ELEMENT DISTRIBUTION IN WATER AND SEDIMENTS OF AN ACID MINE DRAINAGE DISCHARGE LAKE (pH ~1) OF THE Zn-Pb(-Ag-Bi-Cu) DEPOSIT, CERRO DE PASCO (PERU)[1]

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Abstract: A study of an acidic lake (pH ~1) resulting from the deposition of copper leaching spoil waters and acid mine drainage of the Zn-Pb (-Ag-Bi-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 (87) mg/L Cu, 180-746 (493) mg/L Zn, 13-63 (48) mg/L As, 2.2-5.3 (2.9) mg/L Pb, 11205-42300 (29250) mg/L SO_4^{-2} and an acidity of 14480-21440 (16775) mg/L $CaCO_3$. Lake water mean values did not differ significantly from values measured for discharge water. Within the lake water body most element concentrations increased with water depth.

Infiltrated acidic waters dissolved the limestone bedrock under formation of argillaceous gypsum, overlying dissolving calcite. In the precipitating gel-like matter and upper parts of dissolved bedrock, heavy metals enriched in composition to the lake water. X-ray fluorescence data show for this kind of sediment concentration ranges and mean values of 0.76-12.38 (5,98) wt% Fe_2O_3, 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. Heavy metals are most likely fixed by organic matter (15 wt% TOC) in form of chelate complexes. The high amounts of organic carbon in the upper part of the sediments most likely results from the discharged spoil waters of the Cu extraction plant. Hydroxides formed during first steps of the infiltration of the bedrock dissolve during later steps of the lake water bedrock interaction.

Additional Key Words: limestone bedrock, copper extraction spoil water, chelate complexes.

Introduction

The extremely acidic Lake Yanamate (pH~1) with a surface area of 3 km^2, located 2.5 km south of the city of Cerro de Pasco in the Central Andes of Peru, was hydrogeochemically and mineralogically studied. Located at an altitude of 4350 m above sea level, the annual mean temperature is 4.2 °C. The annual mean precipitation of 1025 mm/a is slightly higher than the annual mean evaporation of 988 mm/a. The lake bedrock and the surrounding lake basin of 10 km^2 consists of limestones of the Triassic-Jurassic Pucará formation and the Tertiary Pocobamba formation (Jenks, 1951) (Fig. 1). The basin is divided by the Cerro de Pasco fault, which also crosses the open pit of the Cerro de Pasco mine, 4 km to the north. Loose sediments within the basin were eroded by glacigenous activity. The same process led to the formation of an end moraine south-west of the lake and successively to the natural Lakes Yanamate and Huaygacocha. The lakes were separated by the Pampa Yanamate, a shallow swell of lacustrine sediments. The swell was water covered during the sampling period.

Since 1981 the lake was used as a deposition pond for acid mine drainage (AMD) originated from the Miocene age Pb-Zn (-Ag-Bi-Cu) deposit of Cerro de Pasco and additionally from 1981 until 2001 for spoil water from the Cu solvent extraction process, containing kerosene and Acorga® M-5615, either an aldoxime or ketoxime (EPA, 1994), designed for copper extraction.

During a first mineralization step a 1800 x 300 m measuring quartz-pyrite body formed, representing 90% of the entire ore body (Einaudi, 1977). Ward (1961) describes different lithogenic types of pyrite, some containing greater amounts of As (up to 10%, Petersen, 1965). Most important ore minerals are sphalerite, galena and tennantite-tetrahedrite in the primary zone and covelitte and chalcocite in the oxidized enrichment zone. The most important sources of mine water were: (1) the Cerro de Pasco-fault infiltrated the Raul Rojas open pit and the underground mine; and (2) rain water collected by the Raul Rojas open pit, that subsequently infiltrated in the underlying mine works. In July 2003, the discharge rate was 9.5 m^3/min and the lake water level was 14 m higher than before discharge began. The discharge resulted in an estimated lake volume increase from originally 3 km^3 to 25 km^3. In October 2003, discharge was stopped and AMD was treated in a water neutralization plant, operated with lime.

