

Hydrogeochemistry and sediment mineralogy of Lake Yanamate – an extremely acidic lake caused by discharge of acid mine drainage from the Pb-Zn-(Cu) deposit, Cerro de Pasco (Peru).

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Abstract: *A hydrogeochemical, geochemical and mineralogical study of an extremely acidic lake (pH 1.0) formed by the deposition of spoil waters of a copper leaching plant and acid mine drainage (AMD) of the Pb-Zn-(Cu) deposit Cerro de Pasco is presented. The data shows for the lake water concentration ranges and mean values of 1440-7180 (4330) mg/L Fe, 33.5-105 (88) mg/L Cu, 180-746 (500) mg/L Zn, 13-63 (49) mg/L As, 2.2-5.3 (2.9) mg/L Pb, 3735-14100 (9891) mg/L S and an acidity of 14480-21440 (16775) mg/L as CaCO₃. The mean values of concentrations in lake water do not differ significantly from the values measured for the discharge water. Within the lake water body most element concentrations increase with depths. Infiltrating acidic waters dissolve the limestone bedrock and form a layer of gypsum in the form of argillaceous and gel-like matter, overlying a layer of dissolving calcite. The thickness of the gel-like layer varies between 4 and more than 40 cm, probably given by the highly variable lake bottom surface. In the gel-like newly precipitated matter and upper parts of dissolved bedrock, heavy metals concentrate in composition to the water body. X-ray fluorescence data show for this kind of sediment concentration ranges and mean values of 0.76-12.38 (5.98) wt% Fe₂O₃, 51-3980 (1301) mg/kg Cu, 275-8034 (3822) mg/kg Zn, 43-5781 (898) mg/kg As, 21-1310 (261) mg/kg Pb, 0.7-11 (6.2) wt% S. Due to the low mineralization of this gel-like matter it is not clear if heavy metals are well fixed and so may easily remobilize by a drop of the lake water level or a change of geochemical conditions. The lake water level did not drop as expected from a water balance modeling. This can be explained by the precipitation of gypsum within the limestone bedrock and clogging of fractures with a resulting decrease of the infiltration rate.*

1 Introduction

A case study of the discharge of AMD into a natural lake is presented. To our knowledge, this is the only studied case, where the bedrock of the discharge pond consists of limestone, an highly reactive rock for the neutralization of AMD.

Geography and Geology. The Lake Yanamate is located in the Central Andes of Peru within the ecological region Puna at 4360 m above sea level. Annual mean temperature is 4.2 °C. The mean annual evaporation of 883 mm/a (Upamayo station, 1981-1999)

exceeds slightly the mean annual precipitation of 848 mm/a (Paragsha station, 1976-1999). The main wind direction is NE-SW with mean wind speed of 1.5 m/sec (Cerro de Pasco station, 2002-2003). The lake basin comprises 10 km² of karst topography, formed by the limestone formations Chambará (Pucará group) and Casapalca (Jenks, 1951) mainly consisting of calcite and in parts dolomite with some shale interbeds (Figure 1). Before the lake was used as a holding pond, a former grassland divided the Lake Yanamate from the Lake Huaygacocha located to the SW. Below the grassland, the Cerro de Pasco fault passes with a NW-SE trend, dipping 65°-90° to the east, dividing the two limestone formations. The lake basin was formed by glacial erosion, causing the direct contact of the water body with the underlying limestone bedrock. The bedrock topography is highly variable. An end moraine forms a natural dike on the west side of the lake, now elevated by an artificial dam in respect to the increased lake water level. All surface outflows of the lake are blocked by small artificial dams.

