

13.7.2013 by Taina Laiho

NanoGeo Finland Ltd

NanoGeo Finland Ltd is a Finnish startup company. Business of NanoGeo Finland Ltd is based on the utilization of nanoscale structures and properties of geological (mineralogical) material vermiculite. Vermiculite mineral is heated and by that way its capability to absorb ammonium ions is increased. In the waste water containing ammonium ions and in the gaseous environment containing ammonia, ammoniumvermiculite will be formed. Ammoniumvermiculite can be used to fertilize plants. Nitrogen is one of the most important nutrients. If the nitrogen contained in the waste waters that is produced by mankind could be recovered and used as fertilizer in agriculture and forestry, it would be of great importance.

Samples

Vermiculite, $(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, belongs to the group of phyllosilicates and it has an open layered structure much like mica. The 2:1-layer structure of vermiculite consists of two tetrahedral sheets bound to either side of an octahedral sheet via the plane of basal oxygen atoms. The outer two planes of the layer are formed from the basal oxygen atoms. A part of tetrahedral sites are occupied by trivalent cations instead of Si^{4+} . This substitution results in an excess of the negative charge per formula unit, which is compensated by cations in the interlayer space. In vermiculites compensating cations are hydrated Mg^{2+} in many cases.

Method

A crystal forms a three-dimensional lattice in the space and when a radiation with a suitable wavelength hits such a lattice, diffraction of the radiation occurs. An ideal powder sample consists of numerous amounts of randomly oriented tiny crystals. When a powder sample is placed in a monochromatic X-ray beam the X-rays will be diffracted from the crystal planes of the sample according to Bragg's law:

$$2d_{(hkl)} \sin \theta = n\lambda,$$

in which $d_{(hkl)}$ is the interplanar spacing for the plane with Miller index (hkl) , θ is the diffraction angle, n is the order of reflection and λ is the wavelength of the used X-ray radiation. Having a suitable wavelength various X-ray diffraction procedures have been widely used in the field of materials science. They can be used to study crystal structure, polymorphism, crystallinity and crystallite properties of the sample, for instance. Moreover, X-ray diffraction is commonly used in qualitative and quantitative analysis. This information can be utilized when structure of vermiculite is studied.

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Experimental setup

XRD is a normal method to characterize interlayer distances of vermiculite. PETRA III is one of the foremost 3rd generation synchrotron facilities in the world due to its low emittance storage ring that creates a very small and highly brilliant source. Such a source is ideally suited for experiments at extreme conditions since they require hard x-rays with high brilliance and a small focus. Beamlines P02 is designed to meet these needs by providing two experimental stations for Hard x-ray diffraction. One station (P02.1) is dedicated to High Resolution Powder Diffraction (HRPD) at ambient pressure and high/low temperatures. The ability to create extreme conditions is complemented by time resolved diffraction capabilities in order to explore the kinetics of physical processes during a phase transition. This beamline was utilized in these studies. The brilliance of the beam is 10^{19} ph / s / 0.1% bw / mA, beam energy is 60 keV and resolution is $DE/E = 2 \times 10^{-4}$.

Large flakes of vermiculite were ground using a knife-mill and sieved. Particles of size 77-125 μm were used for the studies (figure 1). During the measurement the powder was kept in polyimide capillaries with a diameter of 0,032". The following scanning electron microscopy (SEM) image presents flakes of vermiculite. Grinding of vermiculite caused delamination and breaking of the layers. The obtained vermiculite flakes were about 5-20 μm thick. Before imaging, vermiculite flakes were covered with a thin layer of gold to prevent charging of the surface.

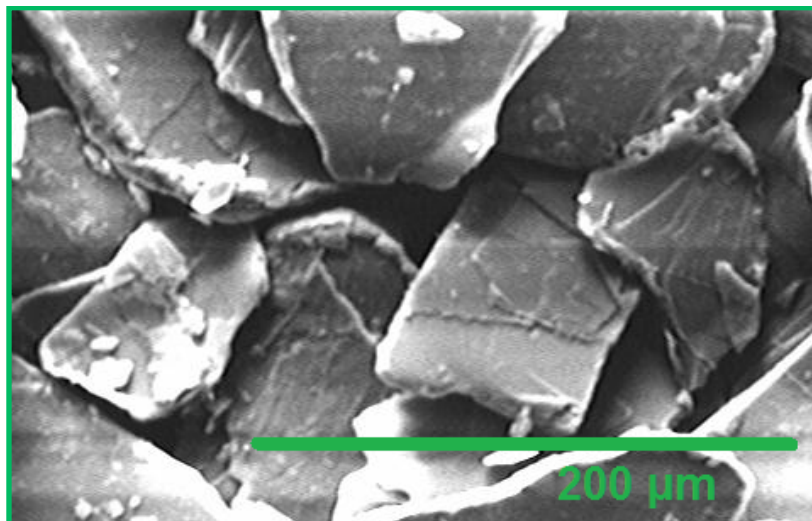


Figure 1. Vermiculite flakes imaged with scanning electron microscopy.

