Copper Enrichment and Secondary Mineralogy in Porphyry Copper Tailings Deposited into a Marine Environment, Bay of Chañaral (Atacama Desert, N-Chile)

Christian Wisskirchen1*, Bernhard Dold1,2, Jorge E. Spangenberg1

1 Institute of Mineralogy and Geochemistry, University of Lausanne, CH-1015 Lausanne, Switzerland. (c.wisskirchen@yahoo.com; Jorge.Spangenberg@unil.ch)
2 Departamento de Geología, FCFM-Universidad de Chile, Plaza Ercilla 803, Santiago de Chile, Chile. (bdold@ing.uchile.cl)
* Actual address: Golder Associates S.A., Magdalena 181 – Piso 3, Las Condes, Santiago, Chile. (cwisskirchen@golder.cl)

Abstract
Porphyry copper tailings (~220 Mt) with initial concentrations of 0.3wt% Cu were discharged into a marine bay. Different Cu enrichment processes for the tailings were evaluated by mineralogical-geochemical and stable-isotope analyses. After 36 years of sulphide oxidation, the oxidation zone is characterized by formation of gypsum and jarosite (pH 2.6-4.0), with local zones of copiapite ($Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2•20H_2O$) resulting from high oxidation kinetics and resultant low pH (pH 1.2) induced by tidal water level changes.

Syndepositional heavy mineral enrichment (up to 1.8wt% Cu as sulphides), due to wave action resulted in an increase of oxidation products in the water and successively to the formation of a hardpan cemented with jarosite and gypsum. At an alluvium-tailings contact, paratacamite ($Cu_2(OH)_3Cl$) is found and is attributed to pH increase triggered by the alluvium.

Evaporation-driven capillary transport resulted in efflorescent eriochalcite ($CuCl_2•2H_2O$) and chalcanthite ($CuSO_4•5H_2O$) precipitation at the tailings surface, depending on the initial $Cl:SO_4$ ratio of the solution. In the saturated zone up to 56 g/L Cl and 35 mg/L Cu is present at neutral pH values.

Secondary covellite rims formed on chalcopyrite and enriched Cu up to 0.56wt%. Stable-isotope results showed seawater infiltration along the shore line, which was a carbonate source for the formation of Cu-carbonates whereas elsewhere paratacamite formed.

Key Words: seawater, brine, paratacamite, eriochalcite

Introduction
Geochemical processes and secondary mineralogy of tailings in contact with highly saline solutions can be different from that of tailings in contact with process waters or with rain or groundwater of lower salinity. This is the case at several sites where sulphuric tailings were discharged into near shore environments and are able to oxidize (e.g. Dold 2006; Dold *et al.* 2011). Further, this may also apply at sites where flotation with seawater is seen as an alternative, due to scarcity of water, such as porphyry copper molybdenum mining projects in the hyper-arid Atacama Desert (Moreno *et al.* 2011; Waples *et al.* 2012; Wisskirchen *et al.* 2012). While the geochemistry and mineralogy of porphyry copper tailings deposited onshore is well studied (e.g., Dold and Fontboté, 2001; Smuda *et al.* 2008), the specific characteristics of acid mine drainage (AMD) formation, metal leaching (ML), and secondary mineralogy of porphyry copper tailings in contact with seawater under oxidizing conditions need to be evaluated to develop a conceptual understanding of the processes involved. This understanding is the basis for further modeling of future water quality and is needed to evaluate closure scenarios.

Another paper of this conference (Waples *et al.* 2012) focuses on static and kinetic testing results for tailings in contact with seawater. This current paper evaluates a marine shore porphyry copper tailings deposit after 36 years of oxidation in the bay of Chañaral in Northern Chile. The tailings deposit at Chañaral offers the unique possibility to study the geochemical interaction of porphyry copper tailings and high saline waters, as the waters of the El Salado brine aquifer and marine seawater infiltrate the tailings (Wisskirchen *et al.* 2006). Findings from the Chañaral tailings impoundment can help to understand geochemical processes at similar sites (e.g. Bay of Ite, Southern Peru) and geochemical processes in flotation tailings deposited with seawater.

Site description

At the bay of Chañaral (Northern Chile; 26°20'S and 70°37'W) flotation tailings from the porphyry copper mines Potrerillos (1926-1959) and El Salvador (1959-1975) were deposited throughout the El Salado valley. The Potrerillos Cu-Mo-(Ag) deposit (1.8 Mt Cu) of Eocene age is located 120 km east of Chañaral (Figure 1) and is characterized by three hypogene alteration and mineralization events and supergene alteration. The early potassic and propylitic alterations are responsible for the K-feldspar, biotite, chlorite, quartz, ankerite, and anhydrite content. Associated sulphides are chalcopyrite, bornite, pyrite, molybdenite, minor enargite, sphalerite, and galena (Camus 2003). The El Salvador Cu-Mo-(Au) deposit (5.7 Mt Cu) of Eocene age ($41 \cdot 10^6$ years) is located 100 km east of Chañaral. Early mineralization is characterized by distinctive quartz veins and largely disseminated K-silicate assemblages of alkali feldspar-biotite-anydrite-chalcopyrite-bornite or chalcopyrite-pyrite. K-silicate alteration converted hornblende phenocraysts to biotite-anhydrite-rutile, ilmenite to hematite-rutile, and titanite to rutile-anhydrite. Secondary Cu-sulphides (chalcocite and covellite) extensively replaced chalcopyrite and bornite, but coated pyrite with little or no replacement (Gustafson and Hunt 1975; Gustafson and Quiroga 1995). Both deposits were exploited by underground mining and the ore minerals (Cu-Mo sulphides) separated from the gangue by alkaline flotation (pH 10.5).

The deposition of ~150 Mt of tailings at Chañaral resulted in a marine shore tailings deposit of 4.5 km^2 and a displacement of the shoreline of around 1 000 m towards the west (Figure 1B). Parts of the tailings deposited in the bay formed a submarine tailings deposit. Prior to this, the bay of Chañaral had a beach, limited to the north by beach rocks and eastwards by coarse beach sands with seashells, alluvial, and some fluvial sequences. First peaks of the Coastal Cordillera reaching 600 m amsl (above mean sea level) are located 3.5 km to the east of the tailings beach.