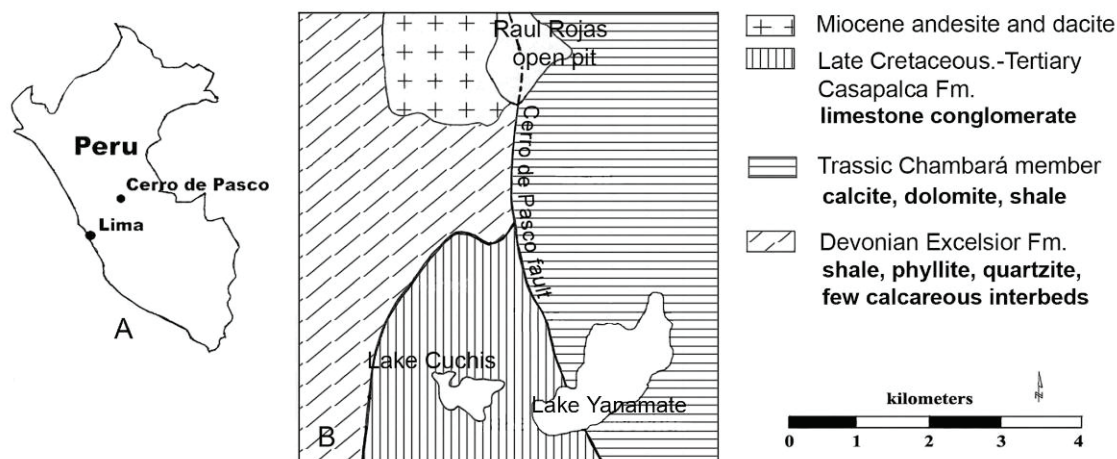


Figure 1: A) Locations map of the study site in Peru. B) Sketch of the local geology around the Lakes Yanamate and Huaygacocha. Note that the sketch shows the former shorelines before discharge started.

Cerro de Pasco mine. The AMD originates from the carbonate-hosted pyrite-rich Zn-Pb-(Cu) ore deposit of Cerro de Pasco, exploited by open pit and underground mining. The deposit has its origin in a 14.5 million years old volcanic vent. In a primary step limestone of the Pucará group was replaced by a quartz-pyrite body measuring 1.8 km N-S and up to 300 m E-W, representing 90 % of the entire ore body (Einaudi, 1977). In some parts the pyrite contains greater amounts of As (≤ 10 wt%), Bi (≤ 1 wt%) and Sb (≤ 1 wt%) (Petersen, 1965). The most important ore minerals are sphalerite, galena and tennantite-tetrahedrite in the primary zone and covellite and chalcocite in the supergene enriched zone. The locally important Cerro de Pasco fault infiltrates water in the underground mine and Raul Rojas open pit. Additionally great amounts of rain water infiltrate in the underground mine, because the underground mine is located directly below the open pit. Since some years the pit water is partly pumped out before it reaches the underground mine and neutral mine waters are separated from the acidic water to be used in the flotation process. During the sampling period the lake received 9.5 m³/min of AMD with pH 1.1, containing 4440 mg/L Fe, 125 mg/L Cu, 784 mg/L Zn, 48 mg/L As, 4 mg/L Pb, 10625 mg/L SO₄ and 18720 mg/L acidity as CaCO₃.

History of Lake Yanamate. The lake is used since 1981 as a holding pond for AMD and between 1981 and 2001 for spoil water of a copper extraction plant, which processed *in situ* leachate waters. The lake volume increased from 3 km³ in 1981 to 25 km³ in 2003,

resulting in a 6 times larger lake surface of 3 km² in 2003 and an increase of the water level of 14 m. The deepest point found during sampling was 41 m. Since 2001 the discharge was decreased in expectation of a water level decrease as a first step of a remediation plan. Contrary to that, the lake level remained high. The discharge pipeline ends 200 m away from the shoreline of the lake. The discharge water eroded a 4 m deep flow channel in the limestone and enters the lake through a cavity. In accordance with the dominating wind direction the discharge plume always moved to the west when observed.

The objective of this study is to investigate the hydro-geochemistry of the water body, the geochemistry and mineralogy of the newly precipitated sediments and the water-rock interactions within the underlying lake bedrocks to evaluate the geochemical processes within this system.

