

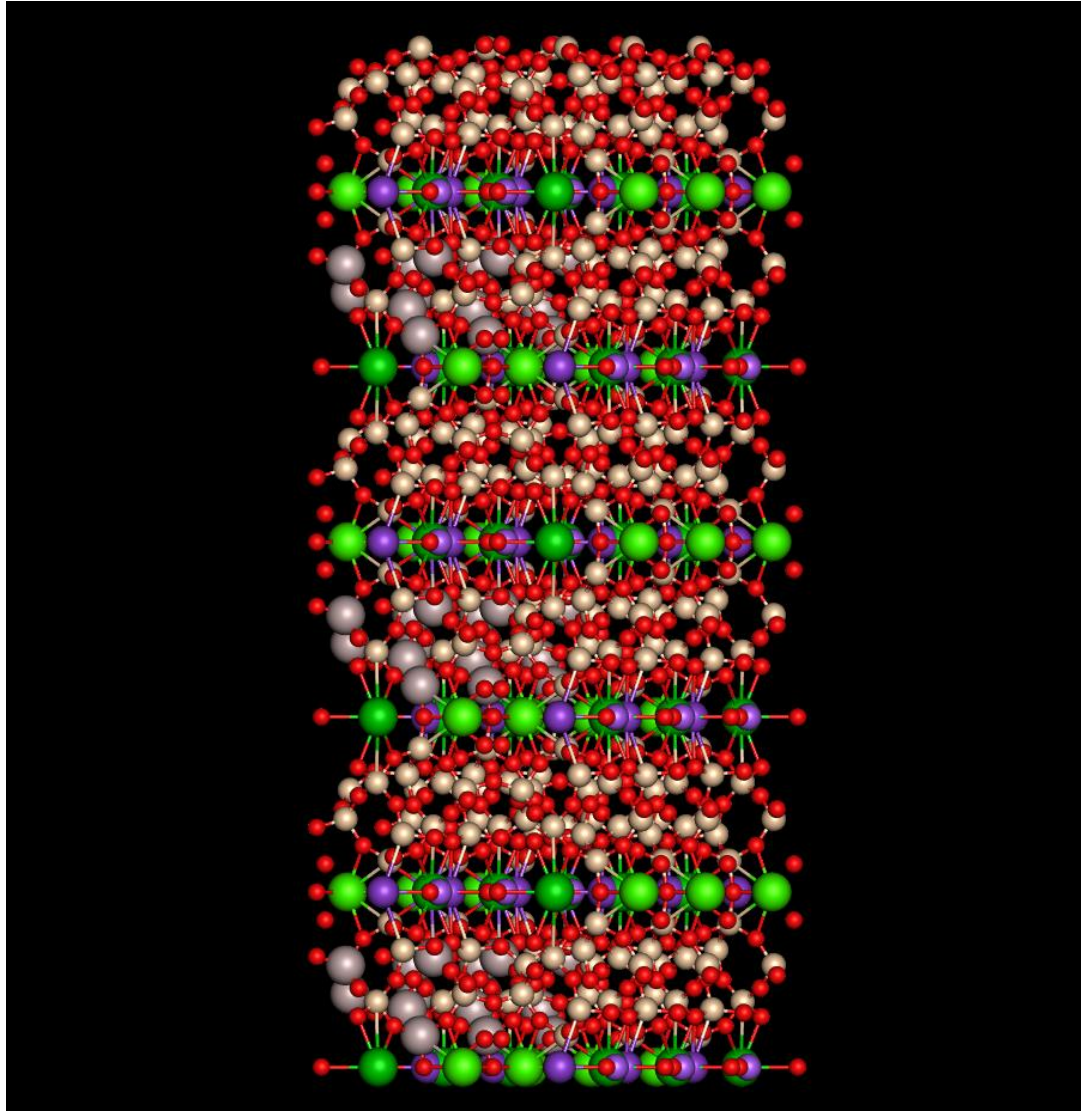
Microporous minerals: A comparative analysis of mineral structures and contaminant uptake potential