The objective of this study was to investigate the spatial distribution of physico-chemical parameters and element concentrations in the water and sediments of the two lakes to understand the geochemical processes, which controlled the distribution of heavy metals and SO_4^{-2} in the water column and the water-rock interactions at the lake bottom. To our knowledge, this is the only studied case, where the bedrock of a discharge pond consists of limestone, an highly reactive rock for the neutralization of AMD.
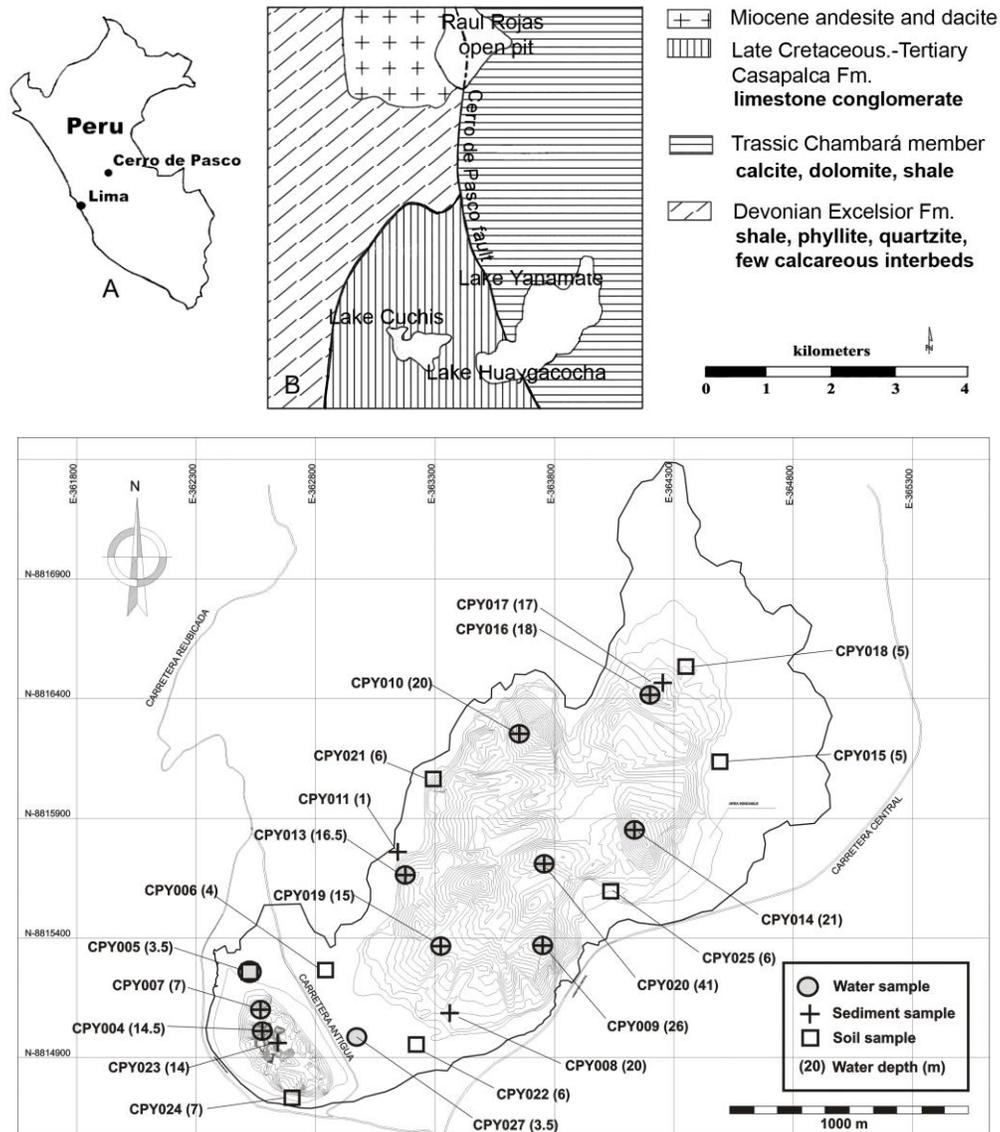
Figure 1: A) Locations map of the Cerro de Pasco region in Peru. B) Simplified map of the local geology, the open pit, and the Lakes Yanamate and Huaygacocha. The two lakes were connected during the sampling period. C) Sampling point map and bathymetry of the Lake Yanamate.