2 Methodology

2.1 Sampling and field methods

Sampling took place in the cold and dry period (July 2003). A total of 45 water-column samples were taken at 11 stations with depths of 0.5 m, 5 m and continued in 5 m steps until the lake bottom was reached (Figure 2). The samples were taken with a peristaltic pump and in-line filter (0.45 µm pore size). The physicochemical parameters (temperature, pH, Eh and electrical conductivity; equipment by WTW[®]) were measured in-line. Because of the low pH environment, a relatively high error in the measured pH values is expected, due to the calibration with pH 4 and 7 standard buffers. Two samples were taken in HDTP bottles and stored by 4°C immediately. A third sample was taken for the titration of acidity following the protocol of Ficklin and Mosier (1998) to a titration end point of pH 8.3 measured with a pH-probe. Before titration samples were boiled after addition of H₂O₂ to oxidize ions possibly existing in reduced state to include subsequent released hydrogen from e.g. iron-hydroxide formation. One sample was taken from the discharge water.

12 cores divided in 44 sub-samples of the lakes sediments and a set of 9 cores in 41 sub-samples of the soils of the inundation zone were sampled with a stainless steel sampler by gravity coring or hammering, depending on water depth. One sample was taken of a delta-like zone near the discharge point. The sedimentological characteristics, grain size, color and occurrence of organic material were described and pH measured, using a WTW[®] pH-meter with the pH-electrode Sentix SP. Sub-samples were taken directly in the field, dried in the laboratories of the mine (<30°C) and the water content was determined, by the difference in weight before and after drying.

Sediment samples were taken at the same sampling points as the water-column samples, determined by the points of greatest depth within the lake with help of the bathymetric map and own water level measurements. Two reference samples of soil and one water sample were taken at a smaller lake of similar bedrock formation.

2.2 Mineralogical methods

All sediment and soil samples were analyzed by X-ray powder diffraction (XRD), using a Seifert XRD 7 with CuKα X-radiation and secondary C-monochromator. The diffractograms were recorded from 2θ=5-100°, with 0.05° step size and 2 s count time

per step. From selected samples thin sections were prepared and analyzed by microscopy.

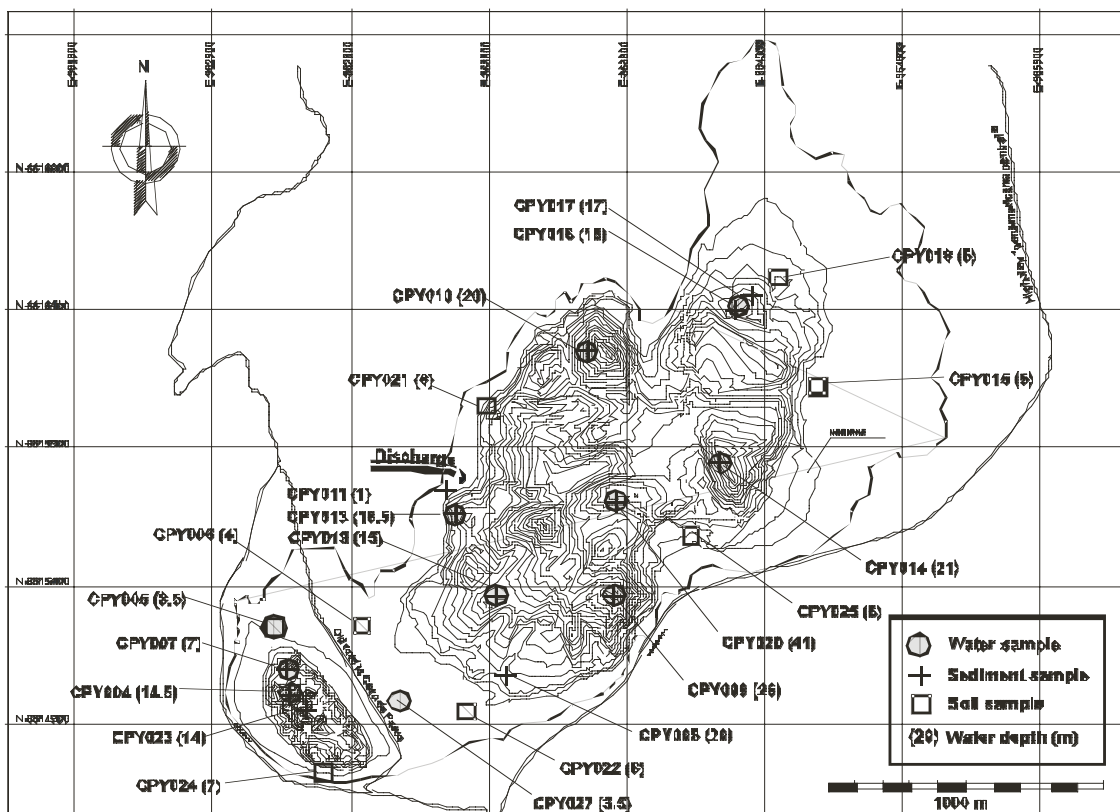


Figure 2: Sampling point positions and bathymetric map of Lake Yanamate (base map from GEMA, 1997).

