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Geochemistry of highly acidic mine water following disposal into a natural lake with carbonate bedrock

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ABSTRACT

Acid mine drainage (AMD) from the Zn–Pb(–Ag–Bi–Cu) deposit of Cerro de Pasco (Central Peru) and waste water from a Cu-extraction plant has been discharged since 1981 into Lake Yanamate, a natural lake with carbonate bedrock. The lake has developed a highly acidic pH of ~1. Mean lake water chemistry was characterized by 16,775 mg/L acidity as $CaCO_3$, 4330 mg/L Fe and 29,250 mg/L SO_4. Mean trace element concentrations were 86.8 mg/L Cu, 493 mg/L Zn, 2.9 mg/L Pb and 48 mg/L As, which did not differ greatly from the discharged AMD. Most elements showed increasing concentrations from the surface to the lake bottom at a maximal depth of 41 m (e.g. from 3581 to 5433 mg/L Fe and 25,609 to 35,959 mg/L SO_4). The variations in the H and O isotope compositions and the element concentrations within the upper 10 m of the water column suggest mixing with recently discharged AMD, shallow groundwater and precipitation waters. Below 15 m a stagnant zone had developed. Gypsum (saturation index, $SI \sim 0.25$) and anglesite ($SI \sim 0.1$) were in equilibrium with lake water. Jarosite was oversaturated ($SI \sim 1.7$) in the upper part of the water column, resulting in downward settling and re-dissolution in the lower part of the water column ($SI \sim -0.7$). Accordingly, jarosite was only found in sediments from less than 7 m water depth. At the lake bottom, a layer of gel-like material (~90 wt.% water) of pH ~1 with a total organic C content of up to 4.40 wet wt.% originated from the kerosene discharge of the Cu-extraction plant and had contaminant element concentrations similar to the lake water. Below the organic layer followed a layer of gypsum with pH 1.5, which overlaid the dissolving carbonate sediments of pH 5.3–7. In these two layers the contaminant elements were enriched compared to lake water in the sequence $As < Pb \approx Cu < Cd < Zn = Mn$ with increasing depth. This sequence of enrichment was explained by the following processes: (i) adsorption of As on Fe-hydroxides coating plant roots at low pH (up to 3326 mg/kg As), (ii) adsorption at increasing pH near the gypsum/calcite boundary (up to 1812 mg/kg Pb, 2531 mg/kg Cu, and 36 mg/kg Cd), and (iii) precipitation of carbonates (up to 5177 mg/kg Zn and 810 mg/kg Mn; all data corrected to a wet base). The infiltration rate was approximately equal to the discharge rate, thus gypsum and hydroxide precipitation had not resulted in complete clogging of the lake bedrocks.

1. Introduction

Management of acid mine drainage (AMD) is a major problem for the present day mining industry. Sulfide-rich deposits tend to produce highly acidic waters, if no carbonate minerals neutralize the effluents (Plumlee and Logsdon, 1999). Pit lakes have become a subject of increasing importance in environmental geochemistry, due to the closure of open pit mines (Castro and Moore, 2000; Geller et al., 1998; Sánchez España et al., 2008). The main sources of acidity and metals in pit lakes include oxidation of sulfides from coal and metalliferous deposits or backfill, water from interconnected flooded underground mines or dissolution of sulfates by water flushes (Bowell and Parshley, 2005; Castendyk et al., 2005; Denimal et al., 2005; Knöller et al., 2004; Pellicori et al., 2005). In most pit lakes, the sources of contaminants are diffuse and difficult to apportion. In pit lakes with carbonate wall rocks or carbonate-containing veins the system is buffered to slightly basic pH, limiting the solubility of most metals (Shevenell et al., 1999).

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Conclusive interpretation by modeling of data sets for a number of pit lakes has suggested control of aqueous element concentrations by mineral equilibrium (Eary, 1999). Addition of lime is still the only successful method to increase the alkalinity of highly acidic pit lakes. Addition of nutrients (phosphate or organic matter) to stimulate the microbiological activity in order to increase the pH has only been applied with good results for pit lakes with pH >3 (Koschorreck et al., 2007).

For AMD neutralization, carbonate minerals are an alternative to lime, because of their lower cost. Several studies have been carried out in recent years to investigate the interactions of carbonates with mine effluents, and their application to AMD neutralization and metal retention (Komnitsas et al., 2004; Simon et al., 2005; Webb and Sasowsky, 1994). For low mineralized AMD, anoxic and oxic limestone drains have been used successfully (Cravotta and Trahan, 1999; Santomartino and Webb, 2007). However, the problem of armoring of the carbonate grains and clogging of the limestone drains by precipitation of Fe- and Al-hydroxides and gypsum still limits the life-span of these treatment systems (e.g. Cravotta, 2008; Rose et al., 2004).

In this article, results are presented of a detailed geochemical study of a natural lake within a carbonate bedrock used as an AMD storage facility for the polymetallic Zn–Pb(–Ag–Bi–Cu) deposit Cerro de Pasco (Central Peru). The AMD with a pH $\sim$1 has been discharged without treatment into Lake Yanamate ($\sim$3 km^2) since 1981. The formation of AMD at Cerro de Pasco and its handling has been studied with regard to the Excelsior waste rock dump and tailings partly underlying it (Dold et al., 2009; Smuda et al., 2007). Additionally, spoil waters with high concentrations of kerosene from a solvent extraction-electrowinning (SX-EW) plant were discharged into the lake until August 2001. The geochemical approach used in this first case study of a discharge pond in carbonate rocks combines major and trace element concentration of waters and sediments, H and O stable isotopes of waters, and mineralogical data. The code PHREEQC V2 (Parkhust and Appelo, 1999) was used to model element speciation and mineral precipitation or dissolution in the water column and at the water–sediment interface. The new data set and geochemical modeling provided insights into the lake chemistry, in particular the formation of secondary minerals, the interactions in the AMD-carbonate system, and the migration of contaminant elements.