Marvin Osorio, Geology '21

Advisor Christopher Oze

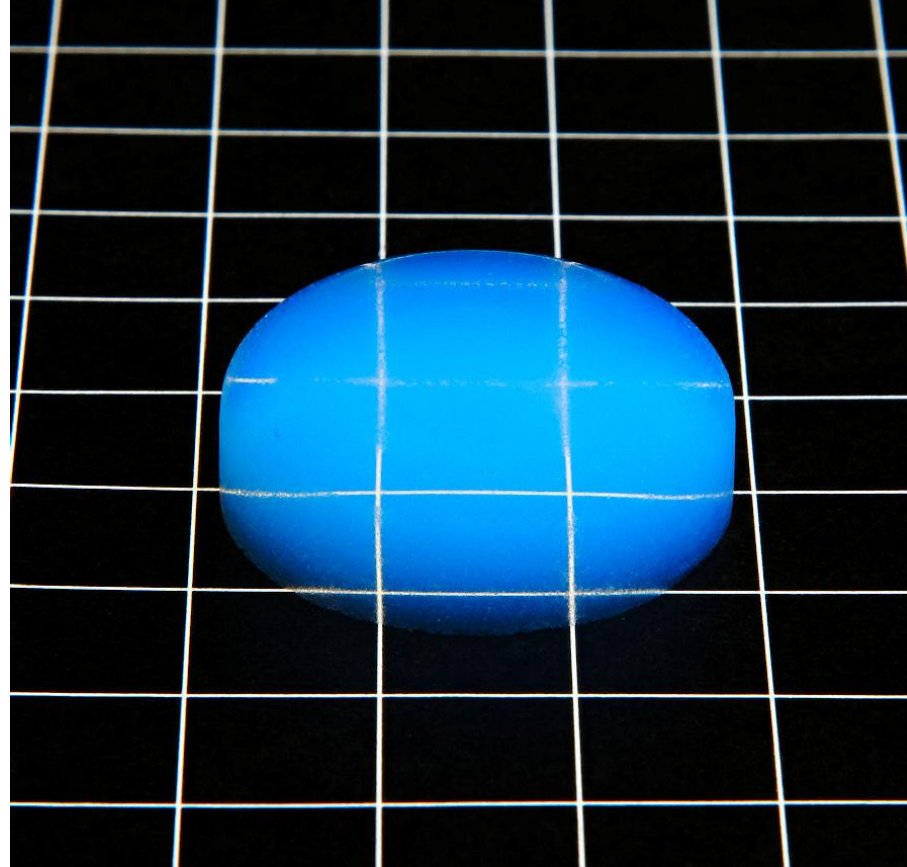




What are microporous minerals?

- In short, microporous minerals are those which exhibit a substantial amount of pore spaces or cavities in their structures. Pore spaces are caused by bonds at the atomic scale.
- Notable minerals which exhibit microporous properties are zeolites and clay minerals. Other such minerals are a recently discovered rowleyite and the man-made aerogel.



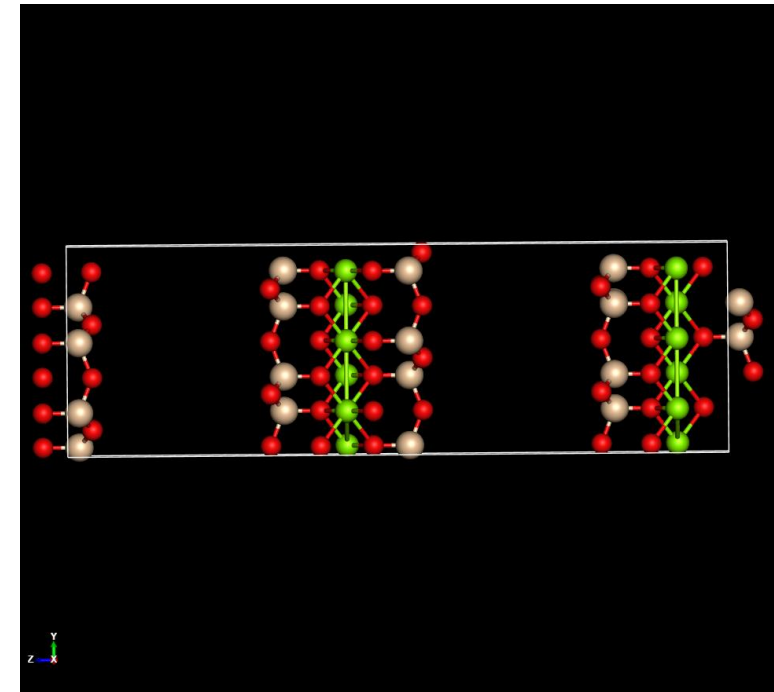
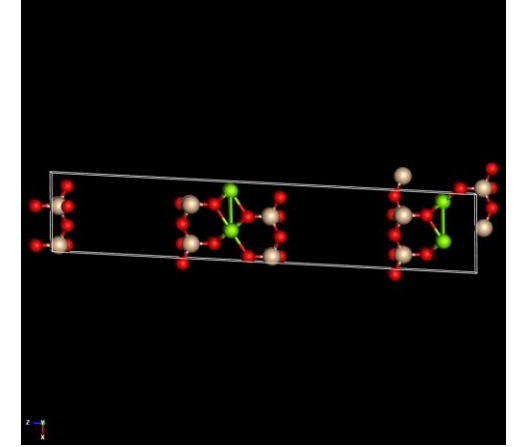
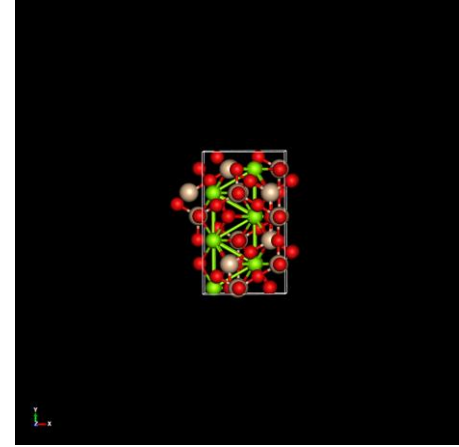


