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► **To cite this version:**

Chloé Fourdrin, Aarrachi Hanane, Christelle Latrille, Faiza Bergaya, Jean-Philippe Renault, et al..  
Dynamics and reactivity of water in natural montmorillonites. 16th International Clay Conference,  
Jul 2017, Granada, Spain. cea-02339001

**HAL Id: cea-02339001**

**<https://cea.hal.science/cea-02339001>**

Submitted on 30 Oct 2019

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## DYNAMICS AND REACTIVITY OF WATER IN NATURAL MONTMORILLONITES

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The radiolytic decomposition of water has significant impact in the nuclear industry. H<sub>2</sub> radiolytically formed by water decomposition might lead to explosion and overpressure hazards in the waste package. In the context of high level radioactive waste management, heterogeneous materials such as clay minerals (or concrete) are possible candidates around the waste package. For instance, bentonite, which major component is montmorillonite (Mt, the most representative swelling clay mineral of the smectite group), is foreseen in France as backfilling material for its swelling and retention properties. However, the significant amount of water present in the interlayer space and between the particles might enhance the H<sub>2</sub> production under irradiation, and despite the environmental significance, only a few studies discuss the water radiolysis in those systems. In this context, we have decided to investigate the dynamics and the reactivity of water molecules confined in natural montmorillonites from Camp Berteau, Marocco.

Ultrafast infrared spectroscopy of the O–D stretching mode of dilute HOD in H<sub>2</sub>O probes the local environment and the hydrogen bond network of confined water [1]. The dynamics of water molecules confined in the interlayer space of montmorillonites and in interaction with two types of cations (Li<sup>+</sup> and Ca<sup>2+</sup>) but also with the negatively charged siloxane surface was studied. The results evidenced that the OD vibrational dynamics was significantly slowed down in confined media: it went from 1.7 ps in neat water to 2.6 ps in the case of Li<sup>+</sup> cations with two water pseudolayers (2.2–2.3 ps in the case of Ca<sup>2+</sup> cations) and to 4.7 ps in the case of Li<sup>+</sup> cations with one water pseudolayer. No significant difference between the two cations was noticed. In this 2D confined geometry (the interlayer space being about 0.6 nm for two water pseudolayers), the relaxation time constants obtained were comparable to the ones measured in analogous concentrated salt solutions. Nevertheless, and in strong opposition to the observations performed in the liquid phase, anisotropy experiments evidenced the absence of rotational motions on a 5 ps time scale, proving that the hydrogen bond network in the interlayer space of the clay mineral is locked at this time scale.

Lastly, the impact of confinement on the reactivity under irradiation of confined water molecules was investigated. The radiolysis of water confined in natural montmorillonites was studied as a function of the composition of the montmorillonite, the nature of the exchangeable cation, and the relative humidity by following the H<sub>2</sub> production under electron irradiation [2]. It was shown that the main factor influencing this H<sub>2</sub> production was the water amount in the interlayer space. The effect of the exchangeable cation was linked to its hydration enthalpy. When the water amount was high enough to get a basal distance higher than 1.3 nm, then a total energy transfer from the montmorillonite sheets to the interlayer space occurred, and the H<sub>2</sub> production measured was very similar to the one obtained in bulk water. For a basal distance smaller than 1.3 nm, the H<sub>2</sub> production increased with the relative humidity and thus with the water amount.

### References:

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