2. Site description

Lake Yanamate is located 5 km south of the Cerro de Pasco deposit at the northern end of the Puna plateau between the Western and Eastern Cordillera of Peru (Fig. 1A and B). This lake is part of the mining facilities of the Cerro de Pasco mine, at present operated by Volcan Corporation S.A.A. and previously (until 1999) by the former state company Centromin S.A. Currently the deposit is exploited by means of both underground and open pit mining. Cerro de Pasco is one of the largest polymetallic resources of the world. Accumulated past production and known reserves include $\sim$175 Mt @ ±7% Zn, 2% Pb and 3 oz/t Ag. Further, 1.2 billon oz of Ag and 2 million oz of Au, and an equivalent of ±50 Mt of Cu have been produced, largely before 1950 (Baumgartner et al., 2008). The deposit is dominated by a 1800 × 300 m quartz-pyrite body formed by replacement of Triassic limestone, representing 90 vol.% of the entire ore body (Enaudi, 1977). Different types of pyrite have been described, some of them containing up to 10 wt.% As (Petersen, 1965; Ward, 1961). The main ore minerals are sphalerite–galena, pyrrhotite, enargite, luzonite, tennantite, marmantite, arsenopyrite and chalcopyrite (Enaudi, 1977). Final hydrothermal and hypogene activities resulted in mineral associations dominated by pyrite–hematite–realgar and covellite–bornite, respectively. Supergene processes formed an enrichment blanket of chalcocite and covellite (Petersen, 1965). The sources of mine water were: (1) groundwater of the Cerro de Pasco fault zone infiltrating into the open pit and the underground mine and (2) rainwater accumulating in the open pit, that subsequently infiltrated into underlying mine works (Luna Bernal and Delgado Venero, 1985). Old mine works on Cu minerals were used for *in situ* leaching with highly acidic solutions. The Cu was extracted in a SX-EW plant using kerosene as a solvent with addition of 4 vol.% Acorga

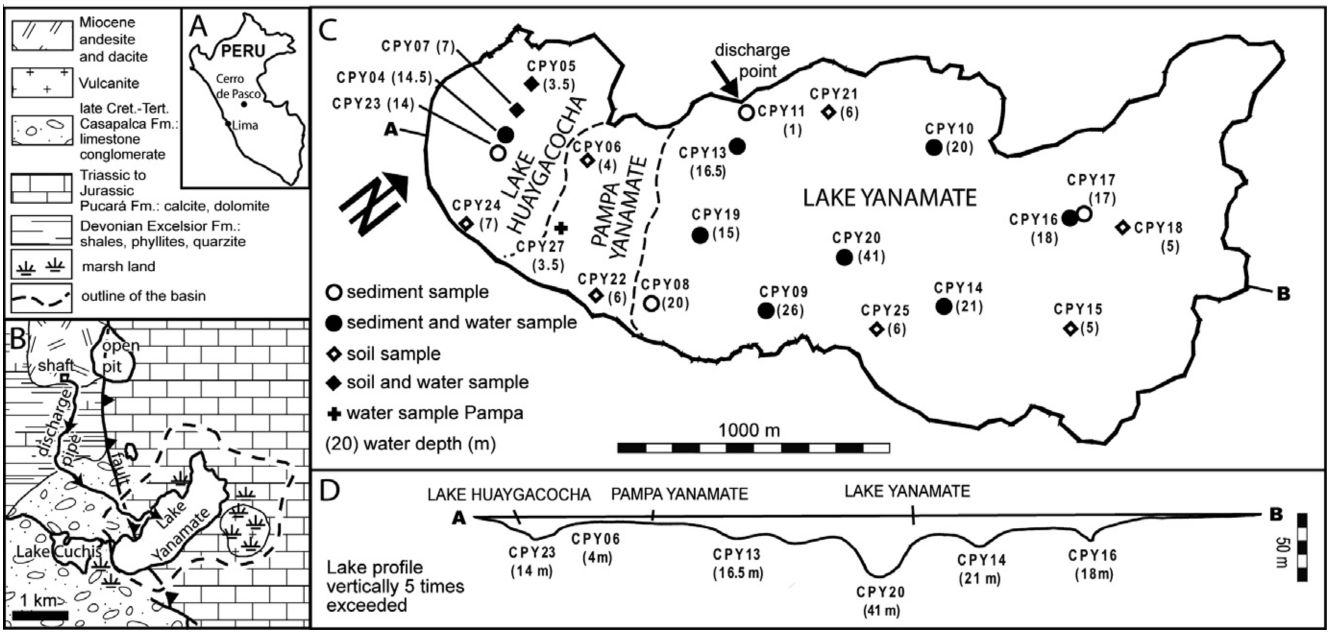

Fig. 1. (A) Location map of the Cerro de Pasco region in Peru. (B) Map of the local geology, the open pit, discharge pipe, and Lake Yanamate. (C) Map of Lake Yanamate and Lake Huaygacocha with sampling points. (D) Cross-section of the lake basin from west to east. The two lakes were connected during the sampling period due to the water level being 14 m higher than before discharge began in 1981.