Density Functional Theory Calculations on Anorthite-SO_2-H_2O

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This presentation describes the models and results of calculations performed to understand the interaction of anorthite in the presence of SO_2, or SO_2 + H_2O. Henley et al.[1] proposed that porphyry copper formation could occur due the $H_2S_{(g)}$ from magmatic gas plumes reacting with Cu^{2+} in groundwater. The hypothesized source of the $H_2S_{(g)}$ is from the reaction of the calcic-feldspar mineral anorthite ($CaAl_2Si2O_8$) and magmatic $SO_{2(g)}$[1]. In anhydrous conditions, those authors provided experimental evidence suggesting that this reaction dominates[1]:

$$2CaAl_2Si2O_8 + 3SO_{2(g)} \rightarrow 2CaSO_4 + 2Al_2SiO_5 + 2SiO_2 + 0.5S_{2(g)}$$ (Reaction 1)

When H_2O is present, the reaction is

$$3CaAl_2Si2O_8 + 4SO_{2(g)} + H_2O_{(g)} \rightarrow 3CaSO_4 + 3Al_2SiO_5 + 3SiO_2 + H_2S_{(g)}$$ (Reaction 2)

$H_2S_{(g)}$ is more stable than $S_{2(g)}$, when H_2O exists and reaction (2) is spontaneous. Reaction (2) could provide a source of $H_2S_{(g)}$ to react with Cu^{2+} to form copper sulfides.

Three hypothesized pathways for this mechanism are explored:

1. *Hypothesis 1* - The $SO_{2(g)}$ molecules in reaction (1) react to form SO_4^{2-} that reacts with Ca^{2+} to form anhydrite.
2. *Hypothesis 2* - $SO_{2(g)}$ reacts with Ca^{2+} through dipole-ion interactions to excise Ca^{2+} from the surface prior to $CaSO_4$ formation.
3. *Hypothesis 3* - H_2O molecules interact with the $SO_{2(g)}$ molecules in reaction (2) to form sulfuric acid, that reacts with the anorthite surface.

[1] Henley RW, King PL, Wykes JL, Renggli CJ, Brink FJ, Clark DA, Troitzsch U (2015) Nature Geoscience 8:210–215.