

Model crustal fluids at high P and T : Implications for aluminum transport

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Fluid-rock interaction associated with metamorphism and magmatism causes mass transfer in the Earth's crust. To understand metasomatism in model crust at high P and T , we investigated the solubilities of K-feldspar (K-fsp), muscovite (ms) and corundum (co) in H_2O at 700 °C and 10 kbar. Starting materials of natural microcline, single corundum crystals, reagent $KSi_3O_{6.5}$ (KS3) and specpure H_2O were reacted in a piston-cylinder apparatus. Fluid compositions were determined by weight loss of K-fsp and co and phase-equilibrium bracketing methods. K-feldspar and ms dissolve incongruently at the investigated pressure. With increase of 0.021 to 0.45 m KS3, Al increased from 0.012 to 0.170 m and coexisting mineral assemblage changed from co, through ms, to K-fsp. Our results locate two invariant points: I1, co + ms + fluid (0.082 m Al, 1.32 m KS3) and I2, K-fsp + ms + fluid (0.16 m Al, 2.69 m KS3). Total solubility of Al and SiO_2 in the presence of dissolved K is considerably higher than in pure H_2O at 700 °C and 10 kbar; e.g., co solubility in the presence of dissolved KS3 is up to fifty times higher than in pure H_2O at the same P and T , and SiO_2 solubility in the presence of K-fsp is at least 0.83 mol/kg H_2O , which is higher than the SiO_2 in H_2O in equilibrium with quartz at the same P and T (0.68 molal). Preliminary experiments at quartz saturation at the same P and T provide the pH buffering assemblages K-fsp + ms + qtz (J1) and ky + ms + qtz (J2) and give nearly identical results. Fluid composition at J2 is 0.07 m Al and 0.098 m KS3, and at J1 is approximately 0.173 m Al and 0.264 m KS3. The results imply that the presence or absence of quartz does not effect the Al solubility for the investigated mineral assemblages. The fluids of the experiments are models of aqueous solutions equilibrated with common crustal bulk compositions such as metapelite and peraluminous and metaluminous granite. The results show that the dissolved Al content in the fluid increases as the bulk rock Al declines; i.e., a fluid in equilibrium with a model metaluminous granite has a higher Al content than one in equilibrium with a model metapelite. The high measured Al concentrations in H_2O -rich fluids indicate that substantial Al transfer may occur at deep-crustal metamorphic conditions, even at low water-rock ratios. The enhanced Al solubility is a strong indication for Al-K and Al-K-Si complexing.

Influence of fO_2 on the precipitation of Fe-poor sulfide minerals

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The Skaergaard Intrusion (East Greenland) differs from other layered intrusions in that it contains disseminated, stratiform Pd-Au mineralizations. In comparison with the classic disseminated sulfide-PGE horizons such as the Merensky reef in the Bushveld Complex or the J-M reef at Stillwater, the Platinova reef occurs at a much higher, chemically more evolved stratigraphic level in the cumulate pile in magnetite-quartz-rich cumulates. Sulfide mineralogy dominated by metal-rich Cu sulfides like bornite, and the noble metals associated with the sulfide are Pd and Au, mostly as alloys with (Cu,Fe)(Au,Pd,Pt). Typical Fe-Ni-dominated sulfides like pyrrhotite or pentlandite are absent.

Several processes have been discussed to explain Cu-enriched, Fe-depleted Pd-Au-enriched sulfide horizons: 1) fractional crystallization of $(Fe,Ni)_{1-x}S$ monosulfide leading to Cu enrichment in the derivative sulfide melt, 2) modification of Fe-Ni-sulfides by infiltration of Cu-enriched postmagmatic fluids, and 3) sulfide oxidation.

To simulate sulfide oxidation experimentally, we add to an $(Fe,Ni,Cu)_{1-x}S$ monosulfide composition varying amounts of hematite and equilibrate these mixtures in welded evacuated SiO_2 glass capsules at temperatures ranging from 1050 (superliquidus) to 700°C (subsolidus). Hematite reacts with the FeS component of the sulfides according to $2 FeS + 2 Fe_2O_3 = 6 FeO + S_2$, raising fS_2 and sequestering FeO to the sulfide melt. In the subsolidus region, the reaction is $6 FeS + 24 Fe_2O_3 = 18 Fe_3O_4 + 3 S_2$, raising fS_2 and stabilizing magnetite. The sequence of oxidation of sulfide species follows broadly the electromotive series, first FeS, then NiS, and finally Cu_2S and CuS, eventually producing Cu-rich sulfides like bornite that coexist with metallic Cu, as observed in the Platinova reef. Microprobe analyses of the first experiments at 1050°C revealed a successive increase in oxygen (O_2) content in the sulfur melt at the expense of S_2 , from < 0.5 wt.% (detection limit) to 7 ± 1 wt.% O_2 in charges with > 30 wt% hematite. Iron also increases with increasing O_2 content in the melt, suggesting that oxygen dissolves in the sulfide melt principally as FeO and/or $FeO_{1.5}$ complexes. In the presence of sulfide melt oxidation to above the fayalite-magnetite-quartz equilibrium is difficult because the FeO component in sulfide melt tends to react with to SiO_2 glass, stabilizing fayalite and constraining fO_2 to near the FMQ equilibrium. In SiO_2 glass, oxidation to beyond FMQ is possible only in the subsolidus temperature region.