Results

It can be seen from all of the measured spectra that the crystallites of the powder sample are oriented preferentially so that the crystal plane with a Miller index of (0 0 2) is oriented parallel to the surface of capillary tube. This phenomenon is typical for the specimen having plate-like particles, as it was the case here.

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The distance between the layers of the sample can be determined from the diffractogram as follows. Since the (0 0 2) peak represents the first order diffraction from those layers all what must be done is to carefully determine the position of the peak and use the Bragg's law.

1) Vermiculite from different origins

The origin of mineral is an important factor. The quality of samples depend on the crystallinity and particle size of phases resulting from the geological origin of clays. That is, the variation in chemical composition of the minerals causes a change in their physical properties. These differences influence on the usability of the mineral. XRD was used in characterization of natural vermiculite from different origins (Finland, Russia and Brazil).

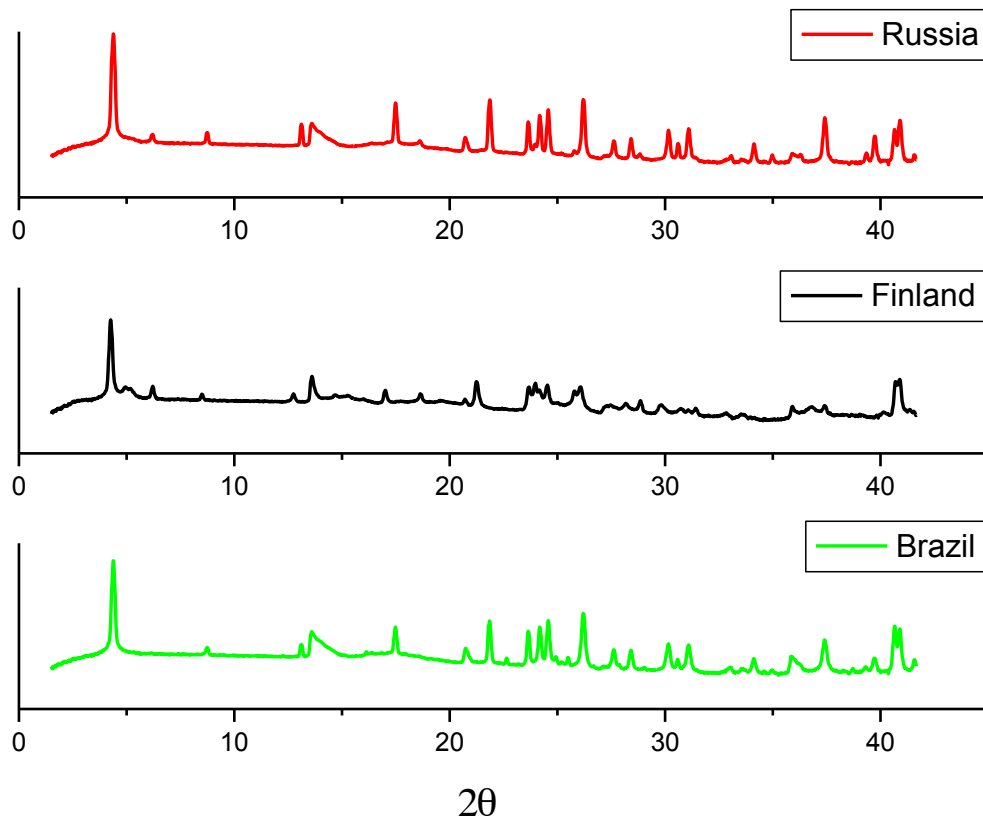


Figure 2. XRD spectra of vermiculites from different origin. (Logarithmic intensity scale.)

