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Experiment Report Form

	Experiment title: Kinetics of in-situ swelling and delamination of vermiculite by hydrogen peroxide	**Experiment number**: A01-2-1289
Beamline: BM01	**Date of experiment**: from: 22 May 2023 to: 24 May 2023 from: 21 Feb 2023 to: 24 Feb 2023 from: 25 Jun 2023 to: 26 Jun 2023	**Date of report**: 13 Sept 2023
Shifts:	**Local contact(s)**: Dmitry Chernyshow, Chloe Fuller	*Received at ESRF: 16 Sept 2023*

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Report:

Main idea

We examined process of swelling of natural clay vermiculite, in H_2O_2, DMSO, DMF, NMF and acetynitrile by synchrotron wide-angle X-ray diffraction, upon complete delamination of vermiculite crystal into the single layers. Vermiculite is a 2:1 layered silicate, composed of 1 nm thin negatively charged sheets kept together by interlayer cations. We have acquired 15 vermiculite samples originating from different areas we exfoliated the most of them into the single nanolayers using DMSO, DMF and NMF, not the other solvents. From our previous XPS experiments and diffraction experiment at BM01 beamline in ESRF, we know that the exfoliation process does not work the same for all of these vermiculite samples, and depends on the type of interlayer cation and charge of the nanosheets. Study of kinetics of reaction promoted by heat, will optimize conditions for exfoliation of vermiculite nanosheets to achieve maximum performance of exfoliation process. However, all liquids intercalated into the all examined samples, including the only one not toxic or harmful-DMSO which opened for us ability to scale up all of our activities we do with synthetic clay, such as CO_2 capture or synthesis of new materials in the clay interlayer.

Background

Vermiculite [1]–[4] shown in Figure 1 is a 2:1 phyllosilicate, consisting of 0.95 nm thin, negatively charged single nanosheets [5], [6], kept together by electrostatic interaction due to the charge compensating cations present in the interlayer, ensuring charge neutrality of the crystals. Structural formula is $(Si_{4-x}\ Al_x)^{IV}(Al_{2-y}\ Mg_y)^{VI}O_{10}(OH)_2,(x+y)M^+$ (dioctahedral) and $(Si_{4-x}Al_x)^{IV}(Mg_{3-y}M_y{}^{3+})^{VI}O_{10}(OH)_{2,}(x\text{-}y)/2Mg^{2.}$ Individual nanosheet is a "sandwich of sheets" composed from two types of atomic sheets – two tetrahedral sheets sandwiching one octahedral sheet. All tetrahedra and octahedra have metal inside: Al and Si in case of tetrahedral sheet and Al, Mg and/or M^{2+} and $M^{3+,}$ which is a divalent and trivalent metal, for the octahedral sheets. Vermiculite can be found in two different compositions, dioctahedral and trioctahedral. Interlayer cations are exchangeable, if the charge is low enough (around 0.6-0.7 per half unit cell). Exfoliation resulting into the dispersion of single sheets in liquid (water) allows large scale self-assembly production of layered nanocomposites by deposition on surface to form heterostructures, nanocomposites[1] or formation of self-standing thin films[7]. However, exfoliation into the single sheets is complicated by uneven and/or high charge distribution due to the imperfections in the structure, thus practical exfoliability of vermiculite is much more difficult than in the case of low-charge smectites, such as synthetic sodium fluorohectorite, as the charge per half unit cell varies between 0.6 – 1.0.
Even if we deal with the high charge so vermiculite is not expandable in the water as is the case of our synthetic clays fluorohectorite, we demonstrated that we can intercalate different liquids into the interlayer, which was subsequently used for complete delamination into the single sheets.

