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Reversed determination of the reaction: Phlogopite + quartz = enstatite + potassium feldspar + H_2O in the ranges 750–875 °C and 2–12 kbar at low H_2O activity with concentrated KCl solutions

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ABSTRACT

The reaction of phlogopite plus quartz to enstatite, potassium feldspar, and aqueous fluid in the system KMASH-KCl was reversed at 2–12 kbar and 750–875 °C and at low H_2O activities by reversal of the H_2O content of concentrated KCl solutions equilibrated with product and reactant assemblages. Synthetic 1M phlogopite [$KMg_3AlSi_3O_{10}(OH)_2$] and enstatite ($MgSiO_3$) maintained end-member stoichiometry throughout, and the potassium feldspar ($KAlSi_3O_8$) was a high sanidine, based on unit-cell refinements. The broad P-T-X_{H_2O} and narrow reversal ranges of this investigation were possible because of the low and well-defined H_2O activity, yet powerful fluxing action, of concentrated KCl solutions. Solubility experiments on quartz and potassium feldspar in our P-T-X_{H_2O} range showed that fluid-phase solution of silicate constituents was too small to have affected the H_2O activity in the experiments. The new determinations are more definitive than previous work done at very low pressures with pure H_2O or in CO_2-H_2O mixtures. They establish the standard free energy of the reaction in the experimental range with an uncertainty of about 1 kJ and indicate that the synthetic phlogopite has maximal (Al-Si) disorder under our experimental conditions. The standard enthalpy of reaction at 298 K is 106.54 ± 2.0 kJ (2σ) based on our reversals, a value 6 kJ less positive than that currently used by many workers in calculations of biotite stability and H_2O activity in the petrogenesis of high-grade metamorphic rocks. The lower thermal stability that we find for phlogopite requires revision in estimates of H_2O activity of granulite facies metamorphism: typical values for the natural assemblage orthopyroxene-biotite-garnet-potassium feldspar-plagioclase-quartz at deep-crustal metamorphic conditions (750–850 °C, 5–10 kbar) are a_{H_2O} = 0.4–0.6 compared with values of 0.15–0.30 which would have been estimated with previously available data on phlogopite stability. An important consequence of the expanded H_2O activity range of granulites is that alkali chloride solutions of only moderate concentration [X_{H_2O} = 0.5–0.7], which are the values observed in actual fluid inclusions in many kinds of igneous and metamorphic rocks, are a feasible alternative to the vapor-absent conditions considered necessary by many workers based on previous low estimates of a_{H_2O}. Participation of concentrated brines in deep-crust/upper mantle metamorphic processes enables alkali metasomatism and other kinds of chemical transport in an aqueous fluid without large-scale melting of the crust.