

Clay Minerals as an Ancient Nanotechnology: Historical Uses of Clay Organic Interactions, and Future Possible Perspectives

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INTRODUCTION.

The word "clay" has ambivalent definitions (Bergaya, 2000). On one hand it is used to define any soil particle smaller than 2 µm, but on the other hand it includes a large group of microcrystalline secondary minerals based on hydrous aluminum or magnesium silicates that have sheet like structures (Manahan, 2000).

Clay minerals have been part of human existence since antiquity (Murray, 1997; Yuan, 2004) and were used as natural nanomaterials along history for industrial and commercial uses. The first recorded applications were more than 5000 years ago, in Cyprus and Greece,

for bleaching fleece and clothes, and removal of grease and stains from it (Beneke and Lagaly, 2002; Robertson, 1986). Additional uses along history included very thin ceramics in China (Weiss, 1963), cosmetics, internal and external medicine, art and religion, construction, sealing and proofing, and assorted uses in the food industry.

There are at least two points that make clay minerals so active in natural processes, and became the key for their wide applications: (a) The very large surface area that arises from the tiny size of the particles (nano-scale), and (b) The fact that those particles are electrically charged, leading to relatively strong electrostatic interactions.

Johnston (1996) develops the concept of "active sites" adopted from biological macromolecules, and defines six different types of sites that may appear in clay minerals, contributing to its interaction with other substances, yielding unique results: (a) "broken edge" sites and exposed surface aluminol and silanol groups, (b) isomorphic substitutions, (c) exchangeable cations, (d) hydrophobic silanol surfaces, (e) hydration shell of exchangeable cations, and (f) hydrophobic sites on adsorbed organic molecules.

The latter active site leads to very interesting interactions between clay minerals and organic chemicals. Changes on the surface of the clay mineral make it specifically optimized for interactions with different types of chemical compounds: Natural clay are negatively charged, and cations can easily bind to their natural surface while negative or non polar hydrophobic chemicals will be rejected. An hydrophilic behavior will be observed, based mainly on hygroscopic water bound as hydration shell on the exchangeable cations (Lahav, 1983). Adsorption of organic cations (as ammonium based compounds deriving from decaying urine, e.g.) to the clay charged sites, exchanging the original inorganic cations, might exhibit hydrophobic moieties toward the outside surface of the "organoclay" composite. Such new surface might be optimal to bind non polar chemicals. In some cases organic cations may be even loaded in excess (charge reversal), leading to interactions with negatively charged chemicals. Morphological properties of the surface also change due to such interactions (see Fig.1): Whereas natural smectite shows dense platelets, a sponge-like structure can be obtained by the binding of the natural organic cationic polymer chitosan, to

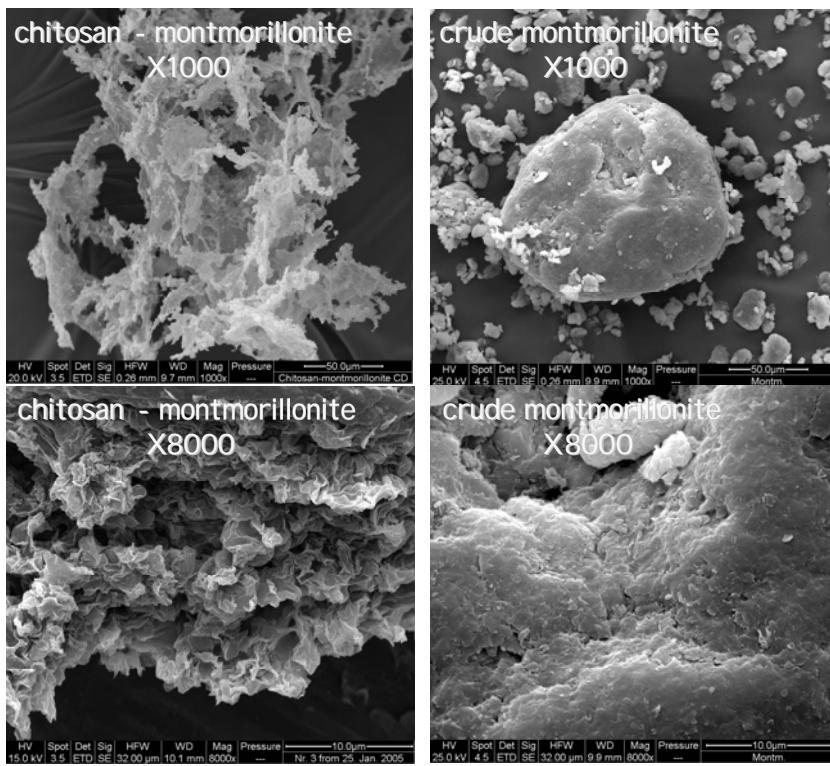


fig 1. An example of the modification in the morphology of a clay mineral (Crude SWy-1 montmorillonite, right pictures) due to the adsorption of organic cations (chitosan-montmorillonite, left pictures). Images are shown at x1000 (upper row) and x8000 magnifications.

montmorillonite (Rytwo and Dultz, 2007, unpublished results).

