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Anhydrite solubility in NaCl-H₂O solutions at high P-T: Applications to sulfur cycling

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More sulfur is subducted than is degassed at volcanic centers globally [1]. This imbalance may result in part from undetected, diffuse S degassing via deep magmatic/metamorphic fluid flow and sulfate precipitation [2]. To explore this hypothesis, we measured the solubility of anhydrite by gravimetry in H₂O-NaCl solutions at 6-14 kbar pressure, 600-800 °C and NaCl mole fractions (X_{NaCl}) of 0-0.3 in piston-cylinder apparatus. In initially pure H₂O, CaSO₄ molality (mol/kg H₂O) is low (0.01-0.04), though it is ~100 times larger at 10 kbar than at the same temperature at 1 kbar. $f\text{O}_2$ was not buffered in most experiments. Unbuffered experiments gave solubilities quite close to values at $f\text{O}_2 = \text{HM}$, because of self-buffering of CaSO₄-H₂O mixtures to high $f\text{O}_2$. Solubility is five times higher at $f\text{O}_2 = \text{NNO}$ due to H₂S in the fluid.

There is a large increase in CaSO₄ solubility with X_{NaCl} . At 800 °C and 10 kbar, $X_{\text{NaCl}} = 0.3$, CaSO₄ molality (m_{anh}) increases 200 times above the pure H₂O value. Regression of the measurements leads to the formula:

$$\log[m_{\text{anh}} - m_{\text{anh}}^0] = -1.533 + 0.00291T + 0.0413P \\ + [1.441 + 0.000160T]\log(X_{\text{NaCl}})$$

where T is temperature in Kelvins and P is pressure in kbar, and m^0 is molality in initially pure H₂O. The predicted dependencies of anhydrite solubility on X_{NaCl} and T are so great at 10 kbar that critical mixing between sulfate-rich hydrosaline melts and aqueous salt solutions is probable at 900 °C at $X_{\text{NaCl}} \leq 0.3$.

Volatile-laden mafic magmas intruded into the deep crust at plate margins may evolve concentrated salt-rich C-O-H-S solutions during crystallization, which could have important implications for sulfur transport processes. These include Pinatubo-type S-rich volcanism, oxidized granulite-facies metamorphism (e.g., Wilson Lake, Labrador), anhydrite-hematite mineralization in Abitibi-type shear-zone Au ores, and porphyry Cu-Mo ore formation. The high sulfate carrying capacity of saline fluids and the potential for S transfer to the crust as sulfide minerals become stable during cooling, suggests that sequestration in crustal fluids and/or minerals may in part account for imbalances in the S cycle.

References

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The role of volatiles on the physical properties of mantle minerals

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Our understanding of the role of volatiles in Earth and other terrestrial planets has advanced enormously during the last ~10 years due to (1) the extension of laboratory studies to higher pressures (higher fugacities), and (2) the development of defect-related atomistic models of dissolution of volatiles in minerals combined with thermodynamic analysis. Two issues are of particular importance to Earth sciences which I will review in this presentation: thermodynamics of volatile solubility and the role of hydrogen in the mechanical properties of minerals.

One of the key concepts in analyzing the thermodynamics of volatile-bearing systems is that the effects of volatiles on physical properties depend strongly on pressure through two factors: effects through the pressure dependence of fugacities of volatile species and the effects through the pressure dependence of relevant enthalpies (enthalpy of dissolution, enthalpy for thermal activation), i.e., the “activation volume” effect. The fugacities of these species increase significantly with pressure, whereas the activation volume effects usually suppress the solubility or the rate of relevant processes such as diffusion or deformation. Consequently, the net pressure dependence of relevant properties is controlled by a delicate balance of two competing factors. I will discuss a few examples of such an interplay including the solubility of hydrogen, carbon and the rate of deformation in olivine.

In more detail, the influence of volatile (such as hydrogen) on physical properties varies from one process to another. An important example is the enhancement of plastic deformation in olivine by hydrogen. The laboratory studies at various hydrogen fugacities (to ~15 GPa) demonstrate that hydrogen enhances deformation of olivine in an anisotropic way: deformation in one orientation (one slip system) is enhanced more than another. This results in changes in lattice-preferred-orientation (LPO) that controls seismic anisotropy. The conditions under which a particular LPO dominates have been determined in the lab and the scaling laws to extrapolate these results to Earth are formulated. Implications of these results on geodynamic interpretation of seismological observations will be discussed.