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2) Heat induced structural changes

Thermal behavior of vermiculite has been studied a lot. As a function of temperature the layer distance of vermiculite (about 1,6 nm) at first diminishes (to about 0,9 nm) and then starts to increase again, and the structure breaks at the end and vermiculite will become exfoliated. Different response to the heating due to the different origin of vermiculite is relevant knowledge in order to manufacture GeoTrap for ammonium absorption. Vermiculite samples from different origin were studied as a function of temperature. Temperature was increased from 25 °C to 580 °C and the speed was 5 °C per minute. XRD spectra were measured continuously during heating. Measurement time of one spectrum was 30 sec.

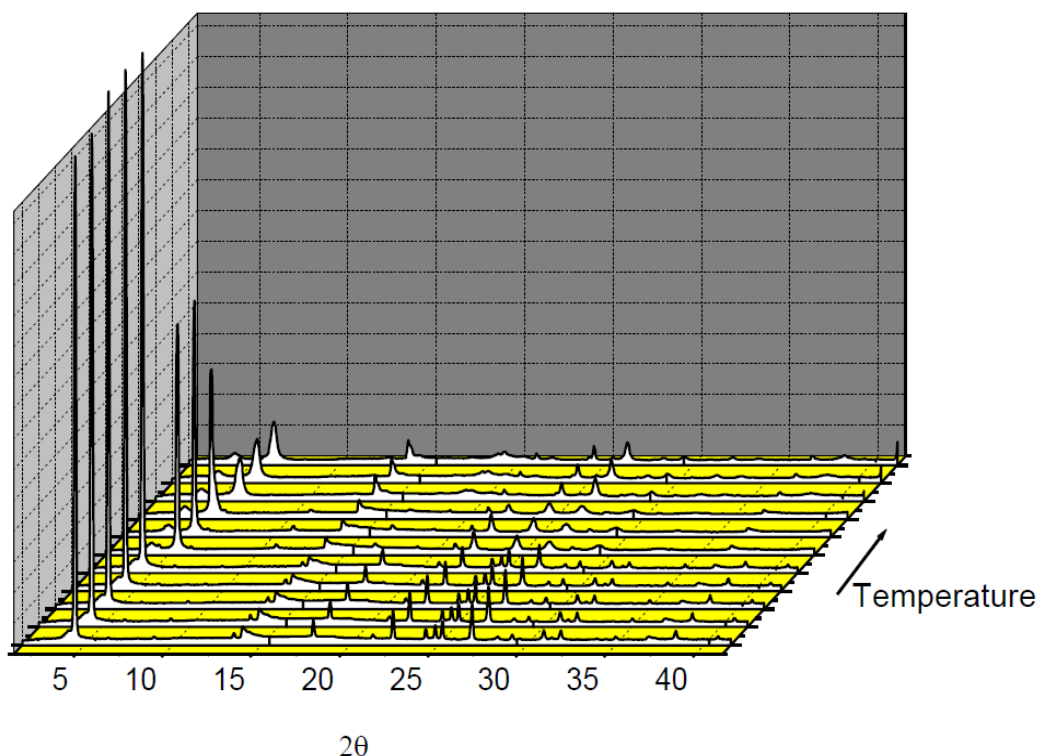


Figure 3. Temperature induced changes in Russian vermiculite.

During heating to a temperature up to 580 °C the vermiculite is dehydrated and exfoliated. During the heating, crude vermiculite passes through five discrete structural transformations, caused by the step-wise dehydration of vermiculite. Each dehydration step corresponds to the shrinking of the lattice dimensions of the vermiculite crystal. The first three steps of dehydration are reversible, whereby the second and third dehydration steps take place at temperature ranges of 190-280 °C and 300-440 °C, respectively. The last two dehydration/dehydroxylation steps are irreversible, leading to consequent decomposition of the vermiculite to talc and, further, to enstatite $Mg_2Si_2O_6$. During the first three dehydration steps H_2O is released from the lattice, but during the last two steps OH is released. The reversibly

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dehydrated vermiculite can be hydrated back in an aqueous solution, and the compressed lattice is getting expanded back to the initial state.

3) Absorption into GeoTrap

GeoTrap is a vermiculite based product of NanoGeo Finland Ltd. It has been developed to absorb ammonium ions into its lattice structure, but some nitrogen is also adsorbed to the surface. In addition to nitrogen, also some metals can be adsorbed to the GeoTrap. Determining of compounds on the surface and in the material is needed. Natural vermiculite and GeoTrap samples after different chemical treatments with ammonium nitrogen and some metals (Zn, Pb, Cd and Fe) were studied.