TYPICAL USES OF CLAY MINERALS.

Several typical examples of the use of clays along the history might be presented. This work will focus only on a few of them.

1. The use of clay minerals in laundry and bleaching of wool and cloth: The term "fullers' earth" usually used for clay minerals arrives from the Latin term "fullo", which indicates "working in the removal of oil from clothes" (Robertson, 1986). As mentioned above, the oldest archeological findings of clay used for such purpose was found in Cyprus, at wool dumps dated from 5000 BC. In Rome, clay and soil were combined with decaying urine to enhance the process, indicating one of the oldest reported uses of clay-organic interactions. Romans even developed a commercial system dedicated to collect products from public urinals, in order to sell the products for laundry use.

2. Chinese Porcelain: Porcelain has been made in China probably since the 6th or 7th century A. D. Quartz, feldspar, and kaolin were then, as now, the raw materials employed. The name "kaolin", for china clay derived from old deposits on the mountain Kao- ling in China. Observations had been made since the 9th century about the fact that "chinese have particularly fine clay which they use to make drinking vessels with the delicacy of glass; although they are made of clay." Such items had great strength, were shaped perfectly by hand, and have wall thickness of less than 0.4mm! During Mongol domination (1280-1368) the knowledge was lost. Ceramics from the following Ming dynasty was not as thin as before, even they tried to use the most plastic kaolin deposits they found. Only till the end of the Ming dynasty (1644) thin ceramics appear again, but in this case those were made from illite, which has-a-priori a considerably higher plasticity than kaolin, making it easier to handle. The secret of ancient Chinese kaolin-based porcelain must therefore lie in some technique enabling delicate items to be formed from kaolin of poor plasticity, which would normally be expected to require clays of extremely good plasticity. Weiss (1963) showed that by mixing kaolinite with urea and aging it "The kaolinite crystals did not dissolve, but the urea-based chemicals

penetrated into the crystal lattice and increased the distance between the kaolinite layers from 7.2 to 10.7 Å. Rheological behavior of kaolin does indeed increase strongly with this pretreatment. A kaolin of low thixotropy subjected to this treatment yields a material surpassing the best ceramic kaolins and approximating sodium bentonites.

3. Cosmetic uses: Clay has been used around the world for centuries by indigenous people as an important medicinal and cosmetic tool ("Mountain Rose Herb", 2008). Clays, as French Green clay (illite) and Rhassoul clay (a smectite), are used externally for skin conditions and for cosmetic purposes. In Mesopotamia mixtures of clays were used as soap an other facial- and skin-care ointments. In Egypt, "red ochre" (a pigment made from naturally tinted clay minerals, with relatively large amounts of hydrated Fe(III)) was used for lips and cheeks

4. Medicinal uses: In the second century A.D., Galen, the Greek philosopher and physician, was the first to record the use of clay by sick or injured animals (AboutClay.com, 2006). Uses appear to be worldwide: The Essenians (near the Dead Sea), The Amargosians (predecessors to the Aztecs), and other natives in North, Central and South America, Africa and Australia recognized the benefit of clays as a dietary supplement or as a healing aid. Several clay providers' web sites propose therapeutical applications. Uses are wide and some of them even have special definitions, ("Pelotherapy": medical treatment by mud baths). Although some uses are rather esoteric, part of the proposed applications are well-understood: adsorption of toxins from skin or internally by clay organic interaction processes, adsorption of mercury and other heavy metals by ion exchange (Eyton's Earth, 2006), use as an alkalizing agent, supplying alkali exchangeable cations, etc.

5. Fining and clarification of juices, oils and wines: Clays were and still are applied in order to avoid secondary turbidity, especially in white wines. The scientific base of this application lies on the fact that during fermentation, most proteins in wine decompose due to the alcohol and low pH. In white wines there is a relatively high concentration of proteins resistant to the process (proteolysis resistant- "PR"- proteins),

most of them positively charged and with relatively low molecular weight. When the temperature of the wine increases due to exposure to sun or high heat at transport conditions- those proteins coagulate, forming tiny aggregates that disperse light, and wine becomes turbid, usually without any influence on the taste (Eisenman,1998). The positive charge of the PR proteins makes them suitable for binding to negatively charged clay minerals. Thus, clayey soils or bentonite were added to wine at very low concentrations at various stages of preparation. The PR proteins are bound to the clay, and sink as relatively larger aggregates. The process of adding a flocculant to avoid the turbidity due to heating is usually known as "fining", and is used until now in most wineries along the world. "Low stability wines" are, therefore, white wines with high PR-proteins. Several fining agents are in use, as bentonite, polymers, gelatin, polysaccharides and other large organic molecules as dried-milk solids (casein) or dried "egg-white" (albumin) (Morris & Main, 1995).

