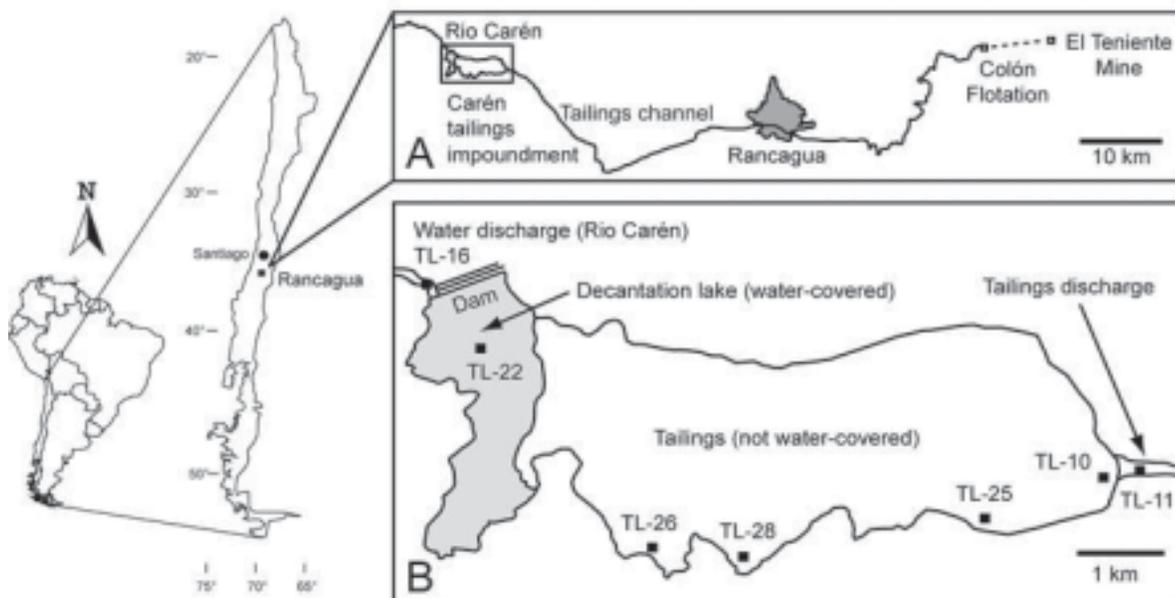
### ABSTRACT

At the active tailings impoundment Carén (surface 22 km<sup>2</sup>, up to 3 vol% sulfides) from the porphyry copper mine El Teniente (Chile) initial steps of primary mineral alteration and geochemical changes after deposition were studied. The variations of  $\delta^2\text{H}_{\text{water}}$ ,  $\delta^{18}\text{O}_{\text{water}}$ ,  $\delta^{18}\text{O}_{\text{sulfate}}$ ,  $\delta^{34}\text{S}_{\text{sulfide}}$ , and  $\delta^{34}\text{S}_{\text{sulfate}}$  values were used to trace sources of water and dissolved  $\text{SO}_4$ . Water in the tailings impoundment changed from pH 9.2-10.2 at the tailings discharge to pH 8.7-7.4 at a downstream decantation lake. Decanted water contained up to 3.5 mg/L Mo, 9  $\mu\text{g/L}$  Cu, 2.7/L Fe, and 1400 mg/L  $\text{SO}_4$ . Sulfide oxidation were observed at the surface of the tailings with metal concentrations in pore water up to 0.20 mg/L Cu and 23.8 mg/L Mo. Dissolved sulfate resulted from the sulfide oxidation process and from dissolution of primary sulfates.

### INTRODUCTION

A study of the initial steps of primary mineral alteration and geochemical changes of tailings at the active tailings impoundment Carén (surface 22 km<sup>2</sup>, Figure 1) from the porphyry copper mine El Teniente (Chile) is presented. The tailings impoundment is constructed in a valley and consists of the discharge point upstream, a zone of water-saturated tailings, a decantation lake and a dam, where decantation water is discharged into a natural river system downstream. The tailings entered the impoundment with pH 9.2-10.2 due to the alkaline flotation process and contained 1-3 wt% sulfides (mainly pyrite). After entering the tailings impoundment, the tailings slurry meanders towards the decantation lake. The slurry current bed moves in an almost constant 4-week-cycle from the northern

to the southern border of the impoundment and back due to the silting up of the current bed by the tailings.



**Figure 1:** Location of the Carén tailings impoundment, Central Chile, and the sampling points

## Methods

At five points in the tailings impoundment, water samples up to a depth of 4 m were taken by piezometer during the winter and the summer periods. Further water samples were taken at the tailings discharge point, the decantation lake, and the discharge of water from the decantation lake. Eh, pH, alkalinity and Fe(II) concentration were measured immediately. Data from a multiple stable isotope study ( $\delta^{34}\text{S}_{\text{sulfide/sulfate}}$  as ‰ VCDT,  $\delta^{18}\text{O}_{\text{sulfate/water}}$  as ‰ VSMOW,  $\delta^2\text{H}_{\text{water}}$  as ‰ VSMOW, details in: Smuda et al., 2006) and geochemical analyses of the water samples (IC, ICP-MS, HG-AAS) were used to trace back main water pathways, mixing of different waters and mineralogical processes of the recently deposited tailings.

