

## Systematics of H<sub>2</sub> and H<sub>2</sub>O evolved from chlorites during oxidative dehydrogenation

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### ABSTRACT

Thermally induced dehydroxylation and oxidative dehydrogenation drive the thermal decomposition of all Fe<sup>2+</sup>-containing phyllosilicates. Whereas the former produces H<sub>2</sub>O gas, the latter results in H<sub>2</sub> evolution. Six chlorites representing the Mg-Fe<sup>2+</sup> 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 Fe<sup>2+</sup> content. Dehydroxylation and oxidative dehydrogenation were tested under inert and oxidizing conditions.

H<sub>2</sub> liberation confirmed the H<sub>2</sub> 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 H<sub>2</sub> evolution, H<sub>2</sub>O (m/z = 18) was released, suggesting that dehydroxylation is a trigger for dehydrogenation. The higher the Fe<sup>2+</sup> content in the studied chlorites, the more intense the H<sub>2</sub> evolution, thus the higher the H<sub>2</sub>/H<sub>2</sub>O ratios. The products of ramp-heating to 1000 °C resulted in varying amounts of newly formed Fe<sup>3+</sup> (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 H<sub>2</sub> and H<sub>2</sub>O evolution produced a feasible model of the thermal decomposition of chlorites.

Despite O<sub>2</sub> availability under oxidizing condition, the Fe<sup>2+</sup> 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 H<sub>2</sub> if released was instantaneously combined with external O<sub>2</sub>, which resulted in an excess H<sub>2</sub>O 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 H<sub>2</sub>O produced by dehydrogenation in the O<sub>2</sub>-bearing carrier gas would result in misleading interpretations of dehydroxylation.

Methodological and geological implications of the TG-MS experiments are discussed. The oxidation of Fe<sup>2+</sup> in all Fe<sup>2+</sup>-containing phyllosilicates proceeds with simultaneous H<sub>2</sub> gas release that is not dependent on oxygen fugacity nor temperature during the mineral formation. Therefore, the correlation between Fe<sup>3+</sup>/Fe<sup>2+</sup> and remaining hydrogen in the structure must be considered during modeling the conditions that involve chlorite as geothermobarometer. H<sub>2</sub> release during heating is proposed as an indicator of oxidative dehydrogenation of Fe<sup>2+</sup>-bearing minerals on Mars.

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