Amount and exact type of protein changes with the grape variety, soil type, weather, etc- and differs considerably from year to year (Ferreira et al., 2002). Thus, winemakers usually make preliminary "try and error" experiments in order to know the amount of clay to add. Large amount might cause unwanted side-taste, and changes in color. Added amounts are usually 0.1-5 g/L (0.01-0.5%). Figure 2 shows a test performed with several clay minerals in order to avoid turbidity after heating in Sauvignon Blanc wine from Galil Mountain Winery, 2006 (Rytwo and Lang, 2007, unpublished results). It can be seen that smectites (SWy-1 and KWK) are considerably more effective in fining than other clay minerals. This is ascribed to the large negatively charged surface area. However, it is interesting to notice that the fining strongly depends on the grape variety: performing the same experiment on Viognier white wine from the same winery- sepiolite yielded the best fining results. We assume that the remaining proteins in Viognier on that season might be non-charged. Since sepiolite adsorbs effectively organic molecules to neutral silanol sites (Rytwo et al, 1998) at amounts considerably larger than smectites, sepiolite achieved better results.

6. Ritual and artistic uses: One of the most scientifically interesting antique

uses of clay organic interactions, is its applications by Maya tribe for the stabilization of "Maya Blue" pigment. (Jose-Yacaman et al., 1996). Despite their age and the harsh weathering conditions, ceramics coloured by Maya Blue have not faded over the centuries. What is even more remarkable is that the colour is resistant to extremes of pH, chemical solvents, bio- and photodegradation. Its composition was unknown until the late 60's, when it was discovered that the pigment is indeed a nanocomposite: a mixture of both organic and inorganic ingredients - a natural clay, palygorskite, and a plant derivative, indigo (Arnold, 2005). What is particularly surprising is that no known organic pigments show such stability. As a result, Maya Blue's chemical complexity and remarkable physical properties have attracted much scientific attention for over 50 years.

The resistance to acids is not due to the role of the indigo, but to the role of the clay (Sanchez del Rio, 2006). Palygorskite and sepiolite clays react with indigo, producing a pigment that does not decolour in acids, as happens for indigo. This is not true for the smectites. The fibrous structure of palygorskite and sepiolite featuring channels is important for stabilization. The description of the chemical bond linking indigo and palygorskite is still the key problem, and will certainly require further studies. The question usually asked is "does the dye enters the channels of the mineral"? Fois et al. (2003) stated based on molecular dynamics simulations that the trapping inside the tunnels

determines its high stability. Several other studies (Chiari and al., 2003; Hubbard et al., 2003) on the other hand, based on thermal analysis and XAFS measurements claim that indigo does not enter the channels neither replace zeolitic water, but is adsorbed on the grooves around the crystal, replacing adsorbed hygroscopic water.

7. Present and future applications: In addition to all uses presented, nanocomposites based on clays and organic compounds are expanding. A review focusing on applications of hybrid organic-inorganic nanocomposites (Sanchez et al., 2006) dedicates a separate chapter to clay-derived nanocomposites due to their importance. Organo-clays receive great interest for applications based on their capacity for selective adsorption of molecules. Thus, they have been used for application in chromatography separations, to remove organic pollutants from air and water, and to develop improved formulation for pesticides, as chemical sensor and molecular sieves, etc. Among other properties we can mention applications based on special structural, gas barrier, antiflammability, or other properties. Interesting photochemical behavior may also arise from the specific structure of those nanocomposites.

REFERENCES.