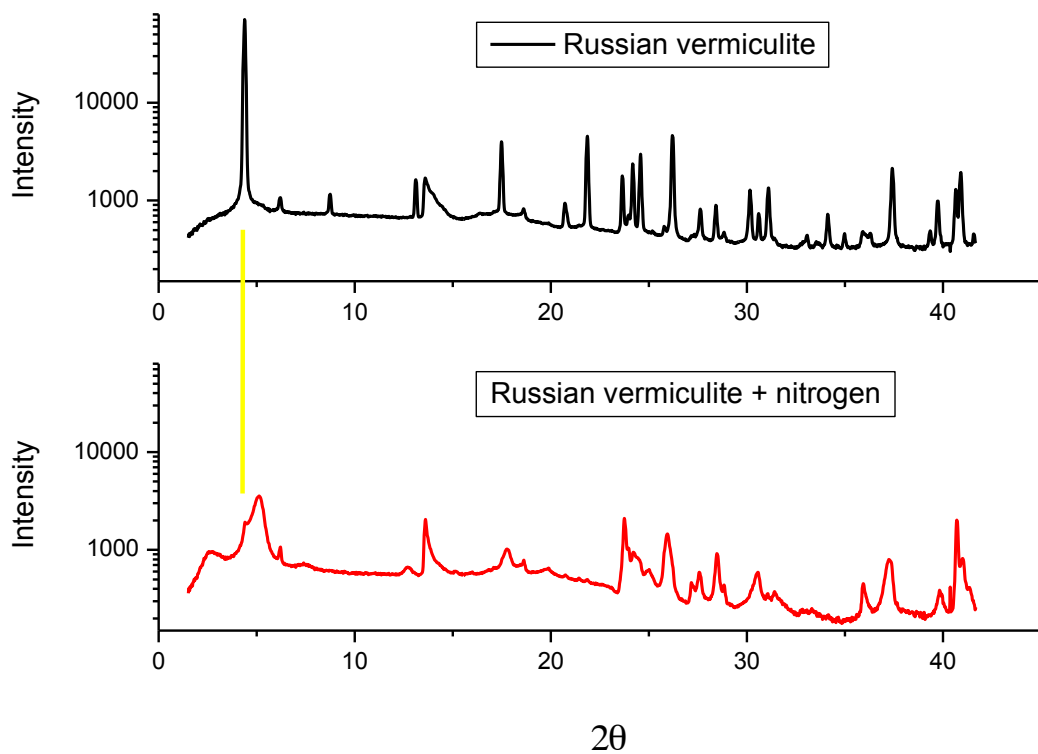


Figure 4. Structural changes are seen in the structure of vermiculite after its chemical treatment with nitrogen solution.

Ammonia is adsorbed by formation of NH_4^+ with interlayer water. First the dissociation of interlayer water is favored by the high $\text{Mg}^{2+}/\text{H}_2\text{O}$ ratio compared to the dilute aqueous solutions. Secondly the cations and water molecules are sandwiched anisotropically between rigid anion sheets with negative charges at fixed points. The exchangeable Mg^{2+} ions are presumed to lie over sites of tetrahedral substitution, and to be co-ordinated to the associat-

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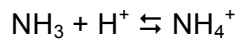
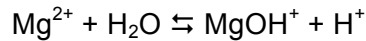
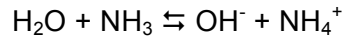
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ed triad of O^{2-} ions. Each Mg^{2+} lies much closer to one silicate sheet than the other and for each sheet only about half of the negative sites will have closely associated Mg^{2+} ions. Thus water ionization will be favored because the resulting NH_4^+ ions will satisfy the remaining negatively charged sites. Possible reactions for NH_4^+ formation by reaction with water are presented following:



Comparison of XRD spectra from natural vermiculite and ammonium treated vermiculite shows clearly, that the NH_4^+ ion causes a contraction of the layer distance and an almost complete removal of the hydration H_2O when it replaces other cations.