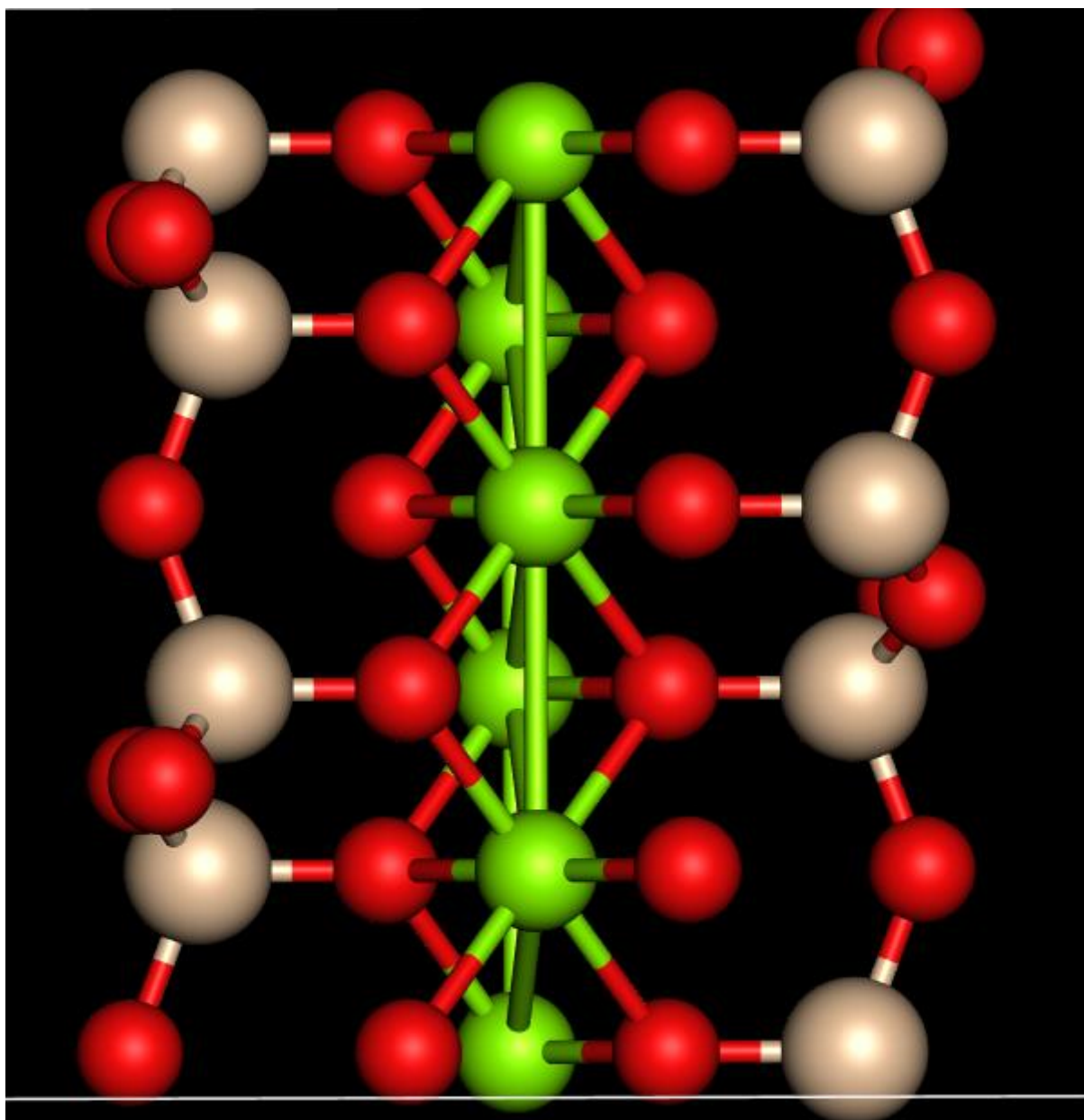
Microporous Minerals



Vermiculite (Clay)