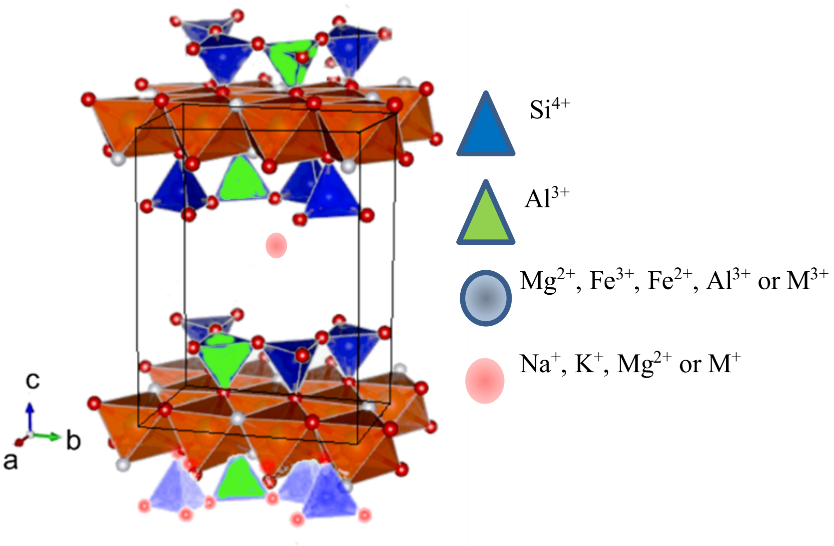

Figure 1. Structure of vermiculite clay, with the metal oxides in the middle layer, SiO_2 encapsulating sheet composed of metal oxides, with the interlayer cation in between the sheets.

Experiment

Vermiculite crystal were first crushed to the fine powder and put into the glass capillaries (diameter 1 mm), closing the capillary with glue in case of the 1WL layer hydrated vermiculite, and using glass wool for samples prepared for in-situ drying. During in-situ drying of samples, samples were heated up upon constant pumping of vapour, from 50-90 ˚C with a rate 60 K/hour and subsequently heated up to 100 ˚C with the same ramp rate and kept at 100 degrees for a time which was necessary for complete drying of the samples.
Dry samples were further exposed to liquid H_2O_2, DMF, NMF and DMSO in order to study in-situ delamination of the layers by these solvents.
Data has been processed using Bubble[8], MEDVED[9] and Fullprof[10] softwares.

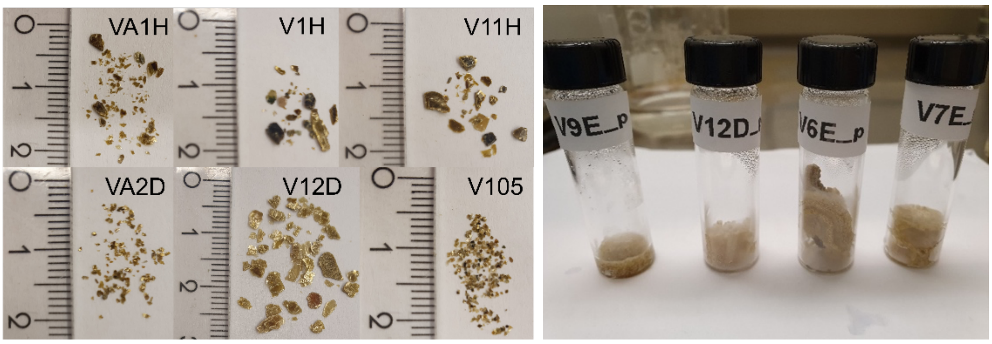

Figure 2. Examples of different vermiculite crystals (left). Swelling of vermiculite crystals in H2O2, where expansion reaches 3 orders of magnitude.

During the in-situ synchrotron experiment to observe dynamics of intercalation, we exposed vermiculite in powder form, loaded in the glass capillary (1 mm diameter) and we exposed it to droplet of individual liquids, which was sucked into the powder just by the capillary forces due to the presence of glass wool and small diameter of capillary. Use of pump to suck liquid into the powder was not needed.

Results

We observed that intercalation happens immediately after exposure of powder vermiculite to liquids we chose. However, in case of H_2O_2, sheets were very much destroyed by H_2O_2 after 10 min of exposure to peroxide, hence this solvent is not very suitable for delamination of vermiculite into the single layers (Figure 3), which lead us to decision not to use it as medium for vermiculite delamination into the single sheets and we rather use other liquids, such as DMF, NMF and DMSO (Figure 3).

