Natural Mg-Fe clinochlores: Enthalpies of formation and dehydroxylation derived from calorimetric study


Abstract

This paper presents the results of the first experimental thermochemical investigation of two natural trioctahedral chlorites (clinochlores). The study was performed with the help of a high-temperature heat-flux Tian-Calvet microcalorimeter. The samples were characterized by X-ray spectroscopy analysis, X-ray powder diffraction, thermal analysis, and FTIR spectroscopy. The enthalpies of formation of clinochlores were found using the melt solution calorimetry method to be: –8806 ± 16 kJ/mol for composition \(\text{[Mg}_4\text{Fe}_{10}\text{Al}_8\text{]}\text{[Si}_8\text{Al}_8\text{O}_{20}\text{]}\text{(OH)}_8\) and –8748 ± 24 kJ/mol for composition \(\text{[Mg}_4\text{Fe}_{10}\text{Al}_8\text{]}\text{[Si}_8\text{Al}_8\text{O}_{20}\text{]}\text{(OH)}_8\). The experimental data for natural samples allowed calculating the enthalpies of formation for end-members and intermediate members of the clinochlore (\(\text{[Mg}_4\text{Al]}\text{[Si}_8\text{Al}_8\text{O}_{20}\text{]}\text{(OH)}_8\)) and chamosite (\(\text{[Fe}_8\text{Al]}\text{[Si}_8\text{Al}_8\text{O}_{20}\text{]}\text{(OH)}_8\)) series. An important feature of the clinochlore structure is the presence of two distinct hydroxyl-containing octahedral layers: the interlayer octahedral sheet and octahedral 2:1 layer; the enthalpies of water removal from these positions in clinochlore structure were determined as: 53 ± 20 kJ/(mol·H₂O) and 131 ± 10 kJ/(mol·H₂O), respectively. These obtained first thermodynamic characteristics of Mg-Fe clinochlores can be used for quantitative thermodynamic modeling of geological and industrial processes including clinochlores of different composition.

Keywords: Clinochlore, chlorite, thermochemistry, microcalorimetry, enthalpy of dehydroxylation, enthalpy of formation

Introduction

Clinochlore is a widespread magnesian chlorite, which is formed during the processes of hydrothermal-metasomatic and metamorphic changes of ultramafic and carbonate rocks; sometimes it is formed in the hydrothermally altered zones around ore bodies. This mineral also occurs as a result of the hypergenic processes in modern sediments, in the weathering crust, and in soils. Several exchange equilibria involving Mg-Fe clinochlores were proposed as geothermometers and geobarometers (Laird 1988). The currently used nomenclature (Bailey 1988; Guggenheim et al. 2006) recommends for clinochlore the following formula \(\text{R}^2\text{Al}[\text{Si}_8\text{Al}_8\text{O}_{20}](\text{OH})_8\), where \(\text{R}\) is dominant octahedral cation \(\text{Mg}^{2+}\): in natural samples the isomorphic admixture of \(\text{Fe}^{2+}\) in this position almost always presents.

The clinochlore structure consists of three-layer packages of 2:1 type, which alternate with the octahedral interlayer hydroxide sheets. The minerals of this group have numerous polytypic modifications with different arrangements of the layers in the structure. An important feature of the clinochlore structure is the presence of two distinct hydroxyl-containing octahedral layers (inside the 2:1 packages and between them) that distinguishes chlorites from other layered minerals. Villiéras et al. (1993, 1994) indicated that the first step of water removal through heating of a magnesian chlorite (dehydroxylation of interlayer octahedral sheet) leads to the formation of a microporous “modified chlorite structure.” Although this dehydroxylation process was explored with the help of various physicochemical methods in the works mentioned above, quantitative thermal characteristics of this process were not determined.

The available data on thermodynamic properties of clinochlores of different compositions are summarized in Table 1. These data were obtained mainly by using evaluations or calculations based on the phase-equilibrium experiments. The results of calculations on the experimentally studied equilibria for clinochlore are given in the reference books and the bulletins on the thermodynamic characteristics of minerals (Robie and Hemingway 1995; Holland and Powell 1998, 2011). Several authors (Hemingway et al. 1984; Gailhanou et al. 2009) studied clinochlores with the different contents of ferrous using an adiabatic calorimetry method; for these substances the low-temperature heat capacities were measured and the values of standard entropies were calculated. The enthalpy of formation of the Fe-rich clinochlore was determined by means of acid solution calorimetry in the work of Gailhanou et al. (2007). Kittrick (1982) calculated the values of Gibbs energy of formation of two samples of the Mg-Fe clinochlores using the solubility data.

The values of the enthalpies of formation for clinochlore with theoretical composition differ significantly from each other. The data for iron-containing species of clinochlore related to the different mineral compositions and therefore it is difficult to use them for modeling \(P-T\) equilibria involving clinochlores and for...