

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: 12 April 2022 to: 16 April 2022	Date of report: 13 Sept 2023
Shifts:	Local contact(s): Dmitry Chernyshov, Vadim Dyadkin	<i>Received at ESRF:</i> 16 Sept 2023
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Report:

Main idea

We examined process of swelling of natural clay vermiculite in water and H_2O_2 , by synchrotron wide-angle X-ray diffraction, in order to determine crystal structure and types of the cations in the interlayer, which affects swelling of these vermiculites and ability to exfoliate and delaminate them into the single sheets.

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 examined types of interlayer cations by swelling them in water, drying at 120 degrees C and exposing them to hydrogen peroxide. Only several types of interlayer cations are hydrated, so we see shift of corresponding (001) diffraction peak to higher d spacing as interlayer expands due to the water intercalation. Moreover, H_2O_2 also affects just selected interlayer cations, which helped us to determine which interlayer cations are present in different samples.

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 $(\text{Si}_{4-x}\text{Al}_x)^{\text{IV}}(\text{Al}_{2-y}\text{Mg}_y)^{\text{VI}}\text{O}_{10}(\text{OH})_2, (x+y)\text{M}^+$ (dioctahedral) and $(\text{Si}_{4-x}\text{Al}_x)^{\text{IV}}(\text{Mg}_{3-y}\text{M}_y^{3+})^{\text{VI}}\text{O}_{10}(\text{OH})_2, (x-y)/2\text{Mg}^{2+}$. 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 and presence of non-hydratable cations, 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 1.2 – 2.0, which is 2 times higher than in the case of synthetic clay.

Even if we deal with the high charge so vermiculite is not totally expandable in the water due to the presence of hydratable cations, as is the case of our synthetic clays fluorohectorite, we demonstrated that we can intercalate different water and hydrogen peroxid into selected interlayers, which was subsequently used for complete delamination into the single sheets.

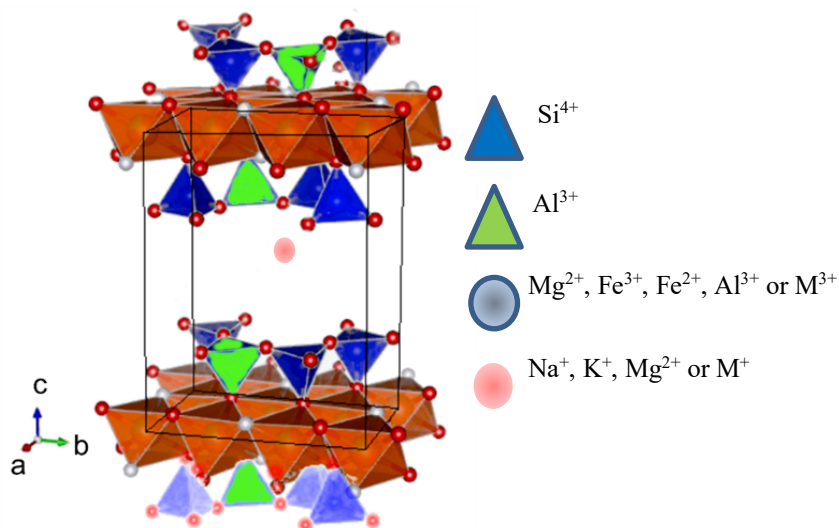


Figure 1. Structure of vermiculite clay, with the metal oxides in the middle layer, SiO_2 encapsulating sheet composed of metal oxides, with the interlayer cation in between the sheets.

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 exposed to water first, then heated up upon constant pumping of vapour, from 50-90 °C with a rate 60

K/hour and subsequently heated up to 120 °C with the same ramp rate and kept at 120 degrees for a time which was necessary for complete drying of the samples.

Dry samples were further exposed to liquid H_2O_2 , in order to study in-situ delamination of the layers. Data has been processed using Bubble[8], MEDVED[9] and Fullprof[10] softwares.

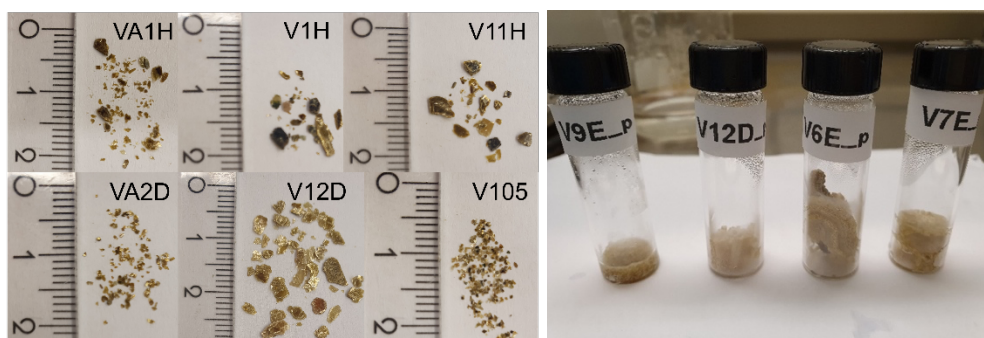


Figure 2. Examples of different vermiculite crystals (left). Swelling of vermiculite crystals in H_2O_2 , where expansion reaches 3 orders of magnitude.

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 water, just several layers were hydrated, which allowed us to determine which cations we have in the interlayer, when we combined these results with elemental analysis we have from XPS (see Table 1.) 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), but it helped us to identify other interlayer cations present in the interlayer.