The biological impact of the tailings deposit has been well studied from 1978 to the present (Castilla, 1983; Ramirez *et al.* 2005). In 1983 it was stated by the United Nations Environmental Program (UNEP), that the area around Chañaral is one of the most contaminated in the Pacific Ocean. During the deposition of tailings into the marine environment, the area was found to be completely sterile regarding sandy beach macro fauna because of the high sedimentation rate (e.g. Castilla and Nealler 1978). After deposition of tailings ceased in the bay of Chañaral in 1975, and at the Caleta Palito 8 km north of Chañaral in 1989, the long term effect of the release of critical elements to the environment has remained. The food chain has not recovered so far. The algal community is dominated by few species. Dissolved copper concentrations exceed seawater complexing capacities; therefore, the copper is bio-available (Stauber *et al.* 2005). The diversity of meiofauna and of benthic organisms correlates negatively with Cu concentrations in pore water of beach sediments or seawater (Lee and Correa 2005; Medina *et al.* 2005). In addition, the finer grain size of tailings compared to the former substrate has inhibited the resettlement with formerly present organisms (Lee and Correa 2004).

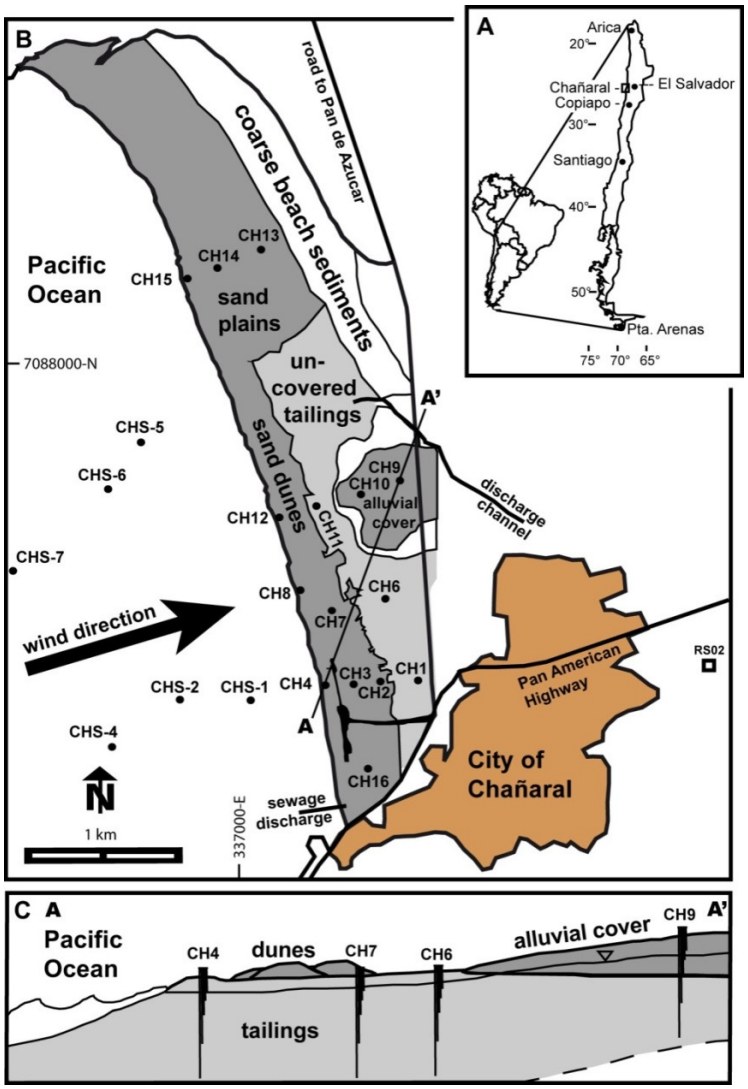

Figure 1: A. Location map of the porphyry copper deposit Bay of Chañaral. **B.** Map of the shore tailings deposit with the surface sediment facies and sampling points. **C.** Vertical sketch of the tailings deposit along A-A'.

Methods

Sampling and field methods

Tailings sediments and pore waters of the unsaturated and the saturated zone were sampled at 15 locations within the tailings deposit (Fig 1B). The oxidation zone above the groundwater level was studied and sampled in detail by excavation of pits. The deeper part of the tailings sediments was sampled by percussion drilling using a 2" tube. Sediments were characterized by means of colour, grain-size, mineralogy, moisture, and paste-pH. Water samples of the unsaturated zone were sampled by squeezing pore water from 3" Aluminium tubes by replacement with soybean oil (Patterson *et al.* 1978). Drive point piezometer nests were installed to sample pore water at depths of 3, 4, 5, 7, and 9 m. Temperature, pH, Eh, alkalinity, and electrical conductivity (EC) were measured during sampling. Samples were filtered through 0.2 µm filters and samples for cations were acidified with HNO_3 suprapure. All water samples were frozen immediately in the field.

Analytical methods

All analyses were performed in the laboratories of the Faculty of Earth Sciences, University of Lausanne. For the stable hydrogen and oxygen isotope analyses of water samples and of precipitated sulphate samples, waters were distilled in a closed system at 110°C before analyses. The stable hydrogen isotope analyses were performed using a Thermo Fisher H-Device connected to a Delta Plus V isotope ratio mass spectrometer (IRMS). For this method, the H_2 gas was produced by reduction of a volume of 1.2 µL water over hot (840°C) chromium within a reactor connected to the dual inlet system of the IRMS. Oxygen isotope analyses were made through equilibration of 0.5% CO_2 in He with 1.2 mL of water for 24 hrs at room temperature followed by extraction in a continuous He flow using a Thermo Fisher Gas Bench II connected to a Delta Plus XL IRMS. The stable hydrogen and oxygen isotope ratios are reported in the delta (δ) notation as the per mile (‰) deviation relative to the Vienna Standard Mean Ocean Water (VSMOW). Distilled lab standards were analytically identical with non-distilled standards. The reproducibility, assessed in terms of the within-run replicate analyses of laboratory standards, was better than 0.3‰ and 0.1‰ (1σ) for δ^2H and $\delta^{18}O$ values, respectively.

Water samples were analyzed for its major elements with Ion Chromatography (IC; Dionex® DX120) and for trace element analysis Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Perkin Elmer ELAN® 6100 DRC) was used. For calibration, two dilutions were prepared of the multi-element standard Merck M6 to meet the concentration range of the samples to be measured and calibration repeated after every two samples. Accuracy and reproducibility (as mean standard deviation) of both methods were better than 3% and 5%, respectively.

