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Research paper

Thermal behavior of chlorites of the clinochlore-chamosite solid solution series: Oxidation of structural iron, hydrogen release and dehydroxylation

Annett Steudel [a,b,*], Reinhard Kleeberg [c], Christian Bender Koch [d], Frank Friedrich [e], Katja Emmerich [a,b]

[a] Competence Center for Material Moisture (CMM), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[b] Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[c] Institute of Mineralogy, TU Bergakademie Freiberg, Brennhausgasse 14, 09596 Freiberg, Germany
[d] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
[e] Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

The thermal reactions of natural trioctahedral chlorites of the clinochlore-chamosite solid solution series were studied by simultaneous thermal analysis supplemented by comprehensive mineralogical analysis. The Fe(II) and Fe(III) amount varied between 0.09 and 4.15 p.f.u. and 0.06 and 0.22 p.f.u., respectively. Content and distribution of Fe(II) determined strongly the thermal behavior. The oxidation of Fe(II) to Fe(III) took place prior or occurred in parallel to the dehydroxylation (DHX) of the interlayer octahedral sheet (IOS). During the oxidation, one electron is transferred to the proton of the octahedral hydroxyl groups forming either H_2 in N_2 atmosphere or reacting further to H_2O in synthetic air (SynA). Thereby, the ratio of mass loss of both DHX of IOS and the 2:1 layers varied in dependency of the Fe(II) position. At high Fe content in chlorites and bulk materials, ferromagnetic phases occurred after heating under N_2.

1. Introduction

Chlorites are rock-forming clay minerals mostly found in low- to medium-grade metamorphic rocks as hydrothermal alteration products of ferromagnesian minerals in igneous rocks and in sediments together with various clay minerals (Deer et al., 1996). The high amount of water bound as hydroxyl groups in the structure makes chlorite as a key mineral in upper mantle mass transport and melting processes in subduction zones (Zanazzi et al., 2009). Furthermore, it determines firing properties of ceramic clays (Barlow et al., 1997) including the thermal activation of clays to produce pozzolans for supplementary cementitious materials. Thus, detailed understanding of the thermal behavior of chlorites, especially dehydroxylation (DHX), is essential in various scientific and engineering fields.

DHX of chlorites occurs above 400 °C in two distinct steps. DHX of the interlayer octahedral sheet (IOS) is followed at higher temperature by DHX of the 2:1 layer (Smykatz-Kloss, 1974; Villiéras et al., 1993). The DHX of the IOS and formation of the "modified chlorite structure" are commonly utilized to identify chlorites in clays also containing 1:1 layer silicates of the kaolinite or serpentine group (e.g., Moore and Reynolds, 1997). While the crystal structure of partially dehydroxylated chlorites was studied in detail (e.g., Brindley and Ali, 1950; Zhan and Guggenheim, 1995) only few studies have focused on the coupled process of Fe^{2+} oxidation and DHX of both the IOS and the 2:1 layer during heating (Caillère and Hénin, 1957; Borggaard et al., 1982; Prieto et al., 1991b). Furthermore, these studies are vague regarding the position of Fe^{2+} within the chlorite structure, the electron transition that is accompanying the Fe^{2+} oxidation and the mass loss ratio of both DHX. Our own preliminary studies revealed a ratio of mass loss for both DHX steps different from 3:1 for ferroan chlorites (see further below).

Trioctahedral chlorites include two octahedral sheets, where the positively charged (+1 p.f.u.) IOS compensates the negative charge (−1 p.f.u.) of the 2:1 layers. Both octahedral sheets are trioctahedral (Guggenheim et al., 2006) and the charge is generated by substitution through trivalent atoms in the IOS or the tetrahedral sheet of the 2:1 layers. The octahedral sheet in the 2:1 layer contains one M1 and two M2 positions. The M1 position is trans-bonded to OH and the M2 positions are cis-bonded to OH. The IOS contains two M3 (mirror plane at the shared edge) and one M4 (with inversion center) positions. Trivalent cations tend to concentrate into the smaller M4 positions (Smith et al., 1997).

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[*] Corresponding author at: Competence Center for Material Moisture (CMM), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

E-mail address: annett.steudel@kit.edu (A. Steudel).