Methodology

Sampling took place during the dry and cold season (June and July). Water samples were taken at depths of 0.5 m, 5 m, and continued at 5 m steps until the lake bottom was reached. Samples were collected at 11 sampling points located above the deepest portions of the lake, until 41 m water depth (Fig. 1). Temperature, pH, Eh and electrical conductivity, and acidity were measured directly in the field. Acidity was measured by titration with NaOH after boiling and the addition of H_2O_2 (Ficklin and Mosier,1999). Samples were filtered through 0.45 µm filters. Lake sediments were sampled by gravity coring at the same stations where water samples were taken (Fig. 2). The cores were divided into 44 sub-samples. A set of 9 cores of the

inundated soils (due to the increased lake water level) were taken by percussion drilling, and where then divided into 41 sub-samples.

Figure 2: A) The unscrewed and opened corer with soil sample CPY007 from Lake Huaygacocha. B) Hoisting the corer with two persons.

Water samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 3000) for major elements, with inductively coupled plasma-mass spectroscopy (ICP-MS; Agilent 7500 C) for trace elements, and the German standard method DIN EN 1189 for dissolved phosphorus. Solid samples were analyzed geochemically by X-ray fluorescence (XRF; Bruker axs S4 Pioneer for major and Spectro XLab 2000 for trace elements) and mineralogically by X-ray diffraction (XRD; Seifert XRD 7). Selected samples were analyzed for total organic carbon (TOC; Eltra Metalyt CS 1000s) or dissolved organic carbon (DOC; Shimadzu TOC5050).

Results and Discussion

Lake Water Chemistry

The mean lake water values were pH 1, 29250 mg/L SO_4^{-2}, 4450 mg/L Fe, 88 mg/L Cu, 504 mg/L Zn, 49 mg/L As, 3 mg/L Pb, and 16850 mg/L acidity as $CaCO_3$, which do not differ significantly from values measured for the discharge water (Table 1). The values are in the order of magnitude slightly below the range for massive pyrite deposits and belong to the highly mineralized AMD waters (Plumlee, 1999).

The lake had only a slight stratification between 5 and 10 m or no stratification during the sampling period, but increasing concentrations with depth, e.g. 3689 mg/l Fe and 26655 mg/L SO_4 at 0.5 m water depth, and 7180 mg/L Fe and 42300 mg/L SO_4 at 35 m depth (Fig. 3).

The mixing of the lake water with rainwater (approximately $4.7 \cdot 10^6$ m³/a natural influx in comparison to $5 \cdot 10^6$ m³/a discharge water) does not result in a bisection of element concentrations, due to the evaporation of lake water. The high concentrations of dissolved P in the lake water originates from llama dung (llamas were feeding around the lake), and entered the lake with the surface runoff.

Results of geochemical modeling (PHREEQCI2 with wateq4f) show, that gypsum, goethite and jarosite are near equilibrium with lake water, possibly forcing element cycling in the water column, through their shallow precipitation, downward settling, and re-dissolution at depth.

Table 1.1: Physico-chemical parameters of Cerro de Pasco AMD and minimal, mean and maximal values of Lake Yanamate. Temp in °C, Eh in mV, electrical conductivity in mS/cm, acidity as $CaCO_3$, S and DP (dissolved phosphor) in mg/L.

	temp	pH	Eh	EC	acidity	SO$_4$	DP
min	6.0	-1.7	588	18.1	14480	11205	12.0
mean	**10.7**	**1.0**	**653**	**24.1**	**16775**	**29250**	**35.0**
max	14.3	1.6	674	31.3	21440	42300	44.0
discharge	21.3	1.1	609	27.4	18720	31875	0.06

Table 1.2: Element concentrations of Cerro de Pasco AMD and minimal, mean and maximal concentration of Lake Yanamate. All concentrations in mg/L.