Major and trace element determinations of bulk samples of beach tailings, submarine tailings of the bay, and of picked secondary minerals were performed at the Institute of Mineralogy and Geochemistry of Lausanne. Samples were milled and prepared for measurement with a wavelength dispersive X-ray spectrometer (Philips® PW2400). Reproducibility and accuracy were better than ±3% and ±5%, respectively. Total Carbon (TC) was determined by coulometric titration with a Ströhlein Coulomat 702 after combustion with O_2. Reproducibility and accuracy was found to be better than ±3%.

Selected samples were submitted to SGS Service Laboratory Toronto (Canada) to be analyzed following a sequential extraction procedure in 7 steps described in (Dold, 2003) (Table 1). Leachates were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

Table 1: Description of the protocol and preferentially dissolved minerals for the applied 7 steps sequential extraction.

Step	Leach (Attack)	Preferentially dissolved minerals
1	Water-soluble fraction (Millipure water shake for 1 h at RT)	Water soluble sulphates and chlorites, e.g. gypsum, chalcanthite, copiapite, halite, eriochalcite
2	Exchangable and carbonate fraction (1 M NH4-acetate (pH 4.5) shake for 2 h at RT)	Calcite, malachite, azurite, vermiculite type mixed layer, exchangeable ions
3	Fe(III)-oxyhydroxides (0.2 M NH_4-oxalate (pH 3) for 1h in the dark at RT)	Schwertmannite, 2-line ferryhydrite, secondary jarosite
4	Fe(III)-oxides (0.2 M NH_4-oxalate (pH 3) for 2 h in a water bath at 80°C)	Goethite, jarosite, hematite, 6-line ferryhidrite
5	Secondary Cu-sulphides and organics (35% H_2O_2 for 1 h in heated water bath)	Covellite, chalcocite, digenite, organics
6	Primary sulphides ($KClO_3$ and HCl attack followed by 4 M HNO_3 boiling)	Pyrite, chalcopyrite, bornite, sphalerite, galenite
7	Residual (HNO_3, HF, $HClO_4$ and HCl digestion)	Silicates

Bulk sediments and samples of secondary minerals were analyzed by X-ray diffraction (XRD) using a Philips® 3020 diffractometer with CuKα and monochromator. Diffractometer settings were 40 kV, 30 mA, 3-80° 2θ, and 0.02° 2θ step size with 2 sec counting time. For selected samples various XRD scans were taken before and after the steps 1 to 4 of the sequential extraction procedure for differential XRD. From selected samples thin sections were prepared using epoxy resin. From samples of a hard pan, sections were prepared with epoxy resin and polished with petroleum, to avoid the dissolution of water soluble minerals. Sections were studied by optical microscopy (transmitted and reflected light) and by Scanning electron microscopy (SEM, Camscan Serie 4) combined with an energy dispersive spectrometer (EDS).

Results and Discussion

Mineralogical and geochemical characterization of primary tailings

The mineralogy of the primary zone of the tailings profile (tailings with no significant influence of weathering) was dominated by quartz, feldspar (albite-anorthite), muscovite, biotite, kaolinite, magnetite, and rutile. Sulphide minerals were pyrite >> chalcopyrite > chalcocite-digenite, sphalerite, and galena ≥ covellite > bornite. By SEM-EDS molybdenite and enargite/luzonite were detected. Total sulphide concentrations were calculated as $S_{sulphide}$ from sequential extraction data of 53 samples (secondary Cu-sulphides leach + primary sulphides leach) and, because of the heterogeneity, corrected for relative length of sample intervals. The tailings contained an average of 0.69 ±1.26 wt% $S_{sulphide}$, or 1.29 ±2.35 wt% pyrite equivalents, respectively. The high variability resulted mainly from the presence of the placer like blankets with 12 wt% pyrite equivalents. The average sulphate concentration (calculated as $S_{sulphate}$ from leaches 1 to 4) was 1.63 wt% $CaSO_4$ equivalents. The TC content in the tailings was below the detection limit (<0.1 wt% TC). Therefore, the tailings at Chañaral are potentially acid producing.

Median grain size of shore tailings was 341 µm and decreased for that of submarine tailings from 160 µm at 0.5 km distance from the shore to 78 µm at 1.6 km from the shore. From sequential extraction data, mean Cu content of the shore tailings was 2834 mg/kg (n=54). Primary tailings of the deeper parts of shore tailings profiles had mean 2 961 mg/kg Cu, compared to 719 mg/kg Cu in a sample of submarine tailings. The deposition in an open bay caused gravity enrichment of coarse grains and heavy minerals (e.g. sulphides) at the beach and successive enrichment in Cu.

Hydrogeology

Stable isotope results were used to identify the origin of pore water present in the marine shore tailings deposit. Most water samples from the saturated zone ranged from −5.1 to −3.8‰ $\delta^{18}O$ and from −51 to −42‰ $\delta^{2}H$ (Figure 2). These water samples plot close to values of −4.3‰ $\delta^{18}O$ and −48.5‰ $\delta^{2}H$ measured for waters of a brine water spring found 40 km east of the shore. The brine water spring had mean concentrations of 21.5 g/L Na, 0.78 g/L Ca, 0.62 g/L Mg, 36.2 g/L Cl, and 2.11 g/L SO_4. Tailings pore waters in the southern transect, e.g. at CH2 at 7m depth, had 28.3 g/L Na, 0.92 g/L Ca, 0.67 mg/L Mg, 42.5 g/L Cl, and 1.81 g/L SO_4, concentrations similar to that of the spring. These results confirm an earlier interpretation that the El Salado brine aquifer flows through the shore tailings deposit into the Pacific Ocean as submarine groundwater discharge (SGD) (Wisskirchen *et al.* 2006). In the northern part of the tailings deposit, mixing of the brine was observed. Water from a well located 2.5 km east of the coast had an isotope composition of −2.2‰ $\delta^{18}O$ and −27.3‰ $\delta^{2}H$, close to the upper limit of mixing. The well water was a mixture of the brine aquifer and a second source of water of heavy isotope composition and lower mineralization, possibly located in the Coastal Cordillera. This unidentified water influenced the northern part of the tailings deposit. At CH14 at 7m depth, pore water had 13.4 g/L Na, 1.0 g/L Ca, 0.60 mg/L Mg, 16.2 g/L Cl, and 2.1 g/L SO_4, concentrations lower than that of the brine. In the south the $Cl:SO_4$ ratio (in equivalents) was 63.6, compared to 20.9 in the north.

