

Systematics of H₂ and H₂O evolved from chlorites during oxidative dehydrogenation

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ABSTRACT

Thermally induced dehydroxylation and oxidative dehydrogenation drive the thermal decomposition of all Fe²⁺-containing phyllosilicates. Whereas the former produces H₂O gas, the latter results in H₂ evolution. Six chlorites representing the Mg-Fe²⁺ series from clinochlore to chamosite and biotite (as an analog of the 2:1 layer in chlorite) were investigated using thermogravimetry coupled to quadrupole mass spectrometry (TG-MS). A fast-ramp heating protocol was applied to identify if and how hydrogen gas was released from the crystal structure and whether it was quantitatively related to structural Fe²⁺ content. Dehydroxylation and oxidative dehydrogenation were tested under inert and oxidizing conditions.

H₂ liberation confirmed the H₂ gas production by oxidative dehydrogenation, as shown by an evolution of the m/z = 2 signal for chamosites, Fe-rich clinochlores, and biotite heated under nitrogen gas atmosphere. Along with H₂ evolution, H₂O (m/z = 18) was released, suggesting that dehydroxylation is a trigger for dehydrogenation. The higher the Fe²⁺ content in the studied chlorites, the more intense the H₂ evolution, thus the higher the H₂/H₂O ratios. The products of ramp-heating to 1000 °C resulted in varying amounts of newly formed Fe³⁺ (from 7 to 22%), however, biotite that converted into oxybiotite underwent almost complete oxidation, indicating a stronger tendency of 2:1 layer to dehydrogenation. The observed concurrent, but independent mechanisms of H₂ and H₂O evolution produced a feasible model of the thermal decomposition of chlorites.

Despite O₂ availability under oxidizing condition, the Fe²⁺ oxidation was not driven by attaching oxygen anions to the phyllosilicate structure, but also by dehydrogenation. Hydrogen was not detected using MS for any tested sample heated in synthetic air because any H₂ if released was instantaneously combined with external O₂, which resulted in an excess H₂O MS signal not matched by mass loss on the TG profiles of chamosite and biotite. Without coupling of the evolved gas analysis with TG, the excess H₂O produced by dehydrogenation in the O₂-bearing carrier gas would result in misleading interpretations of dehydroxylation.

Methodological and geological implications of the TG-MS experiments are discussed. The oxidation of Fe²⁺ in all Fe²⁺-containing phyllosilicates proceeds with simultaneous H₂ gas release that is not dependent on oxygen fugacity nor temperature during the mineral formation. Therefore, the correlation between Fe³⁺/Fe²⁺ and remaining hydrogen in the structure must be considered during modeling the conditions that involve chlorite as geothermobarometer. H₂ release during heating is proposed as an indicator of oxidative dehydrogenation of Fe²⁺-bearing minerals on Mars.

Keywords: Chlorite, hydrogen, evolved gas analysis, dehydrogenation, dehydroxylation, oxidation