Geophysical Research Abstracts Vol. 16, EGU2014-10128, 2014 EGU General Assembly 2014 © Author(s) 2014. CC Attribution 3.0 License.



Effect of fO_2 on phase relationship in basaltic andesites during magmatic differentiation: Control of fO_2 and sulphur speciation in piston cylinder experiments.

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Within the mantle wedge above subduction zones, oxidation reaction take place by interaction of reduced mantle rocks with more oxidized, hydrous fluids, which can cause a local drop of the solidus, resulting in partial melting (2,6,7). The resultant melts are more oxidized that their ocean floor counterparts, which has implications for their subsequent differentiation paths, the speciation of multivalent elements and the solubility and transport of chemical compounds in magmatic systems (1,4,5).

We present a series of sulphur-doped high-pressure experiments conducted to investigate the effect of oxygen fugacity on phase relationships and the behaviour of sulphur in silicate melts. Natural aphyric andesite (FM37) erupted from Laguna del Maule volcano, Chile $^{(3)}$ was selected as a starting composition. Experiments were carried out at 5kbar, 950-1150°C and variable oxygen fugacity conditions. New experiments buffered at Co-CoO and Ni-NiO buffer conditions have been performed using a new "MTB capsule design" developed in order to accurately control fO_2 by means of a double capsule containing metal-oxide buffers and a pyrex sleeve to minimise H_2 diffusion. This new design constrains oxygen fugacity to within ± 0.1 -0.2logf O_2 units of the target value. Before conducting these experiments, the assemblage was tested multiple times at 10kbar, 1000°C over 24-48 hours and demonstrated consistent, accurate fO_2 control.

Analyses of the preliminary experimental run products, from a related Chilean basaltic andesite starting composition, demonstrate a clear effect of fO_2 on phase relationships and the proportion of melt generated during experiments. Under oxidized conditions, as temperature decreased from 1150°C to 1050°C, the amount of melt decreased from 100% to \sim 80%, due to the formation of orthopyroxene, anhydrite and plagioclase. In contrast, in reduced runs the system remains nearly liquid (\sim 5% crystals) down to 950°C due to the change in sulphur speciation and onset of orthopyroxene precipitation at much lower temperatures. The change in temperature from 1150 to 950°C resulted in a drop in S content from \sim 2500ppm to \sim 1000ppm in the melt for oxidized experiments, whereas S slightly increased from \sim 3000 to \sim 3500ppm in the reduced experiments. Quantitative control over fO_2 will allow for more precise determination of phase relations and control of sulphur specification, offering a possibility of detailed reconstruction of metals enrichment in silicate melts.

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