In the southern part of the tailings deposit, isotopically lighter water infiltrated the tailings, plotting on a mixing line between portable water of the municipality of Chañaral (−10.9‰ $\delta^{18}O$ and −80.0‰ $\delta^{2}H$) and

the brine water. At CH1 at 1.3 m depth, pore water had 2.1 g/L Na, 0.12 g/L Ca, 0.08 mg/L Mg, 1.4 g/L Cl, and 0.64 g/L SO_4. Because of its lower density, the sewage formed a plume on top of the brine water. Only at the coastline did pore water consist of seawater in the profiles CH8 and CH12 (upper 3 m; Figure 2) and CH15 (upper 1.6 m). In the south at CH4, seawater infiltration was restricted by the higher hydraulic head of the brine aquifer and the sewage water.

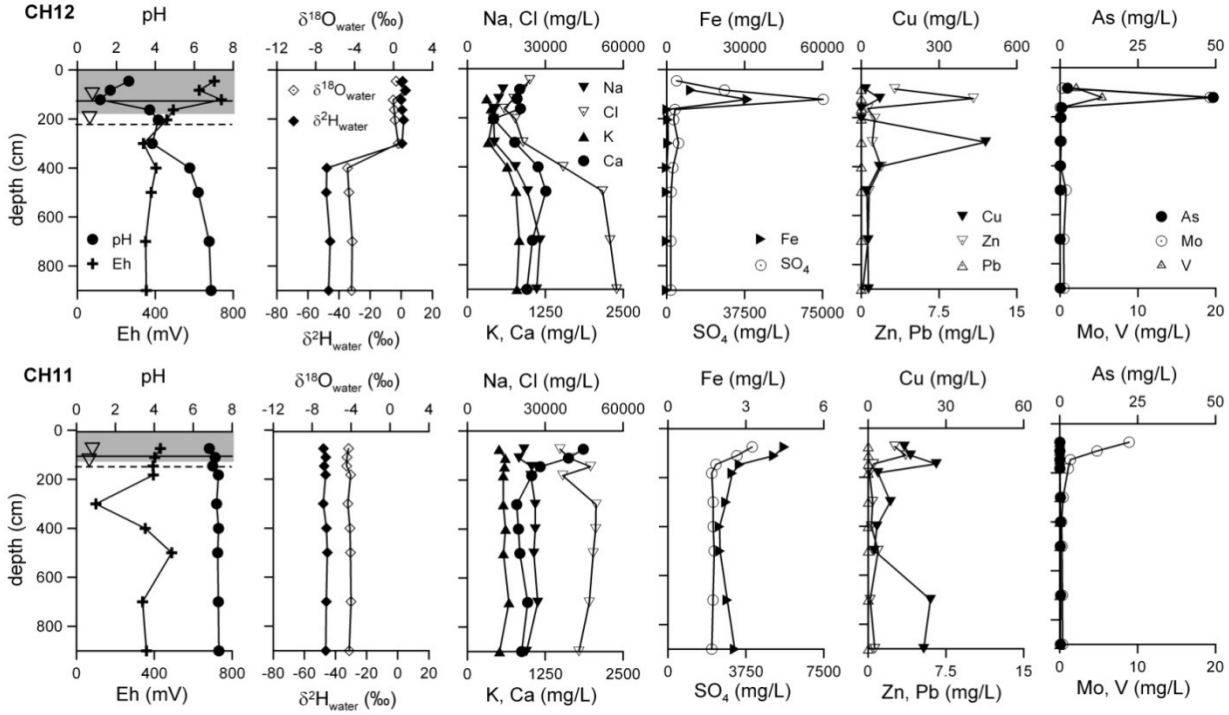

Figure 2: Vertical profiles of the pore water hydrogeochemistry and stable isotope geochemistry of CH12 and CH11 (central transect). Grey zone represents oxidation zone, dotted line represents the water table.

Enrichment processes and secondary mineralogy

Placer-like enrichment blankets

In the northern part of the tailings deposit, where wave action is stronger than in the southern part, an enrichment blanket formed during deposition due to the reworking of the tailings sands by tidal changes (e.g., CH11 at 2 m depth, Figure 4B). The enrichment blanket could be found only at sea level and slightly above, corresponding to the altitude of the beach zone. The high contents of up to 17 wt% Fe and 2 wt% Ti (compared to 1.3 wt% Fe and 0.4 wt% Ti in non-enriched tailings) correlated to XRD findings of heavy minerals (e.g., hematite, pyrite, and rutile). Cu was enriched up to 0.8 wt%. When above the water table, the pyrite enrichment caused the preferred development of oxidation zones (with resultant pH values down to 1.7). These layers of the profiles and in the enrichment blankets were consolidated by the formation of jarosite and gypsum, forming a hard pan (Figure 3). Around pyrite grains, gypsum and jarosite formed distinctive rims (Figure 5A). Water movement was upwards due to capillary rise. Dissolved K was consumed in the lower part of the hardpan and in the upper part of the hardpan only sodium-jarosite formed (detail in Figure 3).

Unsaturated tailings profile

The oxidation zone, which developed pH values between 1.2 and 4, had not reached the water table in most of the profiles and depended strongly on shoreline distance and topographic altitude of the terrain. Near the shore line (e.g., CH12) marine water infiltrated and water level was controlled by cyclic changes. This resulted in cyclic renewal of pore water and pore gas causing high oxidation rates, resulting in low pH values of 1.2 and high dissolved concentrations , such as 31 g/L Fe, 49 mg/L As, 19 mg/L Mo, and 75

g/L SO_4 in the pore water (Figure 2). Secondary minerals in this profile were K- and Na-jarosite ($Na^{+}Fe^{3+}{}_3((OH)_3/SO_4)_2$) showing the same spatial relation as observed within the hardpan. Above the oxidation front copiapite ($Fe^{2+}Fe3^{+}{}_4(SO_4)_6(OH)_2$•20 H_2O) was detected by XRD in rosette-like mineral agglomerates. At the water table (1.8 m depth) and below, pH values were 4 down to 3 m of depth. The oscillation of the water level facilitated the transport of heavy metals and arsenic to the marine environment.

