Vertical distribution of Fe and S species in anoxic water column of Pavin Lake (France): Electrochemical evidence for nanoparticulate FeS

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Recently it has been shown that anodic oxidation of Hg by FeS at around -0.45 V can be used as an analytical protocol for electrochemical determination of FeS nanoparticules in natural waters [1]. The proposed protocol was tested on anoxic samples of Pavin Lake (France) where anodic waves were observed at -0.45 V (vs. Ag/AgCl); these correspond to an electrochemical transformation of particulate and/or nanoparticulate FeS to HgS.

A vertical profile of S(-II) obtained by voltammetric measurements showed that through the whole Pavin Lake monimolimnion layer a majority (~70 %) of S(-II) is in the form of FeS nanoparticulates. Concentrations of dissolved Fe(II) in the Pavin Lake monimolimnion layer are extremly high (up to the 1 mM) supporting our previous conclusion that Fe(II) is controling the speciation and distribution of S(-II) between dissolved and particulate phases [2,3]. At the oxia-anoxia boundary (from 61 to the 64 m), electrochemical measurements indicate presence of colloidal Fe(III) and /or Fe(III) organic species [2].

Thermodynamic calculations predict precipitation of FeS with log Ks value between -3.6 and -3.8 in the Pavin Lake monimolimnion layer. In the upper part of monimolimnion layer most probably precipitation of greigite is proceeding.

It was shown that modification of an Hg electrode with surface formed FeS has significant influence on the voltammetric Fe(II) determination, since cathodic reduction of Fe(II) in such conditions is occuring both on bare (-1.4 V) and on FeS modified Hg surfaces (-1.1 V)[1]; Fe(II) may be underdetermined when only the -1.4 V peak is measured.

[1] Bura-Nakić et al. (2011), Electroanalysis, in press. [2] Bura-Nakić et al. (2009), Chem. Geol. **266**, 311-317. [3] Viollier et al. (1997), Chem. Geol. **142**, 225-241.

Inverse modelling of gas chemistry measurements

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We illustrate the inverse modelling of gas chemistry measurements by using gas compositional data for both quiescent and explosive emissions from the lava lake at Erebus volcano, Antarctica. The multi-component degassing model used needs calibration with experimental data in order to partition correctly the volatile species between their gaseous and dissolved forms. Solubility experiments were made on phonolite lava from the lake for H_2O, and data from the literature were reformatted to obtain the fugacity-based solubilities of CO_2 and S.

The degassing model is based on the hypothesis that the gas phase is buffering the system and controls the balance of volatile species. Two types of calculations are performed, depending on whether the measured gas was in equilibrium with the surrounding melt at the lake surface (case 1), or was emitted in isolation from the lava contained in the lake (case 2). The inversion procedure starts by calculating the equilibrium composition of all the species assumed to coexist at atmospheric pressure. This is not straightforward, as the species that are best measured at the vent and those best constrained in the model do not always match. At Erebus, such discrepancy occurs for H_2S, which is simulated but not measured, and OCS, which is measured but not simulated. Compression is then performed by assuming mass conservation of the volatile elements, either applied to the mixture of melt and gas (case 1), or only to the gas (case 2).

Model results are projections at higher pressures (up to 3 kbar) of the gas composition measured at the surface. At Erebus, we find that the difference between the gas emitted explosively and that emitted passively can be explained by a common source situated at depths corresponding to as little as 300 bars pressure. While quiescent, the lake is either degassing in fully open system, or by the means of a convective system restricted between the surface and depths equivalent to 60 to 300 bars. Additional constraints on the magmatic system are obtained by comparing the simulated melt volatile contents with those measured in melt inclusions. We will discuss the limitations of the main model assumptions (chemical equilibrium, gas buffering of the redox state, and temperature effects).