	K	Na	Ca	Mg	Al	Fe	Cu	Zn	As	Pb
min	11.1	7.4	344	80.6	84.2	1440	33.5	180	12.7	2.2
mean	**31.4**	**18.0**	**397**	**214**	**259**	**4330**	**86.8**	**493**	**48.0**	**2.9**
max	36.4	40.9	466	243	384	7180	105	746	63.1	5.3
discharge	40.6	19.1	391	375	284	4440	125	748	47.8	4.2

Lake bottom sediments

At location CPY013, close to the discharge point, pyrite, sphalerite, anglesite and muscovite settled out of the mine water in form of detrital enriched sediment in the upper 10 cm of the sediment profile, this is also reflected by the geochemical data (Fig. 5). The detritus was contained in a gel-like matrix. At 14 cm depth the core CPY013 had a algae layer. Below no detrital minerals were found, but the matrix had the same gel-like aspect. This proves, that the gel-like matter formed by two different processes: (1) by precipitation and (2) by the dissolution of the bedrock.

The gel-like matter contain high concentrations of organic carbon (mean 16 wt% TOC) in the precipitated material. Core CPY023 had 21.8 and 14 wt% TOC in the upper two samples of gel-like matter. The deeper part of the core, the roots containing argillaceous material had TOC contents between 2.7-4.4 wt%.

XRD results of the gel-like matter showed the presence of gypsum. However, large gypsum agglomerates found in the dried samples were not found in the fresh samples and formed during the drying process (Fig. 4). Most likely the gel-like matter contained gypsum in form of poorly crystalline matter.
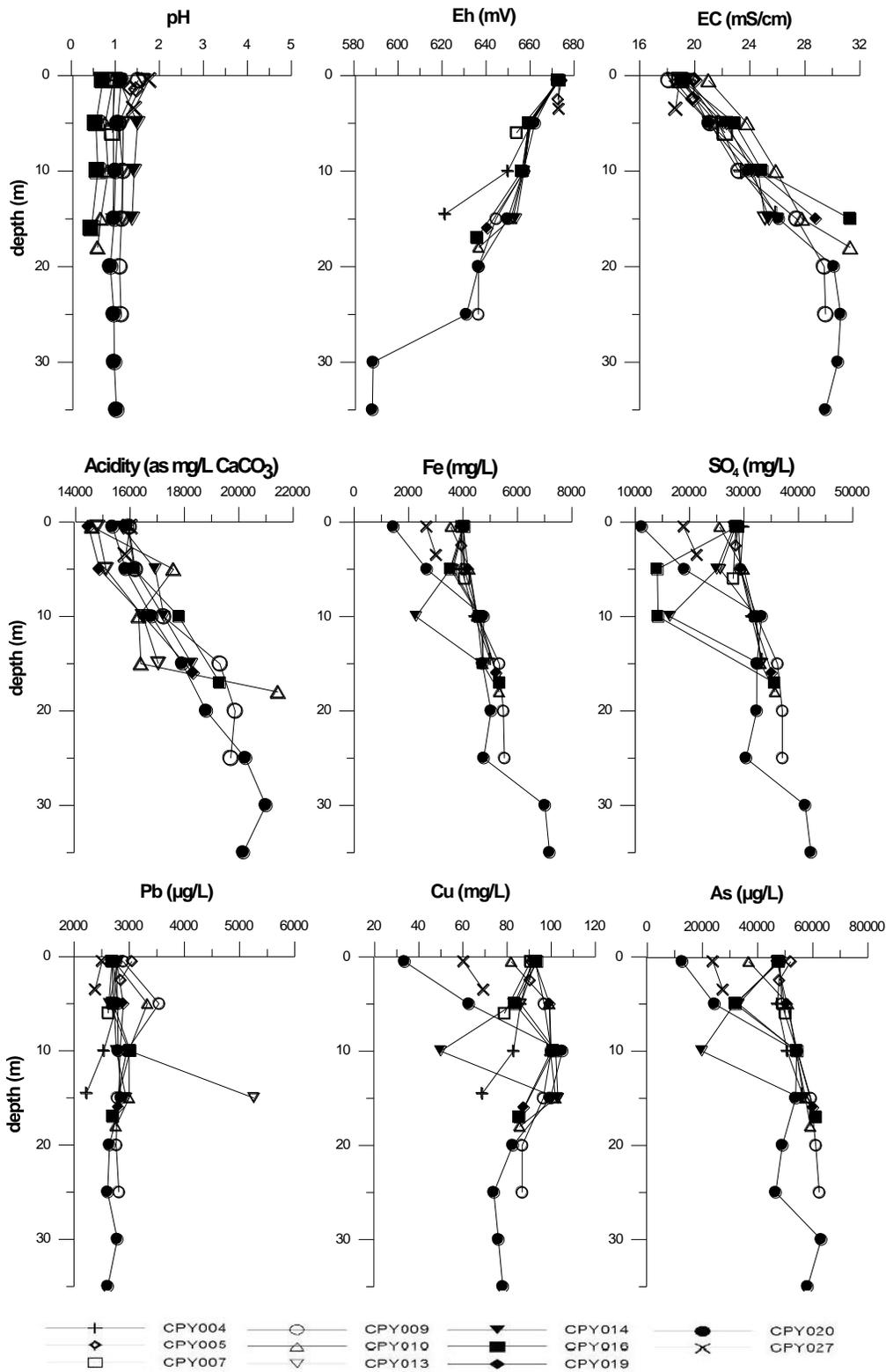
Figure 3: pH, Eh, electrical conductivity (EC), acidity, Fe, SO_4^{-2}, Pb, Cu, and As of 11 water columns sampled in Lake Yanamate and Lake Huaygacocha.
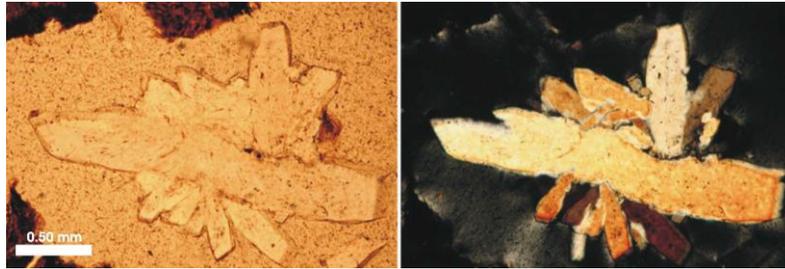
Figure 4: Tertiary gypsum of sample CPY013 (20-30 cm). Under crossed nickels (right) mineral intergrowths can be observed.