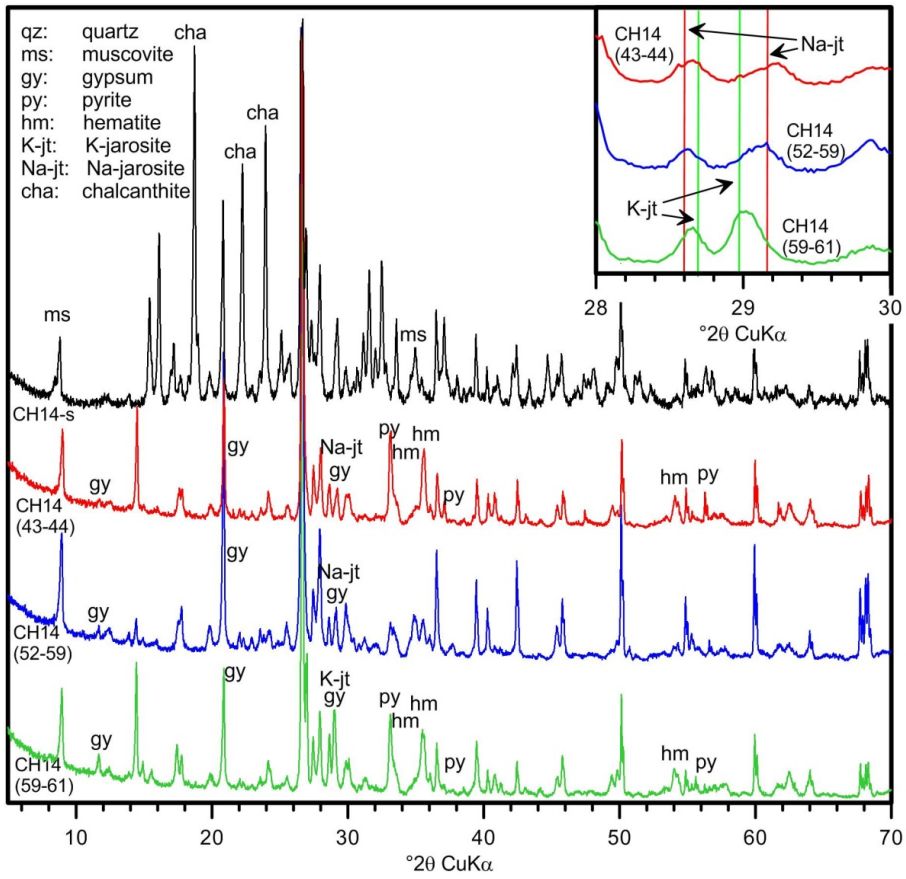

Figure 3: Results of XRD from a handpicked efflorescence salt sample (CH14-s), and sediment samples from the oxidation zone at 43-44 cm, 52-59 cm, and 59-62 cm depth. The detail shows the peak positions for potassium- and sodium-jarosite.

In other profiles, which were less influenced by seawater level changes, the oxidation zone had pH values between 2.4 and 4.3 and was of yellowish- ochre brown color, dominated by jarosite. Paratacamite ($Cu_2(OH)_3Cl$) formed as a green film on the surface of horizons of alluvial material (silt-clay horizons with some carbonate NP) above the oxidation front. Grain size boundaries in the tailings served as capillary barriers within the profile, resulting in the precipitation of efflorescent salts (gypsum, halite).

On top of the tailings deposit, efflorescent salts formed due to capillary transport and evaporation. The mineral association was dominated by eriochalcite ($CuCl_2$·$2H_2O$), halite (NaCl), chalcanthite ($CuSO_4$•$5H_2O$; Figure 3 CH14-s), blödite ($Na_2Mg(SO_4)$•$4H_2O$), tamarugite ($NaAl(SO_4)$•$6H_2O$), gypsum ($CaSO_4$•$2H_2O$), and brushite ($CaHPO_4$•$2H_2O$). Also within the tailings profile oversaturation was reached, and resulted in an upwards sequence of gypsum, halite and eriochalcite, such as at CH6. In the southern part of the tailings impoundment, where Cl:SO_4 ratios (equivalents) were 63.6, eriochalcite formation was favoured, whereas in the northern part, where Cl:SO_4 ratios (equivalents) were 20.9, chalcanthite

formation took place. No direct association between the two Cu efflorescent salts was observed. The presence of phosphates is explained by the presence of bone material and bird excrements at the deposits surface. Where dunes migrated, a crust of up to 10 cm of efflorescent salts (mainly halite and gypsum) was found. The granulometric difference from the tailings to the well sorted dune sands functioned as a migration border, due to the faster evaporation of pore fluids in the fine sands. Wind driven sand led to the abrasion of the efflorescent salts and its transport out of the direct tailings environment.

Due to the mobilization of Cu in the oxidation zone, Cu was depleted and concentrations of as low as 415 mg/kg Cu in CH11 and 337 mg/kg in CH12 were measured for oxidized unsaturated tailings, compared to the average Cu of 2 834 mg/kg (Figure 4).