2.3 Geochemical methods

Chemical composition of bulk samples of the solids was examined by X-ray fluorescence (XRF) with a Bruker axS4 Pioneer for major elements and a Spectro XLab 2000 for trace elements. Water samples were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin Elmer Optima 3000) for major elements and inductively coupled plasma-mass spectroscopy (ICP-MS; Agilent 7500 C) for trace elements and DIN EN 1189 for dissolved phosphorus. Selected samples were analyzed for dissolved organic carbon (DOC; Shimadzu TOC5050), or total organic carbon (TOC; Ultra Metalyt CS 1000s), respectively. Water analyses were used for geochemical modeling with the program PHREEQCI 2 (Parkhurst and Appelo, 1999). The complete set of mineralogical, geochemical and hydro-geochemical data can be found in Wisskirchen (2004).

3 Results and discussion

3.1 Water

The discharge water composition of the Cerro de Pasco mine and the mean lake water composition of Lake Yanamate show values in the order of magnitude typical for

massive pyrite deposits and belong to the highly mineralized AMD waters (Plumlee 1999). The mean lake water has a slightly lower electric conductivity (24.6 mS/cm) than the discharge water (27.4 mS/cm) (Table 1). However, when dilution by rainwater and surface runoff is taken into account (approximately $4.7 \cdot 10^6$ m³/a natural influx in comparison to $5 \cdot 10^6$ m³/a discharge water), a bisection of the element concentrations should occur. In fact, elements accumulate in the lake due to the absence of abundant mineral precipitation suppressed by the low pH ~ 1 . The acidity of the lake water is 16775 mg/L as CaCO₃ in comparison with 18720 mg/L as CaCO₃ in the discharge water. With 4330 mg/L Fe, 49 mg/L As, 18 mg/L Na, and 397 mg/L Ca as lake water mean concentrations, these elements show no significant difference in concentrations between lake water and discharge water (Table 2).

Table 1: Physico-chemical parameters of Cerro de Pasco AMD discharge and minimum, mean and maximum values of Lake Yanamate. DP = dissolved phosphorus.

	T (°C)	pH	Eh (mV)	EC (mS/cm)	Acidity (as CaCO ₃ in mg/L)	S (mg/L)	DP (mg/L)
<i>min</i>	6.0	-1.7	588	18.1	14480	3735	12.0
<i>mean</i>	10.7	1.0	653	24.1	16775	9750	35.0
<i>max</i>	14.3	1.6	674	31.3	21440	14100	44.0
<i>discharge</i>	21.3	1.1	609	27.4	18720	10625	0.06

Table 2: Element concentrations of Cerro de Pasco AMD discharge and minimum, mean, and maximum concentration of Lake Yanamate. All concentrations in mg/L.

	K	Na	Ca	Mg	Al	Fe	Cu	Zn	As	Pb
<i>min</i>	11.1	7.4	344	80.6	84.2	1440	33.5	180	12.7	2.2
<i>mean</i>	31.4	18.0	397	214	259	4330	86.8	493	49.0	2.9
<i>max</i>	36.4	40.9	466	243	384	7180	105	746	63.1	5.3
<i>discharge</i>	40.6	19.1	391	375	284	4440	125	748	47.8	4.2

Only dissolved P is significantly more concentrated in lake water (35 mg/L) than in discharge water (0.06 mg/L). The contents of other elements except Ca and As are lower in the lake than in the discharge water, down to a ratio of 0.5. The high phosphorus concentration in lake water originates most likely from llama dung (llamas are feeding around the lake), entering the lake with the surface runoff.

