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Nonaqueous H_2 generation from Fe(II)-phyllosilicates and their H isotope signature

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The majority of broadly-accepted reactions generating H_2 gas in the presence of Fe(II)-bearing rock requires electron transfer between the recrystallizing mineral phases and water, which allows producing H_2 from H_2O. Fe(II)-bearing hydrous (ie. hydroxyl-bearing) minerals, however, can produce H_2 gas directly from their OH groups, without the presence of molecular water. Among commonly occurring rock-forming minerals, amphiboles and phyllosilicates meet the conditions for that reaction. Especially the trioctahedral variety of phyllosilicates can contain exceptionally high proportions of Fe(II) and OH.

Dehydroxylation and dehydrogenation are two competing reactions of Fe(II)-bearing phyllosilicates occurring upon their heating. The former reaction produces one H_2O molecule from two OH groups, leaving one hydroxyl oxygen atom in the structure. In contrast, dehydrogenation employs electron transfer between ^{VI}Fe(II) and hydroxyl H, resulting in the oxidation of octahedral Fe(II) and generation of H radicals forming - under O_2-free conditions - a H_2 molecule at the crystal surface. Dehydroxylation and dehydrogenation are separate reactions, resulting in different products, albeit acting simultaneously. Those two thermal reactions can be distinguished quantitatively and separated kinetically: with dehydrogenation preferred at slow heating and dehydroxylation at fast heating rate. The maximum efficiency of phyllosilicates' dehydrogenation in H_2 production can be as high as the transformation of fayalite to magnetite in aqueous environment.

Depending on their interlayer's environment, dehydroxylation of phyllosilicates may (micas) or may not (chlorite, serpentine) be associated with H isotope fractionation between the hydroxyls remaining in the structure and the released H_2O. Dehydrogenation, however, always results in H isotope fractionation, much stronger than that during dehydroxylation. Such a strong fractionation implies a specific model of proton hopping and long-range electron transfer throughout the crystal structure. Distinct δD signatures of H_2 and H_2O originating from the same mineral pool may be mistaken for the result of H_2-water equilibration in hydrothermal fluids.

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