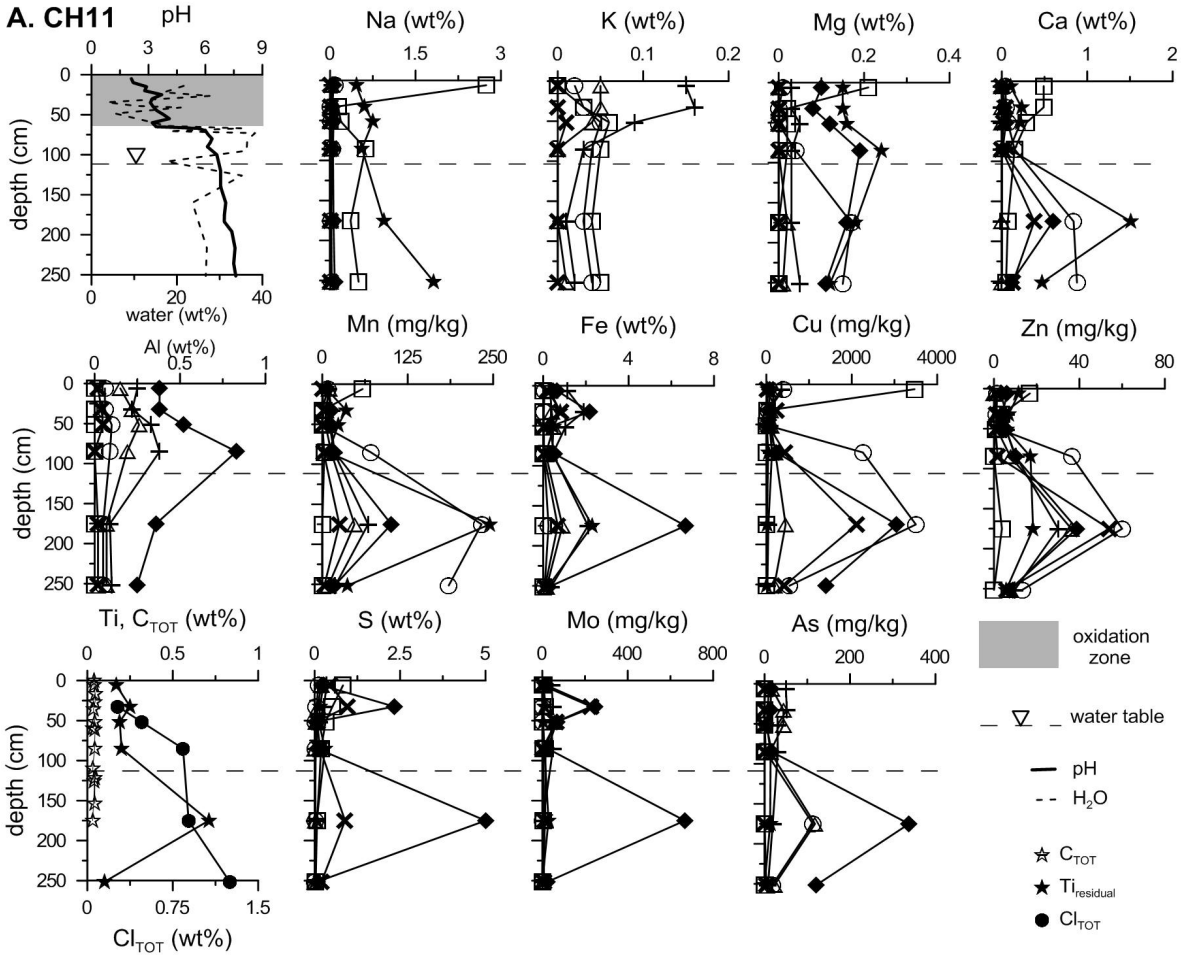

Figure 4: Vertical profiles of tailings paste-pH, water content (wt%), and geochemistry (solids) of locations **A:** CH11 and **B:** CH12 (see Figure 1B) analyzed by a 7 step sequential extraction procedure. Residual fractions of Na, K, and Al are not shown for better visibility.