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The DHX of iron-free clinochlore occurs in two steps:

$$\begin{aligned}\mathrm{DHX_1}:\ & [\mathrm{Mg_2Al(OH)_6}][(\mathrm{Si_3Al})\mathrm{Mg_3O_{10}(OH)_2}]\rightarrow[\mathrm{Mg_2Al(O_r)_3}]\\ & [(\mathrm{Si_3Al})\mathrm{Mg_3O_{10}(OH)_2}]+3\mathrm{H_2O}\\ \mathrm{DHX_2}:\ & [\mathrm{Mg_2AlO_3}][(\mathrm{Si_3Al})\mathrm{Mg_3O_{10}(OH)_2}]\rightarrow[\mathrm{Mg_2AlO_3}]\\ & [(\mathrm{Si_3Al})\mathrm{Mg_3O_{10}(O_r)}]+\ \mathrm{H_2O}.\end{aligned}$$

During DHX_1 three water molecules are released from the IOS between 400 and 700 °C, which results in a mass loss of $\Delta m_1 = 9.72$ mass-%. DHX_2 causes release of one water molecule from the 2:1 layers between 600 and 900 °C, corresponding to a mass loss of $\Delta m_2 = 3.24$ mass-%. The ideal stoichiometric ratio of $\Delta m_1:\Delta m_2$ equals 3:1. Following the second DHX the structure decomposes and forsterite, enstatite, and spinel may form (Villiéras et al., 1993; Barlow et al., 1997).

A solid solution series between the Mg-bearing endmember (clinochlore) and the ferroan endmember (chamosite) exists (Bailey, 1988), but compositional variability affects the DHX and formation of high temperature phases considerably (Barlow et al., 1997). Structural Fe^{2+} lowers the DHX temperature (T_{DHX}) as the Fe—O(H) bond is much weaker than the Mg—O(H) bond with an intermediate thermal stability of the Al—O(H) bond (Caillère and Hénin, 1957). However, the influence of Fe^{2+} oxidation on DHX during heating is not fully understood, yet.

Therefore, the aim of the present study is to unravel the thermal reactions of trioctahedral chlorites in detail.

Hence, in this paper the authors describe the thermal behavior of chlorites of the clinochlore-chamosite solid solution series studied systematically by simultaneous thermal analysis (STA). STA was supplemented by comprehensive characterization of the samples, which involved phase analysis and identification of admixed minerals by X-ray diffraction (XRD), analysis of chemical composition by X-ray fluorescence (XRF) analysis together with determination of amount and distribution of Fe^{2+} and Fe^{3+} by Mössbauer spectroscopy enabling calculation of structural formulae for each chlorite and its thermally treated aliquots. STA enabled detection of evolved gases including hydrogen during heating, and Mössbauer spectroscopy was used to characterize the initial coordination of iron and monitor Fe^{2+} oxidation as the result of the heating.

2. Material

The bulk materials (Chl1b, Chl2b, Chl4b, and Chl5b) of four chlorites (Chl1, Chl2, Chl4, and Chl5) from different locations were investigated. All chlorites belong to the clinochlore-chamosite solid solution series. The locations of Chl1b and Chl2b were unknown. The Chl4b and Chl5b both originate from Switzerland. The chlorite samples differed in paragenesis and particle size. Chl1b and Chl5b contained chlorite crystals of a diameter of 5 mm and larger. Chl2b and Chl4b were characterized by massive aggregates of small chlorite crystals. The bulk material was crushed, mortared, and sieved (<63 μm). The chlorite materials were not purified partly because the available amount was too small and partly because chemical purification could affect the chlorite composition and structure. According to preliminary XRD studies, sample Chl2b contained significant amounts of siderite. Chemical purification treatment would include hot hydrochloric acid (Angel and Scharizer, 2013), which disintegrates chlorites. However, the phase association offered the possibility to study the influence of a common accessory mineral on DHX of the chlorite and crystallization of high temperature phases.