Underlying argillaceous gypsum and/or dissolving argillaceous calcite was found until uncertain depth. Unaltered limestone bedrock was not reached within the primary 69 cm of sediments. Hand specimen of Pucará limestone deposited in the lake for some weeks were intruded by the lake water under successive formation of hydroxides in the rock fractures.

XRF results (Table 2) show that the gel-like material enriches heavy metals, As and SO_4^{-2} in composition to concentrations in lake water.

Table 2: Minimal, mean and maximal concentrations of elements in sediment samples from Lake Yanamate, and mean concentrations of gel-like gypsum, argillaceous gypsum, and argillaceous calcite. LOI (loss of ignition).

	Al_2O3 (wt%)	SiO_2 (wt%)	CaO (wt%)	S (wt%)	P_2O_5 (mg/kg)	K_2O (wt%)	Mn (mg/kg)
min	0.34	2.59	0.28	0.65	<200	0.05	117
mean	2.24	15.03	13.97	6.09	3074	0.41	794
max	7.60	33.10	33.10	11.12	13800	1.50	2235
gel. gypsum	1.22	7.09	8.83	6.48	1920	0.15	1055
arg. gypsum	4.63	28.54	13.77	5.82	7185	0.84	885
arg. calcite	1.89	12.74	24.58	1.90	2242	0.48	623

	Fe_2O_3 (wt%)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	LOI (wt%)
min	0.76	48	275	43	<2	1	16.79
mean	5.27	1089	4746	881	460	16	49.63
max	13.40	3940	27900	5781	8314	103	85.14
gel. gypsum	6.02	1424	4352	1018	254	15	74
arg. gypsum	5.62	652	5135	1121	42	8	
arg. calcite	4.37	75	3274	230	60	10	53.5

