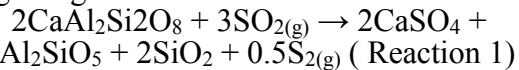


Density Functional Theory Calculations on Anorthite-SO₂-H₂O

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This presentation describes the models and results of calculations performed to understand the interaction of anorthite in the presence of SO₂, or SO₂ + H₂O. Henley et al.^[1] proposed that porphyry copper formation could occur due the H₂S_(g) from magmatic gas plumes reacting with Cu²⁺ in groundwater. The hypothesized source of the H₂S_(g) is from the reaction of the calcic-feldspar mineral anorthite (CaAl₂Si₂O₈) and magmatic SO_{2(g)}^[1]. In anhydrous conditions, those authors provided experimental evidence suggesting that this reaction dominates^[1]:



When H₂O is present, the reaction is
 $3\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{SO}_{2(g)} + \text{H}_2\text{O}_{(g)} \rightarrow 3\text{CaSO}_4 + 3\text{Al}_2\text{SiO}_5 + 3\text{SiO}_2 + \text{H}_2\text{S}_{(g)}$ (Reaction 2)

H₂S_(g) is more stable than S_{2(g)}, when H₂O exists and reaction (2) is spontaneous. Reaction (2) could provide a source of H₂S_(g) to react with Cu²⁺ 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 SO₄²⁻ that reacts with Ca²⁺ to form anhydrite.
2. *Hypothesis 2* - SO_{2(g)} reacts with Ca²⁺ through dipole-ion interactions to excise Ca²⁺ from the surface prior to CaSO₄ formation.
3. *Hypothesis 3* - H₂O 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.