- AboutClay.com (2006): *The history of healing clay* at http://aboutclay.com/history_of_clay.htm
- Arnold D.E. (2005): *MAYA BLUE AND PALYGORSKITE: A second possible pre-Columbian source. Ancient Mesoamerica*, **16**, pp 51-62
- Beneke, K. & G. Lagaly, (2002): *ECGA (European Clay Group Association) Newsletter No. 5, July 2002, page 57- 78*
- Bergaya, F. A. (2000): *Clay science studies in the world, Proceedings of the 1st Latin American Clay Conference Funchal, Madeira, Vol I*, 1-3.
- Chiari, G., Giustetto, R., Ricchiardi, G., (2003): *European Journal of Mineralogy*, **15(1)**, 21-33.
- Eisenman, L., (1998): *Fining and Fining Materials*, 81-96. In *The Home Wemakers Manual*. Del-Mar, CA USA.
- Eyton's Earth, (2006): *Internal uses of Healing Clays* at <http://www.eytonsearch.org/general-uses-clay.php>
- Ferreira, R.B., Picarra-Pereira, M.A., Monteiro, S., Loureiro, V.B., Teixeira, A.R. (2002): *Food Science and Technology J.* **12**, 230-239.
- Fois, E., Gamba A., Tilocca, A. (2003): *Microporous and Mesoporous Materials*, **57/3**, 263-272
- Hubbard, B., Kuang, W., Moser, A., Facey, G. A., Detellier, C. (2003): *Clays and Clay Minerals*, **51(3)**, 318-326.
- Johnston, C.T. (1996): *Sorption of Organic Compounds on Clay Minerals: A Surface Functional Group Approach*, in CMS Workshop Lectures, Vol. 8, *Organic Pollutants in the Environment*, Sahwney, B. ed. The Clay Mineral Society, Boulder CO pp. 1-44
- Jose-Yacaman M., Rendon L., Arenas J., Puche M.C.S. (1996): *Science* **273**:223-225
- Lahav, N. (1983): "Fundamentals of Soil Science" (in Hebrew). Academon Press, Rehovot, Israel.
- Manahan, S.E. (2000): *Environmental Chemistry* 7th Ed. CRC Press, Boca Raton FL.
- Morris J.R. & Main G.L. (1995): *Fining Agent for Wine* at <http://www.uark.edu/depts/ifse/grapeprog/articles/nmc14wg.pdf>
- Mountain Rose Herbs, (2008): *Clays* at <http://www.mountainroseherbs.com/clay-clay.html>
- Murray H.H. (1997): *Clays for our future in H. Kodama, A. R. Mermut & Torrance J. K. (Eds.) Proc. 11th Int. Clay Conf., Ottawa, Canada*, pp 3-11.
- Sanchez C., Julian B., Belleville P., Popall M.J. (2005): *Materials. Chemistry* **15**, 3559-3592
- Sánchez Del Río, M., Martinetto, P., Reyes-Valerio, C., Dooryhée, E., Suárez M. (2006): *Archaeometry* **48(1)**, 115-130.
- Robertson R H S. (1986): Chapter 1- 8. In: *Fuller's earth. A history*. Volturna Press, Hythe, Kent, UK, 1- 83.
- Rytwo, G., Nir S., Margulies L., Casal B., Merino J., Ruiz-Hitzky E., Serratosa, J.M. (1998): *Clays Clay Miner.* **46**, 340-348
- Weiss A. (1963): *Angewandte Chemie International Edition in English* **2**, 697-703.
- Yuan, G. (2004): *J. of Environ. Sci. and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering*, **39**, 2661-2670.

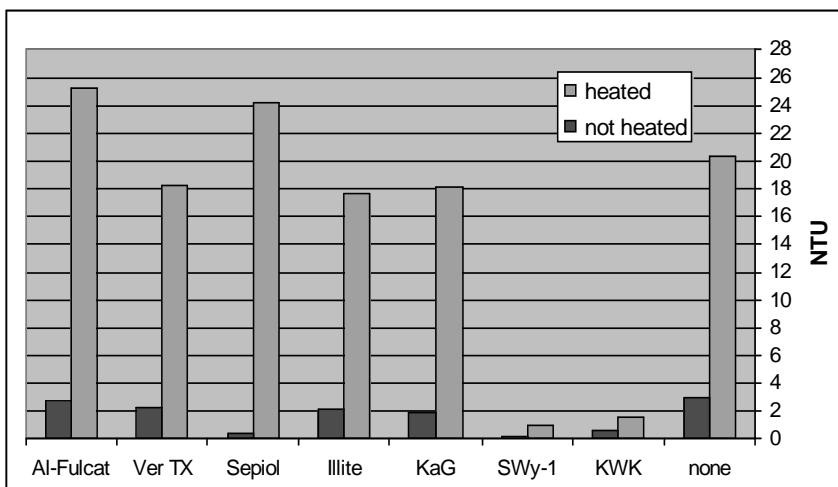


fig 2. Turbidity of heated and non heated Sauvignon Blanc wine, upping adding 0.2% suspended clay mineral. The minerals tested were a pillared clay (Al-FULCAT), Texas vermiculite (Ver TX), Spanish sepiolite (Sep), Silver Hill Illite (Illite), Georgia Kaolinite (KaG), Wyoming SWy-1 montmorillonite, and commercial KWK bentonite (mainly montmorillonite).