The underlying argillaceous grain sized gypsum and dissolved calcite showed decreasing concentrations with depth for As, Pb, Cu, and Cd and increasing concentrations for Zn and Mn (Fig. 5). The increase of Zn and Mn concentrations were interpreted as natural background due to a near Cu-Zn scarn below a small wetland directly east of the lake. Fe showed no detectable trend. Only in a few samples were heavy metal-bearing minerals (anglesite, melanterite, pyrite, jarosite, and siderite) detected.
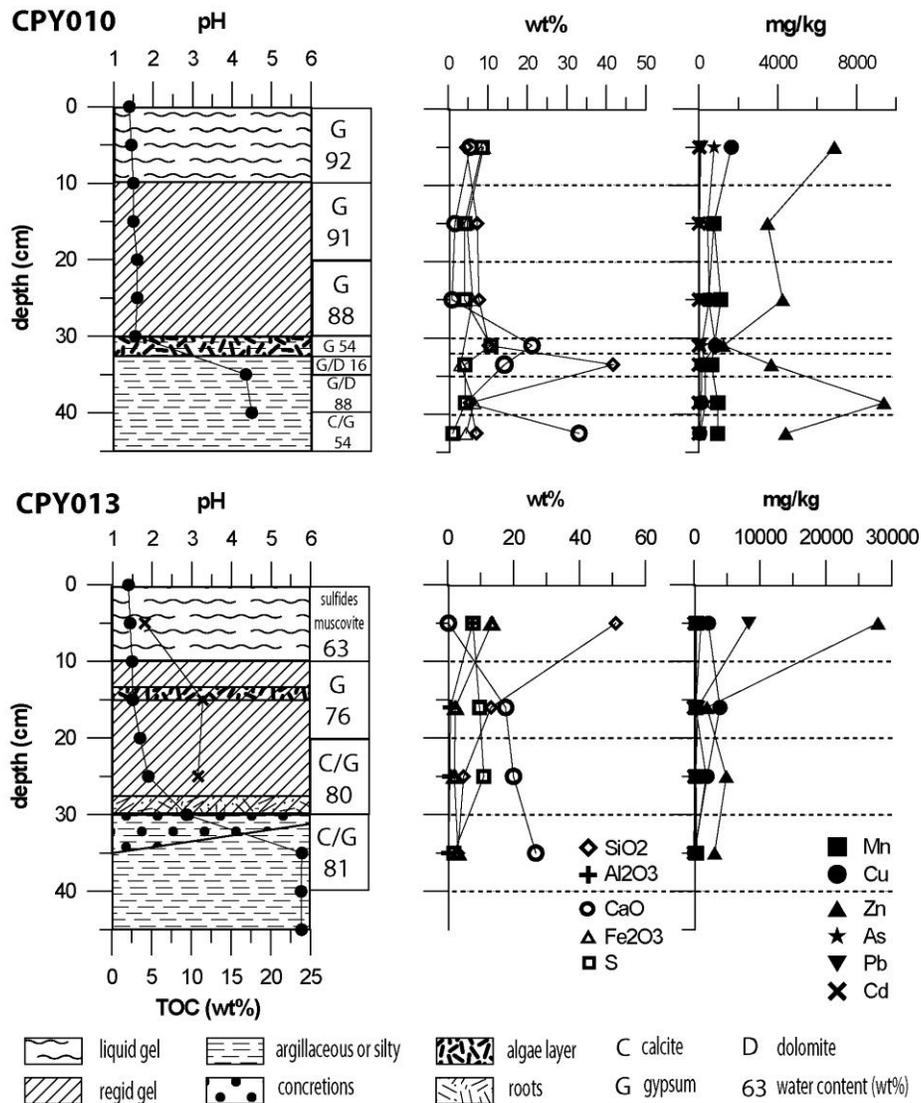
Figure 5: Pore profiles and geochemical data (XRF) of two selected sediment cores of Lake Yanamate: Core CPY013 is located near to the discharge point and core CPY010 is located in the north-central part of the lake (Fig. 1). Water content in percent is given in the right column. Note, that minerals detected by XRD for the gel-like matter may not represent the mineralogy present in the lake, but may result from the sample drying process. Graphs have different scales. For explications see text.

Water-rock interaction model

The interaction of the lake water with the underlying limestone bedrock can be described by a sequence of 4 steps, as follows (Fig. 6):

(1) The experiment with hand specimen showed, that as a first step the acidic water of the lake infiltrate the fractures of the limestone bedrock. In thin sections hydroxides are visible in the fractures.

(2) Under progression of the water-rock interaction, the hydroxide precipitation continues, the pH stabilizes around 5.5, and the limestone dissolves (1st dissolution zone). Also

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geochemical modeling of calcite in equilibrium with mean lake water resulted in a pH of 5.6. Thin sections show hydroxide coatings on residual calcite fragments. XRF results showed high Ca/S ratios. Calcite still dominates over precipitating gypsum.