## Results

*Stable Isotope Analysis.* Tailings water at the tailings discharge point (TL-11, Fig. 1) had a range of 85.1‰ to -89.0‰ for  $\delta^2\text{H}$  and -11.5‰ to -11.8‰ for  $\delta^{18}\text{O}$  indicating a high altitude origin (>1,900 m) of the water used in the flotation processes. At the decantation water discharge point (TL-16) the isotopic range were for  $\delta^2\text{H}$  -68.6‰ to -67.8‰ and for  $\delta^{18}\text{O}$  -9.2‰ to -8.1‰. The

differences between the two sampling sites ( $\sim 20\%$   $\delta^2\text{H}$ ,  $\sim 2\%$   $\delta^{18}\text{O}$ ) were consistent with an evaporative fractionation over the large tailings surface during the whole year. In tailings profiles (TL 22-28), pore water from the surface was enriched in  $^2\text{H}$  during the winter season compared to the summer samples (differences between 8.8‰ and 36.1‰). The evaporation fractionation is suggested to be overprinted by isotopically heavier meteoric water (compared to the high altitude originated tailings waters) during the rainy winter season. In the winter season the  $\delta^2\text{H}_{\text{water}}$  and  $\delta^{18}\text{O}_{\text{water}}$  values increased below 1 m with depth (up to -59.2‰ and -7.8‰, respectively). This isotopic shift could be explained by infiltration of isotopically heavier groundwater into the tailings impoundment. During the dry summer, this contribution was small, and two competing processes controlled the overall  $\delta^2\text{H}_{\text{water}}$  and  $\delta^{18}\text{O}_{\text{water}}$  variations: i) preferential evaporation of isotopically light water, and ii) ascending isotopically light tailings water by capillarity. Small contributions to the variation of the  $\delta^{18}\text{O}_{\text{water}}$  values may be due to the preferential use of isotopically light oxygen in processes of bacterial mediated oxidation of sulfides.

*Water analysis.* Water of the discharged tailings had a pH of 9.2-10.2 and changed to pH 7.4-7.7 at the decantation lake (Table 1), where decantation water is discharged into a downstream natural river system. The maximum concentrations of heavy metals and sulfate in discharged decantation water (2.7 mg/L Fe, 9  $\mu\text{g/L}$  Cu, 3.5 mg/L Mo, 23  $\mu\text{g/L}$  As, 1400mg/L  $\text{SO}_4$ ) were found during the summer period.

**Table 1:** Water data from the tailings and decantation water discharge at the Carén tailings impoundment

	pH	Eh (mV)	Ca (mg/L)	Al (mg/L)	Fe (mg/L)	Cu (mg/L)	Mo (mg/L)	As (mg/L)
Tailings discharge, winter	9.21	214	672	0.738	2.32	0.0260	2.67	0.018
Tailings discharge, summer	10.21	267	719	0.336	2.38	0.0309	3.09	0.016
Clear water discharge, winter	7.41	394	602	0.020	2.07	0.0070	1.31	0.013
Clear water discharge, summer	7.74	410	776	0.064	2.73	0.0089	3.53	0.023

Metal concentrations in pore water from the tailings profiles had their maximum concentrations in the uppermost zone during the summer season (Cu up to 0.20 mg/L, Mo up to 23.8 mg/L). Pyrite grains in the tailings near to the surface had small oxidation rims. This indicated that near to the surface incipient sulfide alteration liberated rapidly heavy metals and sulfate after deposition. In the

surface layer this process was enhanced in the summer, when evaporation resulted in a not water-saturated layer (water level up to 1.14 m below surface) and a lowering of the pH by the subsequent formation of sulfuric acid. For dissolved sulfate another important source was the dissolution of primary gypsum/anhydrite. Fresh alkaline tailings were deposited at the sampling points in a 4-week-cycle saturating the tailings again completely with water. Below 1 m, the pH decreased in the tailings with depth to pH 6.7-8.4, possibly due to neutralization of the bases by the tailings. The concentrations of heavy metals also decreased with depth in the tailings (minimum concentrations: 0.03 mg/L Mo, 0.11 mg/L Cu). This suggested that in the deeper zone the oxidation of sulfides was inhibited due to water saturation and subsequent low availability of oxygen.

## CONCLUSIONS

At the Carén tailings impoundment geochemical water analyses and stable isotope ( $\delta^{34}\text{S}_{\text{sulfide}}$ ,  $\delta^{34}\text{S}_{\text{sulfate}}$ ,  $\delta^{18}\text{O}_{\text{sulfate}}$ ,  $\delta^2\text{H}_{\text{water}}$ , and  $\delta^{18}\text{O}_{\text{water}}$ ) data allow to assess the relative importance of climate, water pathways and different water sources to geochemical and mineralogical changes in freshly deposited tailings. Isotopic enrichment of surface waters indicated high evaporation. Mixing of isotopically heavy meteoric water and groundwater with tailings water explained the  $^2\text{H}$ - and  $^{18}\text{O}$ -enrichment both at the surface and in deeper zones. The  $\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{18}\text{O}_{\text{sulfate}}$  variations resulted from the dissolution of gypsum/anhydrite and the oxidation of sulfides. The secondly mentioned process led in the release of heavy metals, especially Cu and Mo. The oxidation of sulfides was enhanced during the summer period, when tailings areas fell dry and oxygen could enter the uppermost tailings. During the winter the tailings were water-saturated and sulfide oxidation was reduced on the surface of the tailings. Below 1 m depth the pH decreased to circumneutral values, possibly due to neutralization processes. The oxidation of sulfides and the dissolution of primary sulfates resulted in maximum concentrations of 9  $\mu\text{g/L}$  Cu, 3.5 mg/L Mo and 1400mg/L  $\text{SO}_4$  in water at the discharge of the decantation lake.

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