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THERMOCHEMICAL DATA FOR POTASSIC-CHLORO-HASTINGSITE AND DETERMINATION OF AQUEOUS CHLORIDE CONTENTS

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The interaction between Cl-rich fluids and amphiboles in rocks is an area of study useful for understanding geological processes such as the formation of economic deposits, seawater-crust interaction and metasomatism in rocks. This is of interest because Cl aids in the transport of ore-forming minerals, and this data is useful for tracking these hydrothermal fluids in metamorphic rocks. Currently there is very little thermochemical data on Cl-rich amphiboles. Values for ΔH_f° and S° for potassic-chloro-hastingsite ($\text{KCa}_2(\text{Fe}_4\text{Fe}^{3+}(\text{Al}_2\text{Si}_6)\text{O}_{22}\text{Cl}_2)=\text{KCH}$) have been derived here from the upper-thermal stability curve of a K-Cl-rich amphibole.

Synthetic amphiboles close to KCH ($\text{K}_{0.8}\text{Ca}_{1.9}(\text{Fe}_{3.8}\text{Fe}^{3+}_{0.8}\text{Al}_{0.4})(\text{Al}_{1.6}\text{Si}_{6.4})\text{O}_{22}\text{OH}_{0.4}\text{Cl}_{1.2}$) were made at pressures of 3-3.5 kb and 500-800°C in gas vessels pressurized with mixed H_2 -Ar to achieve an f_{O_2} near the NiNiO oxygen buffer. Reversal reactions were done using equal mixtures of the amphibole and its breakdown products in $\text{Ag}_{50}\text{Pd}_{50}$ capsules, locating the boundary at 2kb/735°, 3kb/773°, 4kb/840°, and 7kb/950°C. The end-member reaction is $4\text{KCH} = 4\text{An} + 1\text{Qtz} + 4\text{Hed} + 7\text{Fay} + 2\text{FeCl}_2 + 4\text{Syl} + 1\text{O}_2$. Phases were analyzed by electron microprobe. Ideal activity of KCH was found to be 0.169 in amphibole. A volume for KCH of $295.57\text{ cm}^3/\text{mol}$ was obtained from Rietveld refinements of powder diffraction data for a series of related synthetic amphiboles. C_p (in kJ/mol) of KCH was estimated as $1.15 + 1.04 \times 10^{-4}(T, \text{K}) - 10643.5 / T^2 - 6.40/T^{1/2}$. Combining these data with the activities (AX62, Holland, 2019) and data for the other phases in the Holland & Powell (2011, JMG) database, we are able to calculate $\Delta H^\circ = -10640.6 \pm 7\text{ kJ/mol}$ and $S^\circ = 764.6 \pm 6\text{ J/K}\cdot\text{mol}$ for KCH.

These thermochemical data were used to determine the aggregate Cl activities of the metamorphic fluids that formed the high-grade iron formations of the Beartooth Mtns, Montana (Henry & Daigle, 2018, AmMin). Using the reported mineral analyses, we were able to determine activities of KCH in amph (0.0062-0.021), fs (0.3-0.4), alm (0.2-0.3), and hed (0.4-0.5). Combining these with the rxn $\text{Fs} + \text{KCH} = \text{Qtz} + \text{Alm} + 2\text{Hed} + 0.5\text{Mt} + 0.5\text{FeCl}_2(\text{aq}) + \text{KCl}(\text{aq})$ at 7 kb and 800°C, we can determine the aggregate molality of Cl as 1-9 m, indicating relatively concentrated brines were involved. A clear correlation between the $a_{\text{ideal KCH}}$ and the mCl can also be seen in this locality.

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