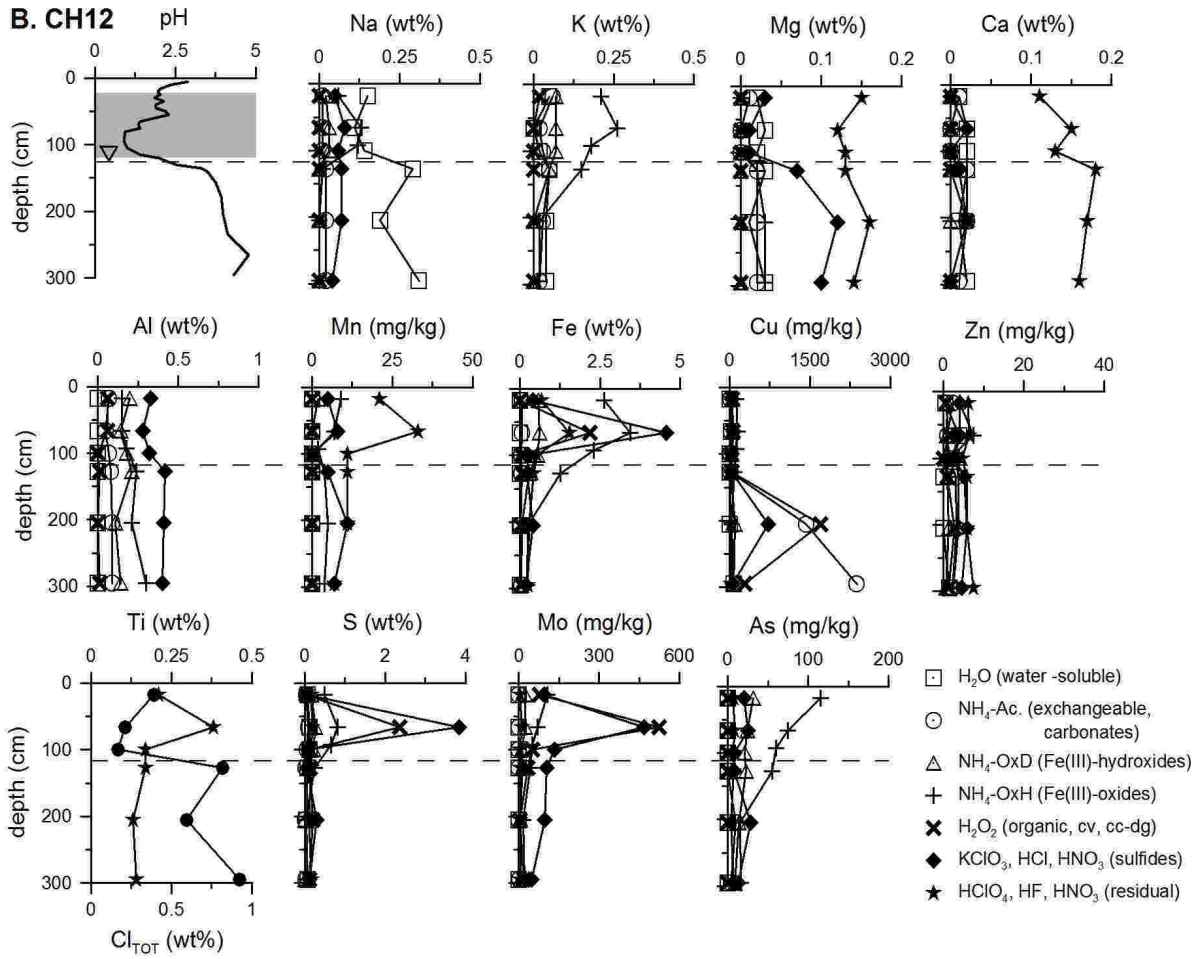

Figure 4 continued

Saturated tailings profile

In general, the aqueous concentration of Cu in natural systems at pH 8 is limited by adsorption. Within the saturated zone of the Chañaral tailings impoundment up to 35 mg/L of Cu were detected in the presence of 56 g/L Cl (see, e.g. CH11 at 7 and 9 m, Figure 2). Most likely, aqueous complexes of Cu with Cl increased the solubility of Cu beyond what is observed in other natural systems without high Cl concentrations (Dold 2006).

In the saturated zone, three different forms of secondary mineral formation were encountered:

- Paratacamite overgrow of chalcopyrite grains that was complete in some cases and also formed in contact with clays, additionally proving its secondary origin (Figures 5B and 5C).
- Below the water table, supergene enrichment formed covellite-digenite and chalcocite rims on chalcopyrite and pyrite (Figure 5D). This enrichment is proved to be secondary by the completeness of the replacement rims, compared to primary rims that were partly broken by milling of the ore. Sedimentary enrichment can be excluded due to the absence of enrichment in Fe and Ti, as found in the placer layers (Figure 4B).
- Malachite and azurite could be detected by optical microscopy. Its presence was restricted to sampling sites along the shoreline (CH4, CH8, CH12, and CH15) and to the profile CH6, where alluvial material containing carbonates were found closely below the water table.

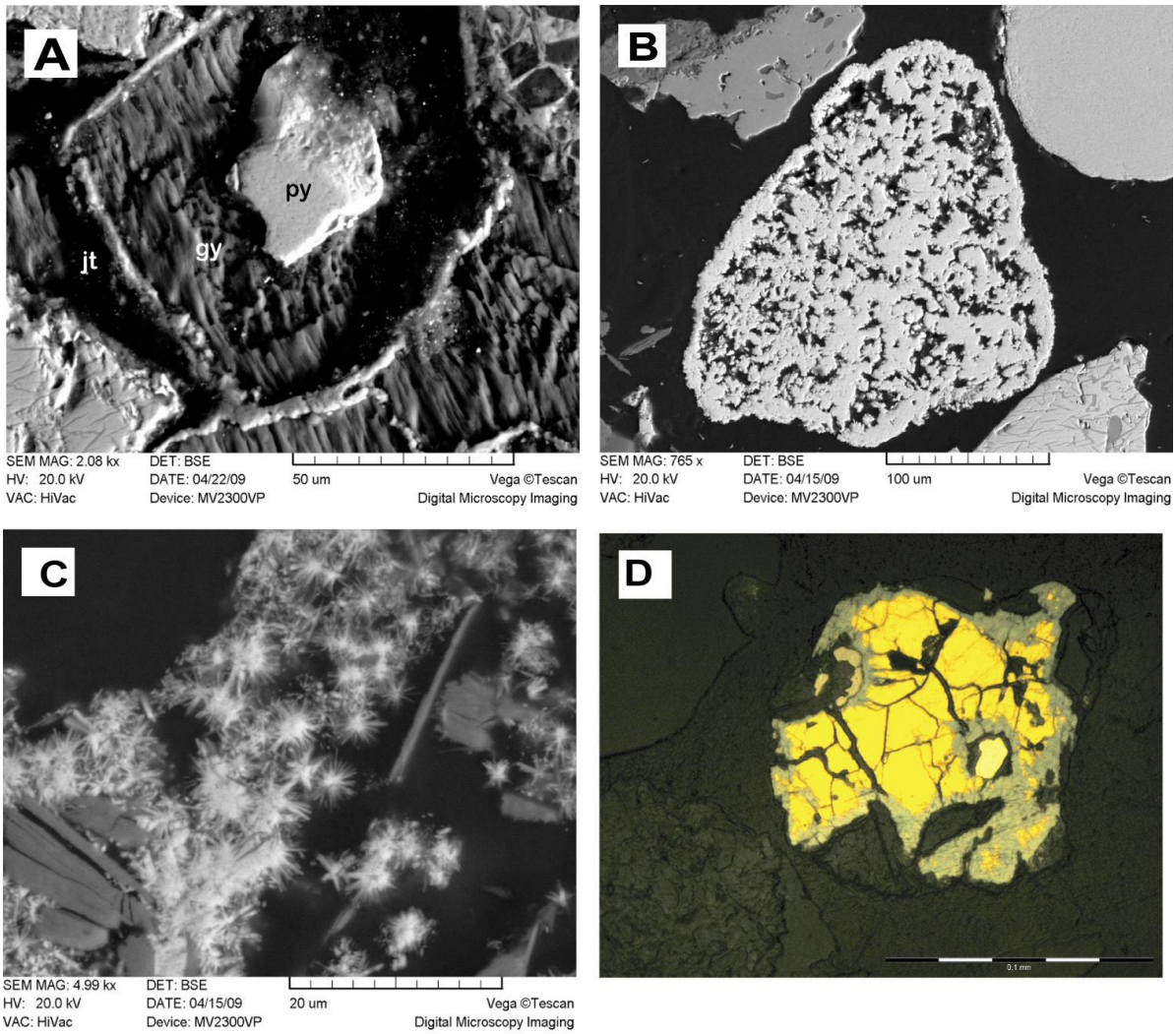

Figure 5: A: Pyrite surrounded by gypsum (gy) and a rim of jarosite (jt) from the oxidation zone of CH14. **B:** Paratacamite replaced and surrounded chalcopyrite widely in the water saturated zone. **C:** Paratacamite intergrowth with clay. **D:** Chalcopyrite with secondary covellite-digenite from CH12 (280-320cm).

Paratacamite and secondary Cu-sulphides were encountered in close relationship, also confirmed by Sequential extraction data. In CH12 at 200 cm depth Cu was found in secondary Cu-sulphides and in the exchangeable fraction. Differential XRD for the water soluble mineral fraction (water leach) and the exchangeable and carbonate fraction (acetate leach) showed the disappearance of paratacamite peaks after the acetate leach, proving that paratacamite dissolves in the acetate leach explaining the high Cu concentrations in this fraction.