The lake showed no homogeneous temperature stratification during the sampling period (Figure 3). In contrast, a lateral variation of the temperature could be observed. In the western part of the lake, where the AMD waters are discharged, the water is warmer, particularly in the upper part of the water column. The exothermic reaction of sulfide oxidation is the reason for this higher temperature of the discharge water. Measured pH showed no depth trend, except slightly higher values at 0.5 m water depth. The Eh decreases with depth, probably influenced by lower concentrations of dissolved oxygen in the deeper water, as a result of the lower exchange of atmospheric oxygen with the deeper parts of the water body.

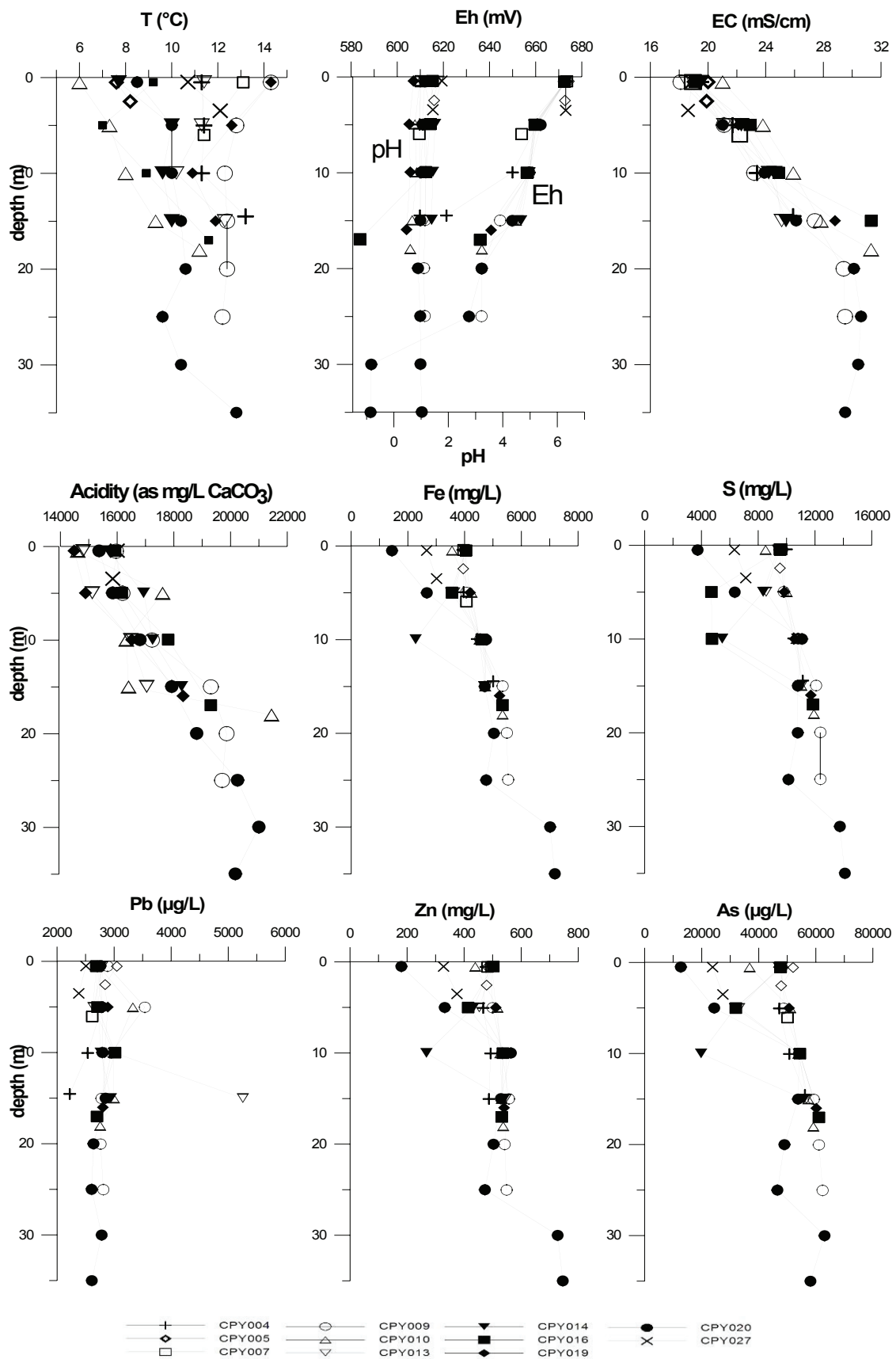


Figure 3: Depth profiles of T, Eh and electrical conductivity, acidity and element concentrations of Fe, S, Pb, Zn and As.

