

Dehydrogenation and dehydroxylation as drivers of the thermal decomposition of Fe-chlorites

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ABSTRACT

In addition to dehydroxylation, thermal decomposition of Fe(II)-bearing chlorites also involves dehydrogenation. Dehydrogenation does not require the presence of oxygen and readily occurs in an inert gas atmosphere via electron transfer between the OH group and octahedral Fe(II). The reaction results in releasing one hydrogen atom that forms an H₂ gas upon diffusing out of the crystallite, and leaves one structural Fe(II) oxidized, to keep the charge balance. Dehydrogenation removes structural hydrogen reducing the amount of OH groups available for dehydroxylation thus H₂O released during heating.

In the present study, the dehydrogenation was tracked thermogravimetrically (TG) for pure chlorites. Clinocllore, Fe-clinocllore, and Mg-chamosite were investigated under various isothermal and ramp-heating conditions under pure nitrogen flow. Thermally altered Mg-chamosite was analyzed ex-situ using Mössbauer spectroscopy, X-ray diffraction (XRD), and infrared spectroscopy.

Dehydrogenation and dehydroxylation were found to occur simultaneously, but by independent mechanisms during the heating of all Fe(II)-containing chlorites. The extent of these reactions was tracked using a combination of total mass loss and degree of Fe(II) oxidation. The dehydrogenation/dehydroxylation ratio varied with heating conditions. The slower the ramp-heating rate, thus the longer time at elevated temperatures before dehydroxylation starts, the greater the dehydrogenation that precedes dehydroxylation. Each studied chlorite had its unique range of isothermal temperatures where dehydrogenation can be enhanced with only minor dehydroxylation. For Mg-chamosite, a narrow range of isothermal temperatures, 390–410 °C, caused—after 48 h of heating—the oxidation of almost 70% of Fe(II), with respect to a maximum ~20% of oxidized Fe(II) after dehydroxylation-dominated ramp heating. Any lower or higher isothermal temperatures than the optimum resulted in a lower amount of Fe(III) and greater total mass losses. Enhanced dehydrogenation led to the formation of a discrete population of a ferric (oxy) chamosite phase, observed in XRD patterns with a *d*-space of 13.91 Å, coexisting with 14.17 Å of the original chamosite. The dehydroxylation and dehydrogenation of chamosite at 450 °C resulted in the broadening of 00 l XRD reflections interpreted as a mixed-layer phase that consisted of original, dehydroxylated, and dehydrogenated layers. Each particular heating protocol enhancing either dehydroxylation or dehydrogenation resulted in different compositions of the product formed after chlorite structure breakdown at 1000 °C.

Even with ramp heating, dehydrogenation can occur, especially with Fe(II)-rich chlorites, decreasing the total mass loss. The procedure for the determination of “structural water” content and “loss of ignition” and “total mass loss” commonly measured in rocks and minerals by thermogravimetric methods can be questioned for Fe(II)-bearing chlorites and hence in the case of all Fe(II)-containing phyllosilicates. In geological conditions, if dehydrogenation occurs prior to chlorite dehydroxylation, the quantity of “structural water” transported within chlorites to the metamorphic environment in subduction zones can be reduced even by 50%. If occurring in natural conditions, Fe(II)-oxidizing dehydrogenation reaction questions the applicability of chlorite in geothermometry. Increased Fe(III)/total Fe ratio results in the miscalculation of chlorite formation temperature as much as by hundreds of degrees Celsius. The presence of Fe(III) as a result of dehydrogenation should be considered for all Fe(II)-bearing phyllosilicates.

Keywords: Chlorite, dehydrogenation, dehydroxylation, oxidation, thermogravimetry, Mössbauer spectroscopy