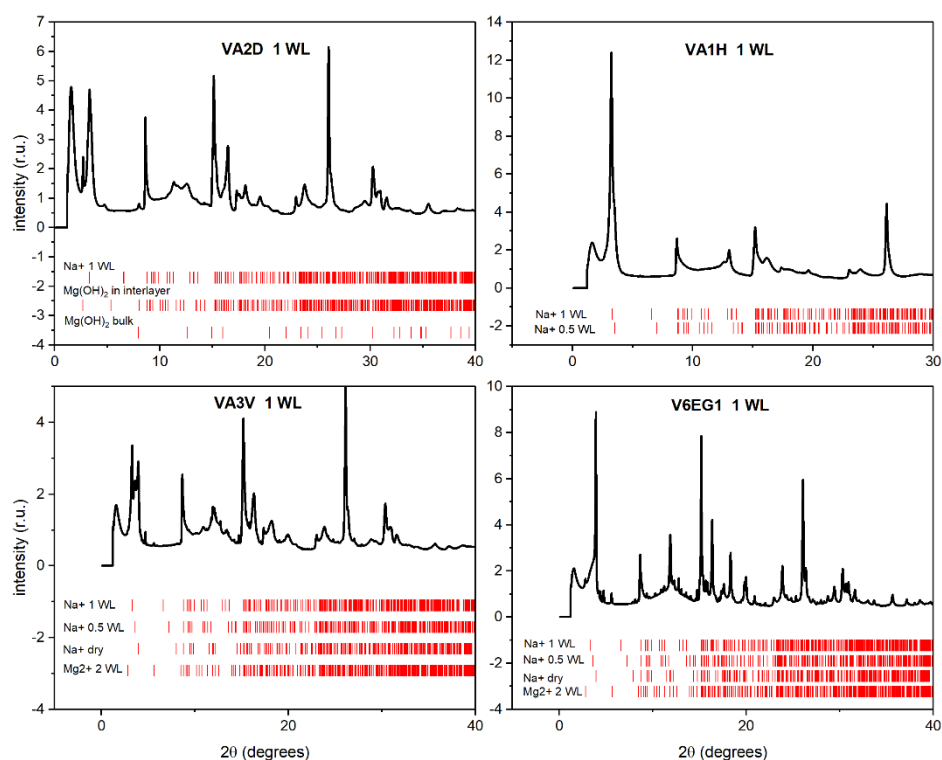


Figure 3. XRD for the 1 WL hydrated VA2D, VA1H, VA3V, V6EG1 samples.

Table 1. interlayer distance d_{001} in XRD patterns for all ions/species present in the interlayer for all samples and sample states, namely 1 WL hydrated, in-situ dried (dry Na sample) and after exposure to hydrogen peroxide. All samples except VA1H and V5D also exhibit presence of non-hydrated Mg^{2+} in the interlayer, with $d_{001} = 9 \text{ \AA}$. *mf* is shortcut for metal fluorides present in the sample. SL represents samples that has been exfoliated into the single layers.

d_{001}/I sample	K	Non-hydr. Na ⁺	0.5 WL Na ⁺	1 WL Na ⁺	1.5 WL Mg ²⁺	2WL Mg ²⁺	Mg(OH) ₂	dry Na sample	H ₂ O ₂
V3V ^{mf}		10.07	11.04	12.16	13.13	14.15		9.91	14.85
		0.92	0.56	1.00	0.33	0.21			
V13V ^{mf}			11.09	12.22		14.26		9.97	14.3
			0.88	1.00		0.30			
VA3V ^{mf,SL}		9.97	11.05	12.04		14.08		9.97	14.2
		0.87	0.70	1.00		0.30			
V2D ^{mf}		10.1	11.27	12.23		14.35		10.1	
		0.87	1.68	1.00		0.82			

V5D^{mf}	10.0	10.08	11.37			10.08	12.69
	8	0.17	1.00				
	0.17						
V12D^{mf}	10.1	10.16	11.37			10.16	
	6	0.16	1.00				
	0.16						
VA2D			11.9	12.4		14.6	
			1.68	1.00		0.88	10.06
V6EG1		10.08	11.01	12.1	14.13		10.08
		2.15	1.15	1.00	0.83		14.15
V7EG1		10.07	11.39	12.32		14.7	10.07
		0.36	0.32	1.00	0.40	0.00	14.8
V8EG4		10.04	11.26	12.22	14.13	14.64	10.04
		0.30	0.34	1.00	0.26	0.28	14.7
V9EG5^{SL}		10.05	11.35	12.33	14.1	14.65	10.05
		0.23	0.33	1.00	0.35	1.31	
V10_5		10.08	11.36	12.29		14.67	10.1
		0.27	0.35	1.00		0.38	
V11H		10.13	11.09	12.15	13.19	14.09	14.9
		0.31	0.97	1.00	0.41	0.30	0.00
V4H^{mf}	10.1	10.1	11.37	12.19	14.08		
	0.11	0.11	0.60	1.00	0.23		10.06
VA1H			11.4	12.24	14.22		9.88
			0.34	1.00	0.00		14.3

Conclusion

We managed to intercalate water and H₂O₂ into the vermiculite interlayer, which allowed us to determine presence of different cations and metal hydroxides in the interlayers.

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