The water chemistry is dominated by the concentrations of Fe, SO₄ (measured and given as S) and acidity. The concentrations of these parameters increase with depth, as most of the elements analyzed. For 0.5 m water depth mean values of 3689 mg/L Fe and 8884.5 mg/L S and at 35 m water depth 7180 mg/L Fe and 14100 mg/L S were measured. However, a distinct density stratification with a mixolimnion and monimolimnion with an intermediate chemocline could not be found. Between 0 and 20 m water depth the electric conductivity, a parameter for the mineralization of the water, shows an approximately linear trend with depth. Water samples taken near the water-sediment interface show values higher than the overall trend. Below 20 m water depth, EC and the concentrations of Fe and SO₄ are not correlated anymore. This is likely caused by the intensified formation of complexes (e.g. FeHSO₄) and the absence of ferric iron, possibly stable in the upper parts of the water body according to modeling with PHREEQC 2.

Because of the constant wind direction a mixing of the lake water can be assumed. More distinct density stratification may occur in the rainy season with a layer of less mineralized water on top of the deeper and more mineralized water.

3.2 Sediments and Soils

Close to the discharge point (CPY011 and CPY013; see Figure 1) pyrite, sphalerite, anglesite, muscovite and quartz settled out in the form of detrital enriched sediment of the deposited mine water (Figure 4). At other locations melanterite or siderite could be detected. In soil cores of the western part of the lake (CPY005, CPY007, CPY024; former Lake Huaygacocha) jarosite was found in the upper 20 cm, but not in the sediment cores (CPY004 and CPY023) of greater water depth. The sediment cores show a sequence of gel-like material, followed by a layer of gypsum and a layer of dissolving calcite, each of argillaceous to silty grain size. Solid limestone bedrock was not reached within the 69 cm of cored sediments.

The gel-like layers had high water contents and for the most part pH 1 – 2. They can be visually distinguished in two types: 1) a fluid one (when occurring it is always found at the top of the core) and 2) a more gelatinous and rigid one. It is assumed, that gypsum and possibly also calcite detected by XRD in these samples formed during the sample preparation and not in the lake. In fact, the gel seems to be a poorly-crystalline or polymer material. It can be assumed, that the algae layer in core CPY013 marks the former lake bottom, supported by the high amount of detrital quartz on top of this layer and low amount of quartz below. Resultant, gypsum layers form by two processes: settling out and by replacement of the limestone bedrock. In CPY020, the gel still consists of calcite. The gel-like layers show a strong enrichment of heavy metals in relation to the concentrations in lake water.

An argillaceous and root-containing layer of CPY023 (14 m water depth) was selected for the detection of total organic carbon (TOC). The four samples have TOC contents of 2.7-4.4 wt%. A 10 cm thick layer of gel-like matter covering the root layer had TOC contents of 21.8 wt% (0-5 cm) and 14.0 wt% (5-10 cm). Kerosene used in the Cu-extraction plant to enrich Cu in an organic phase and was partly discharged with the spoil water into the lake. This artificial influx of organic matter and natural organic matter e.g. from plant parts can not be decomposed in the lake. The microbiological decomposition of organic matter is inhibited by the low pH.