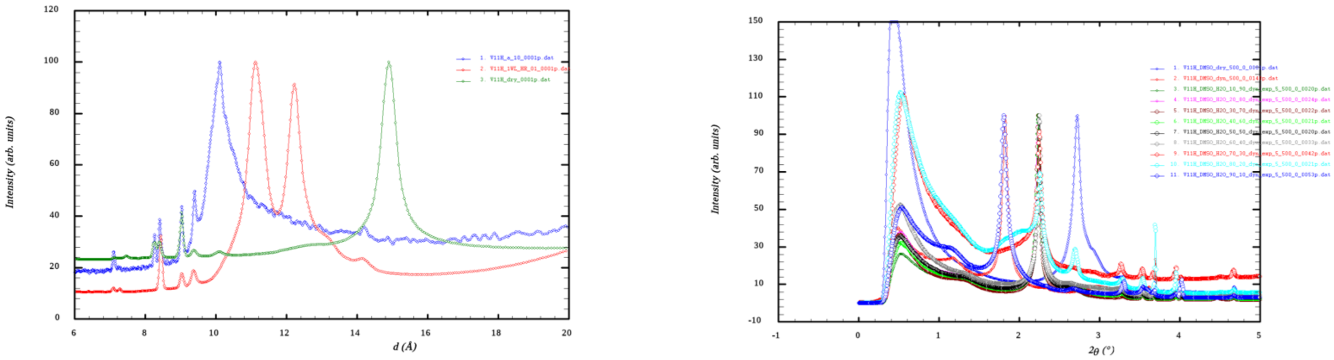

Figure 3. SXRD pattern of 3 vermiculites exposed to H2O2, showing layers with diffferent interlayer cation swell in different way (shift of the first peak on right) – left image. Swelling of the V11H vermiculite in DMSO/H2O with concentration 10-100 % of DMSO. For low content of DMSO, interlayer does not swell (peak at 2 theta 2.8), then we observe partial swelling for concentration up to 90% of DMSO until complete intercalation of DMSO for conc. of DMSO>90 % (right image).

After experiment at ESRF, we managed to exfoliate vermiculite into the single layer (2% yield for H_2O_2, 90% for DMSO). See the AFM topography image. Compete delamination of vermiculite interlayers provides us scale-up for all applications we run on synthetic clays, such as intercalation of CO2 and synthesis of other 2D materials in the clay interlayer.

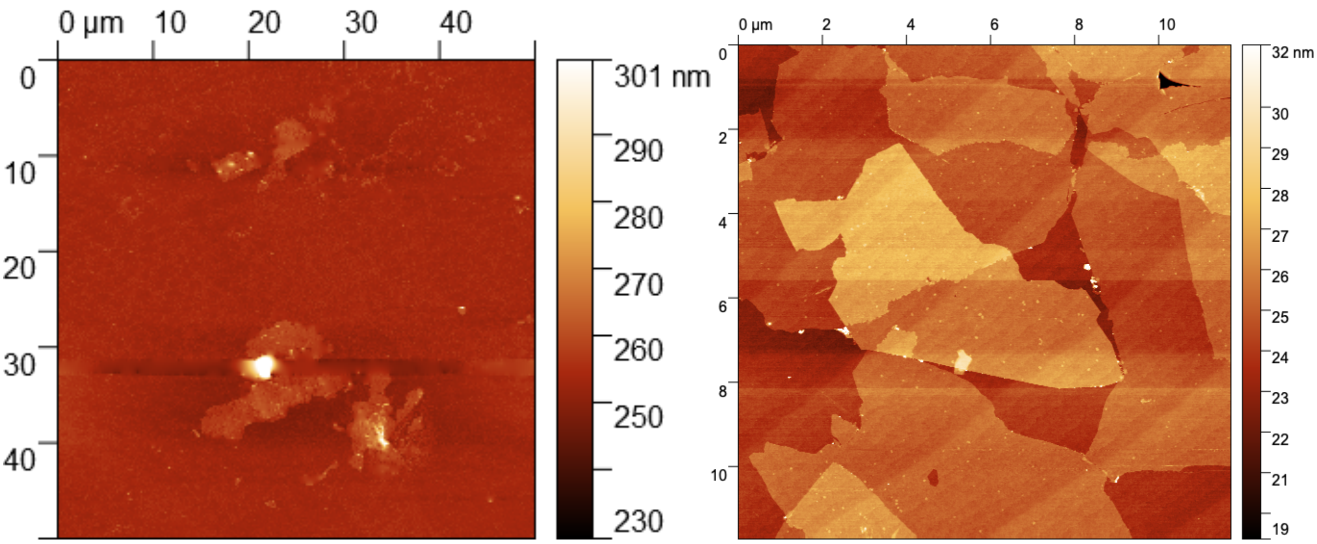

Figure 4. The AFM topography image of vermiculite single sheets from vermiculite intercalated by H_2O_2 – very small and few single layers (left) and DMSO (right), showing many single-layer overlapping nanosheets.

Conclusion

We managed to intercalate H_2O_2, DMSO, DMF and NMF into the vermiculite interlayer, which happens immediately after exposure of powder to these liquids. Following experiments in our lab lead to complete delamination of the layers into the solution of single layers. For scale up of these process, we finally use just DMSO, as it is not toxic and harmful to the environment. Synchrotron experiment allowed us to do scale up of delamination of natural vermiculite clay into the single layer and scale up all applications we have on synthetic fluorohectorite clay, which allow us the transfer of significant part of our application results to industrial level.

References

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