

Regulation of acidity generation and consumption in sediments of acidic mine lakes

C. BLODAU, C. GATZEK AND K.-H. KNORR

Limnological Research Station and Department of Hydrology,
University of Bayreuth, 95440 Bayreuth
(christian.blodau@uni-bayreuth.de)

In acid mine drainage (AMD) polluted lakes, acidity generation and consumption in sediments are regulated by geochemical factors and by seepage of groundwater. We tested the hypothesis that increased inflow of groundwater can shift the sediment from an acid generating to an acid consuming state and examined the chemical factors that control iron and sulfur transformations. In column experiments, schwertmannite bearing sediment, rich in iron, sulphur, and carbon, was percolated (0, 5 and 20 L m⁻² a⁻¹) with two solutions (1/1 mmol L⁻¹ vs. 10/15 mmol L⁻¹ sulphate/ferrous iron, pH 5). A DOC source was added after 46 days (~2.5 mmol C L⁻¹) to ease the carbon limitation of reductive processes. The sediment remained in an iron reducing and acidic state during percolation without DOC. Percolation at a high rate and addition of DOC raised pH values in schwertmannite rich layers from 2.8 to 4.5 – 5. Schwertmannite transformation to goethite partly accelerated by a factor of >2 but effectively buffered proton consumption only at the low percolation rate. With pH increase, iron reduction slowed relative to CO₂ production, sulphate was reduced, and iron sulphides were formed.

In batch experiments we examine the effects of iron sources (schwertmannite, goethite, dissolved Fe³⁺), peat humic acid, and pH (3 – 6) on iron reduction rates. At pH 3, addition of schwertmannite and goethite and dissolved ferric iron strongly increased, and addition of the humic acid decreased iron reduction rates. Goethite promoted iron reduction more strongly than schwertmannite. Raising pH from 3 to 4.5 – 6 strongly decreased iron reduction rates. When the pH was not fixed, addition of schwertmannite increased (6.3 mmol g⁻¹ d⁻¹) and addition of goethite decreased (1.9 mmol g⁻¹ d⁻¹) iron reduction compared to a control (3.9 mmol g⁻¹ d⁻¹). This effect can be attributed to pH values being higher and dissolved ferric iron concentrations being lower in the goethite amended samples, compared to control and schwertmannite treatment. The acidifying effect of schwertmannite was more critical for maintaining high rates of iron reduction than bulk mineral properties.

The study showed that the input of alkalinity and electron donors by percolation may shift the biogeochemical regime from acidity production to acidity consumption. However, the acidifying capacity of schwertmannite transformation is substantial and its kinetics is fast, thus stabilizing the sediments in an acidic state.

Fo 99.8 olivine in basalts: Assimilation of meta-serpentinites or oxidation of magmatic phenocrysts?

M. S. BLONDES¹, M. T. BRANDON¹, P. W. REINERS²,
N.T. KITA³, F.Z. PAGE³ AND J.W. VALLEY³

¹Dept of Geology and Geophysics, Yale University, New Haven, CT, USA (madalyn.blondes@yale.edu)

²Dept. of Geosciences, Univ. of Arizona, Tucson, AZ, USA

³Dept. of Geology, Univ. of Wisconsin, Madison, WI, USA

Rare occurrences of near endmember forsterite (> Fo 95) exist in volcanic lavas, skarns, and metamorphosed serpentinites. We identify olivines, more forsteritic than any published value, in multiple primitive basalt flows of a monogenetic vent in the Big Pine Volcanic Field, CA USA. Here, to provide a framework for understanding the effects of assimilation and alteration processes in basalts, we analyze two competing hypotheses of pure forsterite formation in lavas: incorporation of regenerated olivine from metamorphosed serpentinite or crystallization/alteration in a high *f*O₂ environment. Olivine compositions are bimodal, with flows either having all normal (Fo_{74.9}–Fo_{94.4}) or all forsteritic (Fo_{97.2}–Fo_{99.8}) olivine. Fo composition correlates with increased flow vesicularity but not with the systematic whole rock composition. In many grains, the nearly euhedral forsterite has a hematite and cpx rim, and internal parallel oriented planes of hematite, cpx, and opx.

During peridotite serpentinization and subsequent dehydration, Fe partitions into associated oxides and Ni remains in the serpentine. Thus, regenerated olivines commonly have both low Fe and Ni concentrations. In these lavas, there is a correlative bimodal distribution of NiO. With increasing Mg#, the normal olivines show an increase in NiO whereas it decreases in forsterites to 0.04 wt.%. We therefore can consider a scenario of dehydrated serpentinite originally from the mantle lithosphere incorporated into the ascending melt, with only the forsterite and related oxides remaining.

However, several lines of evidence are inconsistent with an assimilated serpentinite origin, and instead call for late stage oxidation of the melt in air. If metamorphosed serpentinites were selectively incorporated into certain flows, we would expect to see changes in whole rock chemistry as well as a bimodal distribution of both xenocrystic forsterites and phenocrystic normal olivines within single flows, which we do not. A closed system (other than fluids) is also likely because the reintegrated composition of the oxidized assemblage is a normal Fo₈₉ olivine. In addition, four δ¹⁸O analyses by CAMECA 1280 ion microprobe within one forsterite have typical mantle olivine values of 5.42 ± 0.3 ‰ (1σ, 10 μm spots). Continuous oxidation of pre-existing olivine is known to generate pyroxene and oxide symplectites in an increasingly magnesian olivine that exhibit a topotaxial relationship. The BPVF olivines show these requisite reactant phases with the [100] direction of olivine parallel to the [0001] direction of the hematite, and with the symplectite planes parallel to the weak olivine cleavage planes.