

## Solubility of Au in Cl- and S-bearing hydrous silicate melts

R.E. BOTCHARNIKOV<sup>1</sup>, R. LINNEN<sup>2</sup> AND F. HOLTZ<sup>1</sup>

<sup>1</sup>Institut Mineralogie, Leibniz Universitaet Hannover,  
Callinstr. 3, 30167 Hannover, Germany  
(r.botcharnikov@mineralogie.uni-hannover.de)

<sup>2</sup>Dept. Earth and Environmental Sciences, University of  
Waterloo, Waterloo, Ontario, N2L 3G1 Canada

The solubility of Au in Cl- and S-bearing hydrous rhyodacitic and andesitic melts has been investigated at 1050°C, 200 MPa and log $f_{O_2}$  close to Ni/NiO solid oxygen buffer (NNO). Starting materials were dry glasses and fluid sources. Au capsules were used as Au source. The concentrations of Au in the quenched glasses have been determined using Laser Ablation ICP-MS (LA) with special efforts to avoid Au micronuggets. It is concluded that metal micronuggets are experimental artefacts produced by incorporation of Au into the fluids during heating up already in the early stage of the experiment. Once fluids dissolve in the initially dry glass, the precipitation of excess Au causes the formation of the micronuggets. Hence, the micronuggets do not represent quench phases and must be excluded from the analysis. The microanalytical data obtained by LA show that Au concentrations in rhyodacite and andesite vary from ~0.2 to ~1.2 ppm by weight, in general agreement with data for other melt compositions. The Au concentrations do not depend on the melt composition and increase with increasing amounts of Cl and S dissolved in the melt, demonstrating a linear correlation with the apparent activities of Cl and S in the system:

$$\text{Au (ppmw)} = 0.9327 (a_{\text{Cl}^*} \text{ or } a_{\text{S}^*}) + 0.2518; (R^2=0.90)$$

where Au (ppmw) is the weight concentration of Au in the silicate melt and  $a_{\text{Cl}^*}$  and  $a_{\text{S}^*}$  are the apparent activities of Cl and S in the system, respectively. The apparent activities of Cl and S are defined by the simplified linear relationship between volatile concentrations in the melt and activity of volatiles in the system. The maximum activity ( $a^*=1$ ) is assumed to be reached at the saturation of the systems with respect to Cl-rich brine or FeS (pyrrhotite) for Cl and S, respectively. The dependence of Au solubility on the concentrations/activities of Cl and S at a given  $f_{O_2}$  indicates that Au may form not only oxide- but also Cl- and S-bearing complexes in hydrous silicate melts.

## Influence of SO<sub>4</sub> and Mg/Ca on precipitated calcium carbonate

P. BOTS<sup>1\*</sup>, L.G. BENNING<sup>1</sup>, S. SHAW<sup>1</sup>  
AND R.E.M. RICKABY<sup>2</sup>

<sup>1</sup>School of Earth and Environment, University of Leeds, Leeds  
LS2 9JT, UK (\*correspondence: eepbo@leeds.ac.uk)

<sup>2</sup>Department of Earth Sciences, University of Oxford, Oxford  
OX1 3PR, UK

During the Phanerozoic, the chemical composition of seawater has varied significantly [1], causing major changes in the dominant carbonate minerals formed (i.e., the occurrence of calcite vs. aragonite seas; [2]). It is well established that seawater temperature and Mg/Ca ratios strongly influence the mineralogy of the precipitated carbonates [3, 4]. Sulphate, a major constituent of seawater, has also been proposed to have a significant influence on carbonate mineralogy [4], but this effect has so far not been quantified.

Controlled constant addition batch experiments were performed using a wide range of sulphate (0-100 mM) and magnesium concentrations (Mg/Ca 0-5) to determine the effect of these constituents on the calcium carbonate mineralogy. The used concentrations bracketed the estimated range of seawater values through geological time (8-30 mM sulphate and Mg/Ca 1-5.4 [1]).

Our results show that increasing SO<sub>4</sub> concentrations, favoured the formation of aragonite over calcite supporting previous predictions [4]. These results are similar to results in a SO<sub>4</sub> free system, where an increasing Mg/Ca ratio also favours aragonite [this study and 3]. Our findings indicate that existing Phanerozoic seawater models relating to the dominant calcium carbonate polymorph, which used Mg/Ca and temperature only, need to be reconsidered in light of the effect of SO<sub>4</sub>. Additionally, in a magnesium free system, the addition of SO<sub>4</sub> destabilized calcite promoting the formation of vaterite, which although unstable under atmospheric conditions, was the dominant polymorph at 30 mM SO<sub>4</sub>. Increasing the SO<sub>4</sub> concentration further, favoured the formation of aragonite. These results help us evaluate the occurrence of vaterite in rare marine environments (e.g., in the presence of (dissolving) gypsum [5]).

[1] Horita *et al.* (2002) *GCA* **66**, 3733 [2] Sandberg (1983) *Nature* **305**, 19 [3] Morse & Wang (1997) *Geology* **25**, [4] Burton (1993) *Chem. Geol.* **105**, 163. [5] Grasby (2003) *GCA* **67**, 1695.