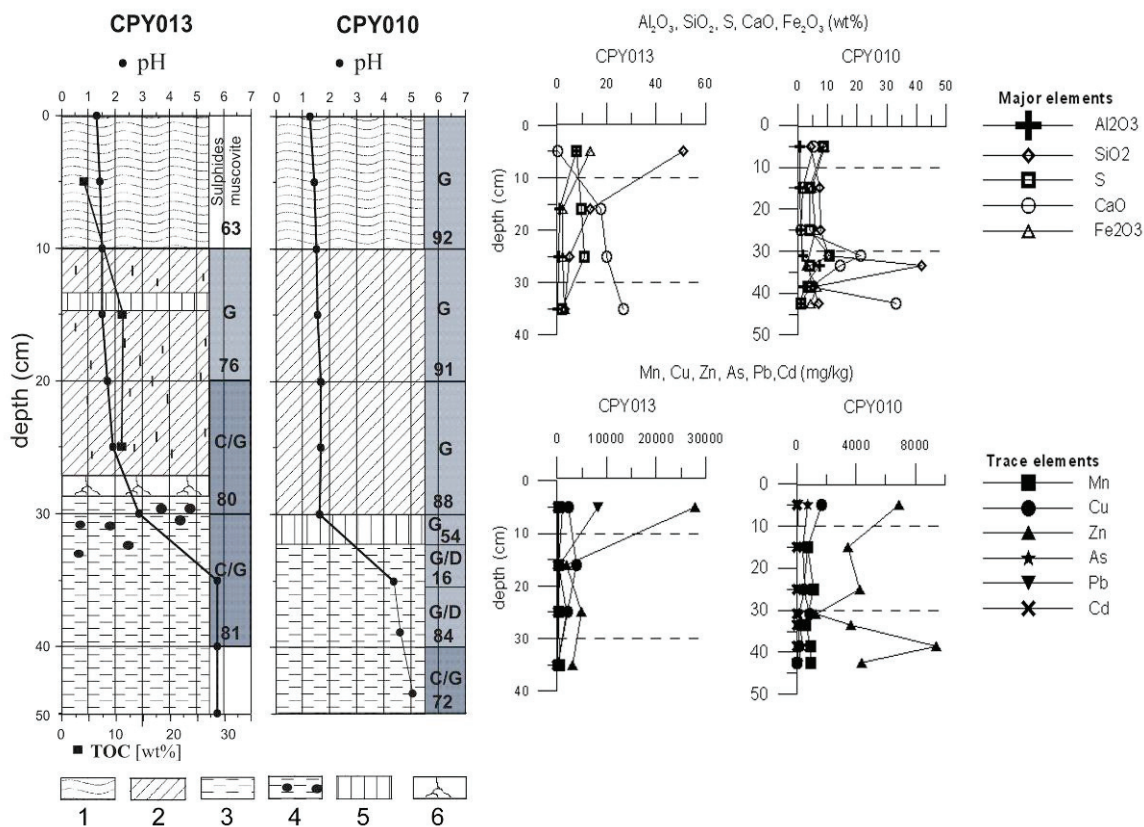


Figure 4: Core profiles and geochemical data (XRF) of two selected sediment cores of Lake Yanamate: Core CPY013 located near the discharge point and core CPY010 located in the NE (Figure 2). Hatchings and abbreviations: 1) fluid gel; 2) gelatinous gel; 3) argillaceous; 4) gravel; 5) algae or algae layer; 6) root layer; G) gypsum; C) calcite; D) dolomite. Water content in percent is given in the right column. Note, that minerals detected by XRD for the gel-like sediments may not represent the mineralogy present in the lake, but may result from the sample drying process.

3.3 Model of limestone bedrock alteration

Rocks of Pucará limestone were put in the lake for some weeks and used for the preparation of thin sections. These thin sections show, that the lake water primary intrudes fractures of the bedrock under precipitation of hydroxides (Figure 5). Under progression of the water-rock interactions, the calcite dissolves under stabilization of the pore water pH at 5.5 in a first dissolution zone. This pH was also modeled for lake water in equilibrium with calcite. Thin sections show hydroxide coatings on residual calcite fragments. If the acid neutralization capacity of the limestone is consumed, formation of gypsum accelerates and hydroxides formed in the first dissolution zone dissolve due to the lower pH of 1 - 1.5. No hydroxides could be found in thin sections of this part of the profile. In the upper part of the profile also gypsum dissolves until equilibrium with lake water is reached. Modeling of the lake bottom water samples showed saturation indices for gypsum of 0.0 to -0.2.

