

## Effect of alkali content and Fe oxidation state on the S oxidation state and solubility in rhyolitic glasses

G. GIULI<sup>1\*</sup>, E. PARIS<sup>1</sup>, R. ALONSO MORI<sup>2</sup>, P. GLATZEL<sup>2</sup>, M.R. CICONI<sup>1</sup>, B. SCAILLET<sup>3</sup> AND S.G. EECKHOUT<sup>2</sup>

<sup>1</sup>School of Science and Technology, Geology division, University of Camerino, ITALY

<sup>2</sup>European Synchrotron Radiation Facility (ESRF), Grenoble, France

<sup>3</sup>Inst. de Sciences de la Terre D'Orleans, UMR, CNRS-UO, Orleans, France

The Fe oxidation state, coordination geometry and <Fe-O> distances have been determined by Fe K-edge XANES and EXAFS for a set of sulphur bearing silicate glasses of rhyolite composition in the aim of determining: 1) the effect of bulk composition on the iron oxidation state and local structural environment; 2) the effect of Fe oxidation state on sulphur behaviour in the corresponding magmas/melts. Glass compositions have been chosen so as to represent S-Cl-F bearing rhyolitic magmas with low to high alkali content. These glasses have been equilibrated at a range of different oxygen fugacity conditions typical of magmatic conditions and ranging from -15.4 to -10.75 log units (at 800 °C, 1.5 kbar). Comparison of the pre-edge peak data with those of Fe model compounds allowed to determine the Fe oxidation state and coordination number for all the glasses analysed. The  $Fe^{3+}/(Fe^{3+} + Fe^{2+})$  ratio varies from 0.25 to 0.80 ( $\pm 0.05$ ) in the glasses studied. Moreover, pre-edge peak data clearly indicate that  $Fe^{3+}$  can be present in [4] and/or [5] coordination according to the alkali content of the glass, whereas  $Fe^{2+}$  is present in [5] coordination units for these compositions. The presence of minor amounts of [6] coordinated Fe cannot be ruled out by XANES data alone. EXAFS derived Fe-O distance in the most oxidised sample (Fe-O=1.85 Å) indicates that  $Fe^{3+}$  is in tetrahedral coordination. For these glass compositions, going from reducing to oxidising condition results in higher fraction of network forming [4] $Fe^{3+}$ , thus increasing the polymerisation of the tetrahedral network. Alkali content has been found to have a very strongly effect on the Fe oxidation state: at a given oxygen fugacity, Fe oxidation state increase noticeably with increasing alkali content. A direct proportionality has been found between the  $S^{2-}/Fe^{2+}$  molar fractions. As Fe oxidation state is known to affect the solubility of  $S^{2-}$  species in silicate melts, Alkali content is expected to play a major role together with oxygen fugacity in the S geochemical behaviour in silicate magmas.

[1] Giuli, G. *et al.* (2002) *Geochim. Cosmochim. Acta*, **66**, 4347- 4353. [2] Giuli, G. *et al.* (2011) *American mineral.*, **96**, 631-636

## Redox dynamics resulting from chemical and physical fluxes in surficial permeable sediments

B.T. GLAZER<sup>1\*</sup>, J. FRAM<sup>1,2</sup>, J.L. MURPHY<sup>1</sup>, K. FOGAREN<sup>1</sup> AND F. J. SANSONE<sup>1</sup>

<sup>1</sup>University of Hawaii, Department of Oceanography, 1000 Pope Rd., Honolulu, HI 96822;

(\*correspondance: glazer@hawaii.edu)

<sup>2</sup>College of Oceanic and Atmospheric Sciences, Oregon State University, 104 COAS Administration Bldg

The upper layers of nearshore permeable sediments are dynamic, active sites of intense redox cycling. Previous research and our preliminary results indicate that vertical redox oscillations in these sediments can be driven by biogeochemical or physical variability, or by episodic events such as severe storms and their associated terrestrial runoff. Further, it can be assumed that each of these forcings operate on different and distinctive time and vertical scales. The current work focuses on central goals of calculating the fluxes of redox-sensitive chemical species in surficial permeable coastal sediments, and understanding the transformations within the highly responsive "zone of reactivity" in the upper centimeters of these sediments.

We have made extended deployments of a custom physical and chemical sensor package in nearshore permeable sediments, as part of a cabled seafloor observatory. Instrumentation includes a multi-channel high-resolution miniature thermistor chain, an in situ electrochemical analyzer (ISEA-III, AIS Inc.), a profiling micromanipulator, oxygen optrodes (Aanderaa), independent temperature loggers (RBR), and a seafloor visualization system, all integrated into the existing physical sensor network observatory (Kilo Nalu Nearshore Reef Observatory, Oahu, Hawaii, USA). Here, we describe on-going work aimed at: (i) improving our understanding of the interaction between these active, carbon recycling sediments and the overlying water column; (ii) examining in detail the temporal and spatial variability of key redox-reactive chemical species; (iii) quantifying the relative contributions of benthic photosynthesis, sand ripple position, currents and waves to redox oscillations; and (iv) integrating fine-scale chemical measurements with porewater velocity modeling to calculate biogeochemical fluxes.