Primary and secondary water content heterogeneity in volcanic glasses

H. TUFFEN¹, J.M. CASTRO², J. OWEN¹ AND J.S. DENTON³

¹Lancaster Environment Centre, Lancaster University, UK (h.tuffen@lancaster.ac.uk, j.owen2@lancaster.ac.uk)

²Institut für Geowissenschaften, Johannes Gutenberg University Mainz, Germany (castroj@uni-mainz.de)

³Los Alamos National Laboratory (jo.denton@yahoo.com)

Spatial heterogeneities in the dissolved water content within volcanic glasses are generated by diffusive degassing and crystallization of melts, as well as subsequent posteruptive hydration of quenched glasses. Characterization of the resultant water diffusion gradients using micro-analytical techniques such as SIMS or synchrotron FTIR allows us to model the timescale of water diffusion and thus key pre-, synand post-eruptive processes. We present a variety of micro-analytical data to illustrate three sources of water content heterogeneity within rhyolitic glasses.

Firstly, enrichment of water in glass surrounding spherulites reflects its expulsion during growth of anhydrous mineral phases. Our diffusion models have placed new constraints on spherulite growth rates within obsidian flows [1]. Secondly, we have found strong water enrichment adjacent to perlitic fractures in subglacially erupted obsidian lavas [2]. Diffusion and cooling models show that perlitisation starts at ~400 °C and occurs over timescale of days [3]. Finally, we have used SIMS analysis to overcome the hydration problem and successfully measure the dissolved magmatic water content of pumices [4]. This provides new insight into magma storage and degassing prior to an exceptionally violent eruption.

[1] Castro *et al.* (2009) *Chem Geol* **268**, 272–280. [2] Tuffen H *et al.* (2010) *Earth Sci Rev* **99**, 1–18. [3] Denton JS *et al.* in prep, *Geology*.[4] Tuffen H *et al.* in prep, *EPSL*.

Studies of near surface redox transitions in crystalline rocks in Sweden and Greenland

E.-L. TULLBORG¹*, H. DRAKE², J. SUKSI³ AND J. SMELLIE⁴

¹Terralogica AB, P.O. Box 4140, SE-443 14 Gråbo, Sweden (*correspondence: evalena@terralogica.se)

²Sebagl of Netural Science Linguistic SE 201.82

²School of Natural Science, Linnaeus University, SE-391 82 Kalmar, Sweden

 ³Laboratory of Radiochemistry, Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki
 ⁴Conterra AB, P.O. Box 8180, SE 104 20 Stockholm

Oxidising groundwater conditions in the near surface of crystalline rock usually change to reducing in the upper 100 m of the bedrock. To detect the depth of this redox transition zone only from groundwater considerations may be difficult because of flow changes and mixing with time. More useful is to use a combination of different geochemical analyses of redox sensitive elements (e.g. Ce, U) in fracture coating samples. These data, together with mapped changes in fracture mineralogy with depth (especially the presence or absence of minerals like Fe-oxyhydroxides and Fe-sulphides), have been shown to mirror the switch from oxidising to reducing conditions [1, 2, 3]. In addition, U-series isotopes can provide time constraints on redox changes contributing to mobilisation and deposition of uranium.

The present study compares new results from close to the ice margin in Greenland (Greenland Analogue Project [4].) with results from two coastal Swedish sites (Äspö and Laxemar) [2, 3]. One of the key questions for the long term safety of a repository for spent nuclear fuel is whether the intrusion of glacial meltwater can maintain its oxidising character to repository depth (~500 m). If that is the case, mineralogical and geochemical evidence should be observed, especially in fracture material from the Greenland drill cores.

The comparison of results shows that although evidence of oxidation (e.g. breakdown of pyrite and formation of Feoxyhydroxide) are documented to greater depth in the Greenland drill cores than at Äspö and Laxemar, it does not exceed 100 m. Also, positive Ce anomalies (indicating Ce^{4+}) are recorded to greater depth in the Greenland drill cores (~ 40 m) compared with Äspö and Laxemar (10-15 m), although still not very deep. Uranium isotopes indicate a transition from mobilisation to deposition in accordance with the other redox indicators, albeit the patterns are complex and the uranium content in the Greenland samples is very low.

- [1] Tullborg et al. (2008) Appl Geochem 23, 1881–1897.
- [2] Landtröm *et al.* (2001) SKB R-01-37. [3] Drake *et al.* (2009) *Appl Geochem* **24**, 1023–1039.
- [4] www.skb.se/GAP.