3. Methods

The chlorite content and accessory minerals were identified and quantified by X-ray diffraction (XRD) analysis of powdered samples (diameter 20 mm, top loading). A Bruker D8 Advance A25 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a LYNXEYE XE Detector (opening degree 2.94° and 192 channels) was used. Patterns were recorded between 5 and 80° 2θ with CuKα radiation, a counting time of 3 s and a step size of 0.02° 2θ, a fixed slit of 0.18°, soller collimator of 2.5° (primary and secondary side) and a knife edge 3 mm above the specimen holder. Rietveld software "AUTOQUAN" (Version 2.8.0; GE Inspection Technologies GmbH, Ahrensburg, Germany) was utilized for quantitative analysis (Kleeberg and Bergmann, 2002). The mineral names were abbreviated according to Whitney and Evans (2010). Mineral abundances were normalized to 100 mass-% and are reported in the following text as %.

The heated samples were also analyzed by XRD for identification of recrystallization products. The available material was not sufficient to prepare standard size powder samples. Therefore, the gently ground material was spread as an ethanol dispersion on a silicon low-background sample holder. Data were recorded between 10 and 70° 2θ with the same instrumental setting as described above.

High temperature XRD measurements were performed on a heating chamber (MRI TC1200, Pysikalische Geräte GmbH now Bruker AXS GmbH, Karlsruhe, Germany) between 50 and 1000 °C in static air to observe the changes of the chlorite structure during heating. The heating chamber was installed in a Bruker D8 Advance (CuKα radiation; counting time of 0.5 s, step size of 0.015° 2θ, a variable slit system, irradiated length 12 mm, a primary soller collimator of 2.3°; a secondary soller collimator of 2.5°) and equipped with a PSD Detector (opening 1.4°). The powder was filled (top loading) in a ceramic holder (internal diameter of 18 mm and external diameter of 24 mm). The data were recorded between 3 and 70° 2θ.

The *00l* basal reflections were used to deduce the amount of Al, Fe and Mg in the structure. The position of the first basal reflection (d_{001}) is related to the amount of Al in the tetrahedral sheet in the 2:1 layers (Brindley, 1961; Brindley and Brown, 1980). The iron distribution between the IOS and 2:1 layers was determined using the intensity ratio of the 003 and 005 reflections. The parameter "symmetry" (D) represents the difference of the number of Fe(II) atoms in the octahedral sheet of the 2:1 layers ($Fe(II)_{O,2:1}$) and in the IOS ($Fe(II)_{IOS}$) (Brindley and Brown, 1980; Moore and Reynolds, 1997). Accordingly, a positive D assigns that the amount of Fe(II) in the octahedral sheet of the 2:1 layers is higher than in the IOS.

Mössbauer spectroscopy was applied to the raw chlorite samples to identify the valence state of iron, the ratio between Fe(II) and Fe(III), the distribution of oxide- and silicate-bound iron, and additionally, to determine the distribution of Fe(II) and Fe(III) in the chlorite structure. Mössbauer spectroscopy was also applied to the heated chlorite samples to identify changes in the abovementioned parameters after heating. Mössbauer spectra were recorded at 295 K with a conventional spectrometer in constant acceleration mode. The spectra were fitted using a sum of Lorentzian doublet and sextets constrained to be pairwise identical. The chlorite components were fitted following Lougear et al. (2000) used to determine the ratio between Fe(II) and Fe(III) in the chlorite, and other components were assigned using values from literature. The isomer shifts (IS) and the quadrupole shifts (QS) of Fe(III) and Fe(II) were used to allocate Fe(III) and Fe(II) to the octahedral positions in the IOS (M3, M4) or in the 2:1 layers (M1, M2). IS and QS of Fe(III) are noticeably lower compared to Fe(II). IS are in the range of 0–0.5 mm/s for Fe(III) and 1.0–1.4 mm/s for Fe(II). QS are in the range of 0.4–1.1 mm/s for Fe(III) and 2.2–2.75 mm/s (rarely 1.7 mm/s) for Fe(II) (Weaver et al., 1967; Lougear et al., 2001; Zazzi et al., 2006; Dyar and Schäfer, 2008). IS of Fe(III) in M4 position is <0.41 mm/s (Zazzi et al., 2006). Tetrahedral Fe(III) has the best constrained parameters with IS = 0.2 mm/s and QS = 0.50 mm/s (Dyar and Schäfer, 2008). The two octahedral positions (M1 and M2) in the 2:1 layers have the same IS but different QS. The QS of M1 is minimal lower compared to M2 (Lougear et al., 2001). The positions M2 and M3 are characterized by similar QS but different IS. The IS of M2 are minimal lower compared to M3 (Lougear et al., 2001).