(3) When the neutralization capacity of the limestone is consumed, the formation of gypsum accelerates and hydroxides formed in the 1st dissolution zone dissolve due to the lower pH of 1 – 1.5 (replacement zone). No hydroxides could be found in thin sections of this part of the profile.

(4) In a 2nd dissolution zone, also gypsum dissolves until equilibrium with lake water is reached. Modeling of the lake bottom waters samples showed saturation indices (SI) for gypsum of -0.2 to 0.0. This material has an aspect of gel-like matter.

On top poorly crystalline minerals or polymers precipitate as gel like matter, as observed, e.g. core CPY013. The high water content of the sediments allows a diffusive exchange with the overlying lake water.
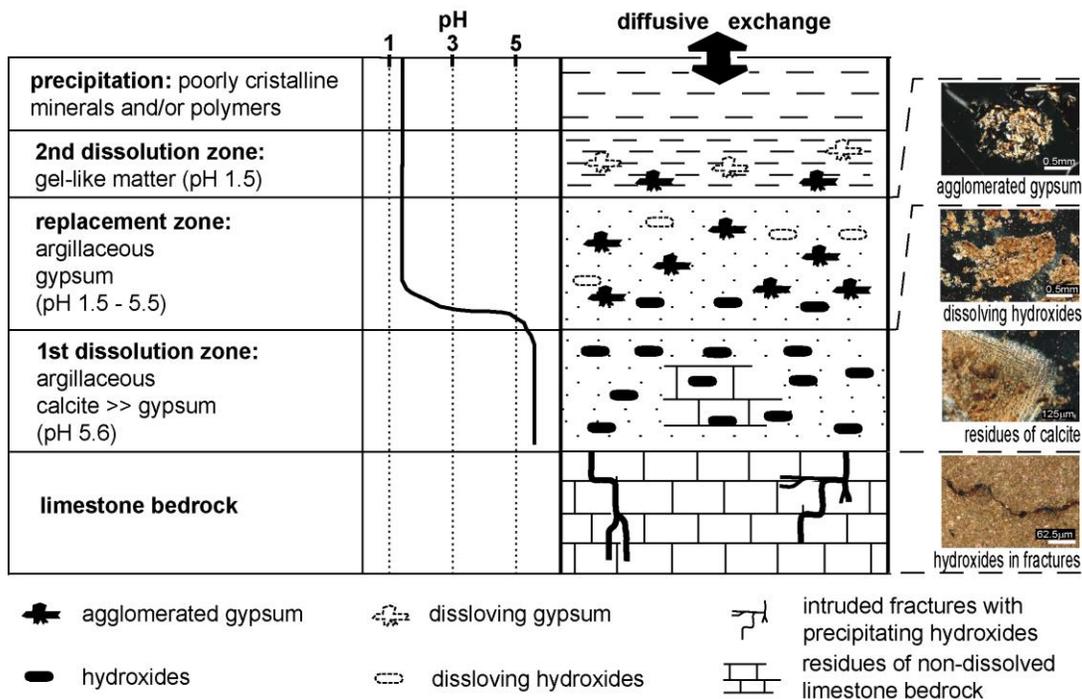
Figure 6: Schematic model of the bedrock alteration due to the infiltration of the acidic lake water (pH ~1) and thin sections under crossed nickles.

Conclusions

The lake water composition was controlled by the low pH, which inhibited the precipitation of most minerals. Only gypsum, goethite and jarosite were found to be near equilibrium with the lake water. During the sampling period (June and July) no or only a very slight lake stratification could be observed. The water column was dominated by a continuous increase of water mineralization and acidity with depth.

Besides the detrital minerals settled out near the discharge point, no heavy metal bearing minerals could be found by XRD. Most likely, heavy metals seem to be associated to the organic matter (up to 21.8 wt% TOC) in the gel-like matter. In some cores, relatively higher heavy metal concentrations were reached in the argillaceous gypsum directly underneath the gel-like matter, where metal-hydroxides were still stable. Successively metal-hydroxides dissolved when the neutralization capacity of the limestone bedrock was exhausted.

Acknowledgements

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