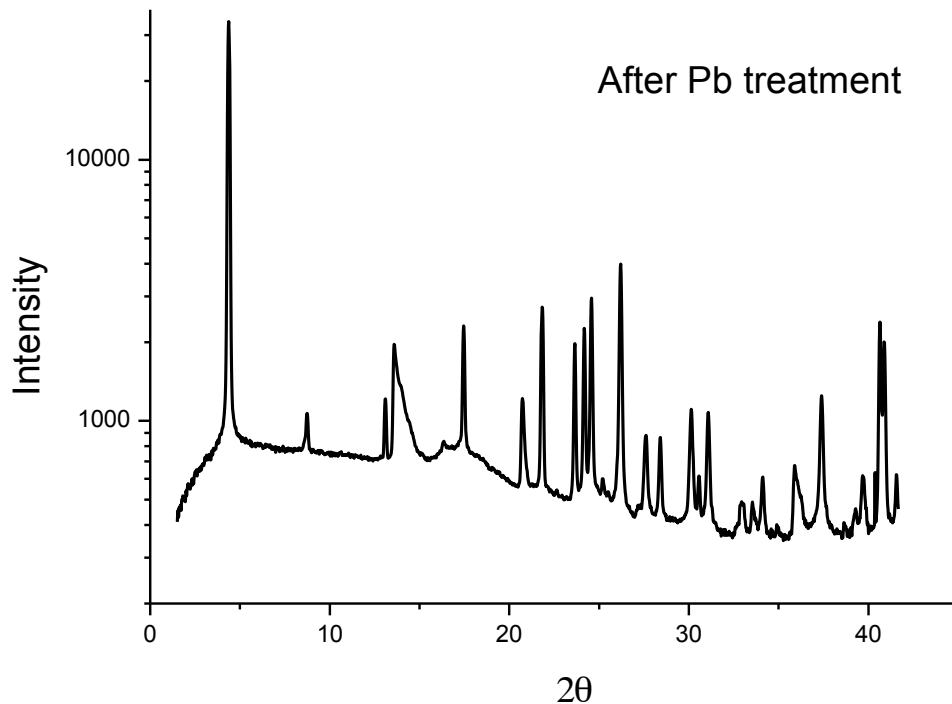


Figure 5. XRD spectrum of heat treated vermiculite after chemical treatment with cadmium solution.

Vermiculite can adsorb heavy metals via three different mechanisms: (1) cation exchange at the planar sites, resulting from the interactions between metal ions and negative permanent charge (outer-sphere complexes) and (2) formation of inner-sphere complexes through $Si-O^-$

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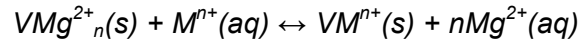
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and Al-O⁻ groups at the clay particle edges. The principal mechanism of interaction is thought to be ionic exchange which can be presented by general equation:



Where V is the vermiculite, Mg²⁺ the magnesium, n is the charges of the cation M in aqueous solution or exchange in solid. This equation shows that for each mol of exchanged magnesium, the same quantity of a cation enters in solid. The amount of exchange is related to properties of cations such as hydration volume and hydration enthalpy of cation. (3) The third mechanism is weak physical adsorption on external surfaces and on the edges of the interlamellar region. Now measured XRD spectra show no metal adsorption induced difference in the spectra.

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Measurements

NanoGeo's measurements

number of measurement	sample	description of sample	file or directory
1	24	Zn <75 µm	Taina_sample_24-00022
2	26	Pb <75 µm	Taina_sample_26-00023
3	15	Kovdor 75-125 µm	Taina_sample_15-00024
4	22	NGT MVTT 75-125 µm	Taina_sample_22-00025
5	25	Cd <75 µm	Taina_sample_25-00026
6	18	GeoSmart-old	Taina_sample_18-00027
7	6	Sokli3 75-125 µm	Taina_sample_06-00028
8	9	Sokli1 75-125 µm	Taina_sample_09-00029
9	12	Brazil 75-125 µm	Taina_sample_12-00030
10	16	Kovdor <75 µm	Taina_sample_16-00030
11	27	Fe <75 µm	Taina_sample_27-00031
12	30	GeoSmart-fresh	sample30-00057
13	08	Sokli3 + N	sample08-00058
14	17	Kovdor + N	sample17-00059
15	14	Brazil + N	sample14-00060
16	20	GeoSmart-old + N	sample20-00061
17	11	Sokli1 + N	sample11-00062
18	12	Brazil	03_sample12_heating
19	6	Sokli3	04_sample06_heating
20	15	Kovdor	05_sample15_heating
21	9	Sokli1	06_sample09_heating

Samples from different origin (different mine): Kovdor, Brazil, Sokli1 and Sokli3

Samples of different size: < 75 µm or 75-125 µm

Samples after different metal containing solution treatment: Zn, Pb, Cd, Fe

Samples after nitrogen treatment: N

Fertilizer that has been used in our latest growth experiment: NGT MVTT

Filtering sand of NanoGeo Finland Ltd.: GeoSmart Fresh, GeoSmart old

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