Conclusions

At the marine shore tailings deposit of Chañaral, the interaction between sea water and a highly saline brine with tailings can be well studied. The contact to the open sea introduces dynamical changes into the system, which are not observed in other tailings systems. The water level changes favour the oxidation kinetics near the shoreline.

The data shows that in a high chlorine system, the mobility of bivalent cations is increased at higher pH conditions. This has to be accounted for in the evaluation of AMD formation in tailings resulting from

seawater flotation systems. Movement of Cu was upwards due to evaporation-driven capillary transport in the upper part of the tailings profile and downwards to the saturated zone in the lower part of the tailings profiles. The presence of high chloride concentrations resulted in the presence of characteristic secondary minerals not commonly observed in other tailings impoundments, such as halite, eriochalcite, and paratacamite present in the non-saturated zone and the evaporative surface crust. Nevertheless, where $Cl:SO_4$ ratios were lower, chalcanthite was the forming efflorescent copper salt. On grain size boundaries efflorescent salt also precipitated within the unsaturated zone above the oxidation zone. Below the water table Cu re-precipitated under formation of rims of calcocite-digenite on sulfide minerals, but also formed paratacamite and copper carbonate (azurite and malachite) where alkalinity was available.

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References

Camus, F. (2003) Geología de los sistemas porfíricos en los Andes de Chile. Servicio Nacional de Geología y Minería, Santiago de Chile.

Castilla, J.C. (1983) Environmental impact in sandy beaches of copper mine tailings at Chanaral, Chile. Marine Pollution Bulletin 14, 459-464.

Castilla, J.C., and Nealler, E. (1978) Marine environmental impact due to mining activities of El Salvador copper mine, Chile. Marine Pollution Bulletin 9, 67-70.

Dold, B. (2003) Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. Journal of Geochemical Exploration 80, 55-68.

Dold, B. (2006) Element flows associated with marine shore mine tailings deposits. Environmental Science and Technology 40, 752-758.

Dold, B., Diaby, N., and Spangenberg, J.E. (2011) Remediation of a marine shore tailings deposit and the importance of water-rock interaction on element cycling in the coastal aquifer. Environmental Science and Technology 45, 4876-4883.

Dold, B., and Fontbote, L. (2001) Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. Journal of Geochemical Exploration 74, 3-55.

Gustafson, L.B., and Hunt, J.P. (1975) The porphyry copper deposit at El Salvador, Chile. Economic Geology 70, 857-912.

Gustafson, L.B., and Quiroga, J. (1995) Patterns of mineralization and alteration below the porphyry copper orebody at El Salvador, Chile. Economic Geology 90, 2-16.

Lee, M.R., and Correa, J.A. (2004) Copper mine tailings disposal: consequences for the interstidal polychaete Saccocirrus sonomacus (Canalipalpata: Protodrilida). Journal of The Marine Biology Association U.K. 84, 603-606.

Lee, M.R., and Correa, J.A. (2005) Effects of copper mine tailings disposal on littoral meiofaunal assemblages in the Atacama region of northern Chile. Marine Environmental Research 59, 1-18.

Medina, M., Andrade, S., Faugeron, S., Lagos, N., Mella, D., and Correa, J.A. (2005) Biodiversity of rocky intertidal benthic communities associated with copper mine tailing discharges in northern Chile. Marine Pollution Bulletin 50, 396-409.

Moreno, P.A., Aral, H., Cuevas, J., Monardes, A., Adaro, M., Norgate, T., and Bruckard, W. (2011) The use of seawater as process water at Las Luces copper-molybdenum beneficiation plant in Taltal (Chile). Minerals Engineering 24, 852-858.

Patterson, R.J., Frape, S.K., Dykes, L.S., and McLeod, R.A. (1978) A coring and sqeezing technique for detailed study of subsurface water chemistry. Canadian Journal of Earth Sciences 15, 162-169.
Ramirez, M., Massolo, S., Frache, R., and Correa, J.A. (2005) Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile. Marine Pollution Bulletin 50, 62-72.
Smuda, J., Dold, B., Spangenberg, J.E., and Pfeifer, H.R. (2008) Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: Implications on sources and mobility of elements during transport and early stages of deposition. Chemical Geology 256, 62-76.
Stauber, J.L., Andrade, S., Ramirez, M., Adams, M., and Correa, J.A. (2005) Copper bioavailability in a coastal environment of Northern Chile: Comparison of bioassay and analytical speciation approaches. Marine Pollution Bulletin 50, 1363-1372.
Waples, J., Wisskirchen, C., and Vasquez, F. (2012) Geochemical Characterization with High Ionic Strength Methods for Arid-Climate Mines Utilizing Seawater. 9th International Conference of Acid Rock Drainage. Ottawa, Ontario, Canada.
Wisskirchen, C., Dold, B., and Spangenberg, J. (2006) Hydrogeochemical and stable isotope study of the watershed "El Salado" valley and its waters infiltrating into the marine shore tailings deposit at Chanaral (Northern Chile). XI Congreso Geologico Chileno, Antofagasta, pp. 671-674.
Wisskirchen, C., Waples, J., Vásquez, F. (2012) Considerations for seawater in mining: approaches to evaluate ARD and metal leaching potential. Water in Mining 2012. 3rd International Congress on Water Management in the Mining Industry. 6th to 8th June 2012, Santiago, Chile.

Acronyms

Ac.	Acetate
AMD	Acid mine drainage
cv	covellite
cc	calcocite
dg	digenite
EC	Electrical conductivity
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IRMS	Isotope ratio mass spectrometer
EDS	energy dispersive spectrometer
h	hour
M	mol
n	number (of samples)
ML	Metal leaching
Mt	Million tons
NP	Neutralization Potential
RT	room temperature
SEM	Scanning electron microscopy
TC/EA	temperature conversion elemental analyzer
TC	Total Carbon
SGD	Submarine groundwater discharge
UNEP	United Nations Environmental Program
VCDT	Vienna Canyon Diablo Troilite
VSMOW	Vienna Standard Mean Ocean Water
XRD	X-ray diffraction
wt	weight