The karst basin allowed the infiltration of water for the most part of the discharge period, but due to the higher volume of gypsum relative to calcite, fractures began to clog in the last years.

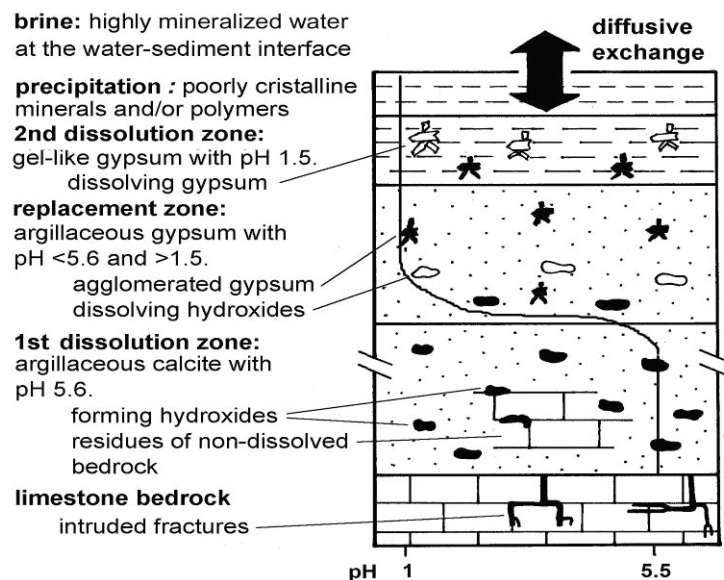


Figure 5: Schematic model of the limestone bedrock alteration due to the infiltration of the acidic lake water (pH ~1).

3.4 Results of modelling with PHREEQC 2 and wateq4f database

Modelling shows saturation indexes (SI, here given for sample CPY10 18m depth) of 0.05 for anglesite, giving a possible explanation of the remaining 2.9 mg/L Pb in lake water. Gypsum is in equilibrium (SI -0.02) with lake water and goethite oversaturated (SI 0.22) after modelling. These are the only oversaturated minerals except hematite, quartz and other types of SiO₂ species for the water samples taken near the water-sediment interface, but hematite does not precipitate from AMD likely, rather it can form by dehydration and reorganisation of ferrihydrate (Fe₅O₇OH*4H₂O, not included in the wateq4f data base) in neutral to alkaline media (Cornell and Schwertmann, 1996). For surface water samples also jarosite was modelled as oversaturated in most samples, possibly due to the higher Eh values. Following this results it seems, that heavy metals others than Fe and Pb co-precipitate, and do not form own minerals.

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References

- Cornell, R.M., Schwertmann, U. (1996). The Iron Oxides. Weinheim, VCH Verlagsgesellschaft mbH.
- Einaudi, M.T. 1977: Environment of Ore Deposition at Cerro de Pasco, Peru. *Econ. Geol.* 72, 893-924.
- Ficklin, W.H. and Mosier, E.L. 1998: Field methods for Sampling and Analysis of Environmental Samples for Unstable and Selected Stable Constituents. In: Plumlee, G.S. and Logsdon M.J. (ed.) The environmental geochemistry of mineral deposits Part A, 249-264, Society of Economic Geologists
- GEMA 1997: Levantamiento batimetrico. Lagunas: Yanamate y Huaygacocha. 17 p.
- Jenks, W. F. 1951: Triassic to Tertiary Stratigraphy near Cerro de Pasco, Peru. *Geo. Soc. America Bull.* 62, 203-220.
- Parkhurst, D.L., and Appelo, C.A.J. 1999: User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259.
- Petersen, U. 1965: Regional geology and mayor ore deposits of Central Peru. *Econ. Geol.* 60, 407-476.
- Plumlee G.S. 1999: The Environmental Geology of Mineral Deposits. In: Plumlee, G.S. and Logsdon M.J. (ed.) The environmental geochemistry of mineral deposits Part A, 71-116, Society of Economic Geologists
- Wisskirchen, C. 2004: Geochemical and mineralogical study of an extremely acidic lake caused by acid mine drainage and copper leaching waters, Cerro de Pasco/Peru. Diploma thesis, University of Leipzig. 142 p.