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PHONOLITES, S-SOLUBILITY, AND SODALITE-HAÜYNE STABILITY

CARROLL, Michael¹, SCALLET, Bruno² and ANDUJAR, Juan², (1)Geology Division, Camerino University, via Gentile III da Varano, Camerino, 62032, Italy, (2)CNRS/INSU-Université d'Orléans, ISTO, UMR 6113, 1a rue de la Férollerie, Orléans, 45071, France

Sulfur solubility in magmas is known to strongly depend on such factors as melt composition, magma oxidation state (fO_2), P, and T. Unlike the more common magmatic volatiles (H_2O , CO_2), sulfur can occur in a variety of forms, mainly controlled by magma oxidation state; the most important S-species in natural systems appear to be H_2S , S_2 , and SO_2 as gas/fluid phase components, and S^{2-} , HS^- , or SO_4^{2-} , as species dissolved in silicate melts. As a result of this complexity (and possible S-rich crystals), it is not always easy to interpret the significance of observed variations in S-emissions in active volcanic systems in terms of what is happening at depth. Furthermore, estimation of S-yields to the atmosphere in older volcanic eruptions requires accurate knowledge of not only how much S was in the pre-eruptive melt (e.g., via melt inclusions), but also an estimate of the mass and fugacities of sulfur species in any pre-eruptive magmatic fluid phase.

We have conducted experiments on S-solubility in a sodic phonolitic melt composition (with, in wt% ~60 SiO_2 , 18.8 Al_2O_3 , 10 Na_2O , 5.5 K_2O), at $T = 930^\circ C$, $P = 50-390$ MPa, using mainly IHPV with controlled H_2 fugacity and S fugacity roughly controlled by using samples with different amounts of S added as elemental S. Oxidation states range from approximately -3 to +3 log fO_2 units relative to the NNO buffer. Depending on the amount of S added, the experiments range from nearly water saturated (low S added) to significantly H_2O undersaturated ($P(H_2O)$ down to $\sim 0.5 \cdot P_{total}$), with significant fugacities of H_2S or SO_2 in the fluid phase, depending on experimental oxidation state. Sulfur solubilities in these alkali-rich phonolites are generally higher than those for dacitic to rhyolitic melts reported in other studies at similar fO_2 and fS_2 conditions. While previous studies have reported anhydrite stable in oxidized, S-rich andesitic to rhyolitic melts, in the studied phonolite we observe the stabilization of S-rich Sodalite (Haüyne) with up to ~12 wt% SO_3 at pressures up to 150 MPa, whereas at higher pressures the phonolitic melts coexist with an oxygen-rich Fe-S-O immiscible liquid, but no anhydrite was observed. Additional work will help understand if Sodalite-Haüyne S (and Cl) contents in natural samples may be useful for estimating pre-eruptive S and Cl activities in magmas.

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Presenting Author

Michael Carroll

Email: michael.carroll@unicam.it

Camerino University
Geology Division
via Gentile III da Varano
Camerino 62032
Italy

Student? N

Bruno Scaillet

Email: bscaille@cnrs-orleans.fr

ISTO, UMR 6113
CNRS/INSU-Université d'Orléans
1a rue de la Férollerie
Orléans 45071
France

Juan Andujar

Email: juan.andujar@cnrs-orleans.fr

ISTO, UMR 6113
CNRS/INSU-Université d'Orléans
1a rue de la Férollerie
Orléans 45071
France

Student? N

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