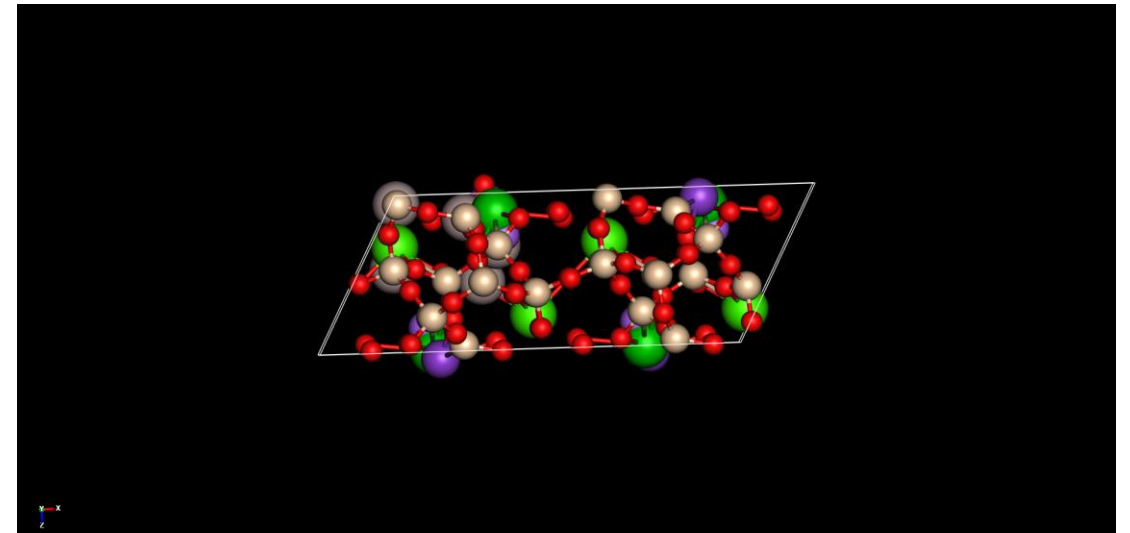
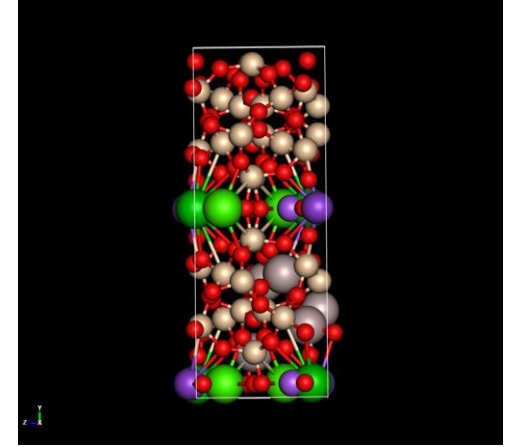
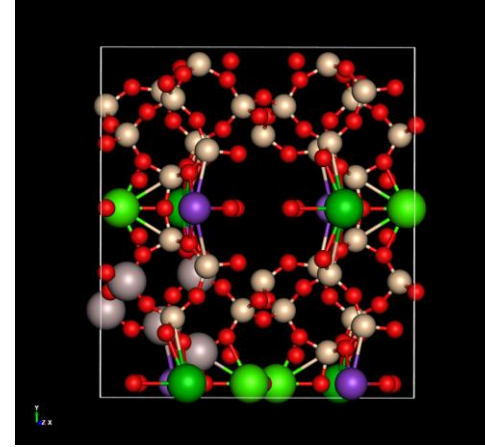
- $(\text{Mg,Fe,Al})_3((\text{Al,Si})_4\text{O}_{10})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
- Vermiculite is a clay mineral which means it has a sheeted structure. It has two tetrahedra sheets and one octahedral sheets.
- Vermiculite is a weathered mica changing the potassium ions between pore spaces to magnesium or iron.
- In the models sheeted structures can be seen in the top right and bottom along with pore spaces where Mg and Fe ions fit.

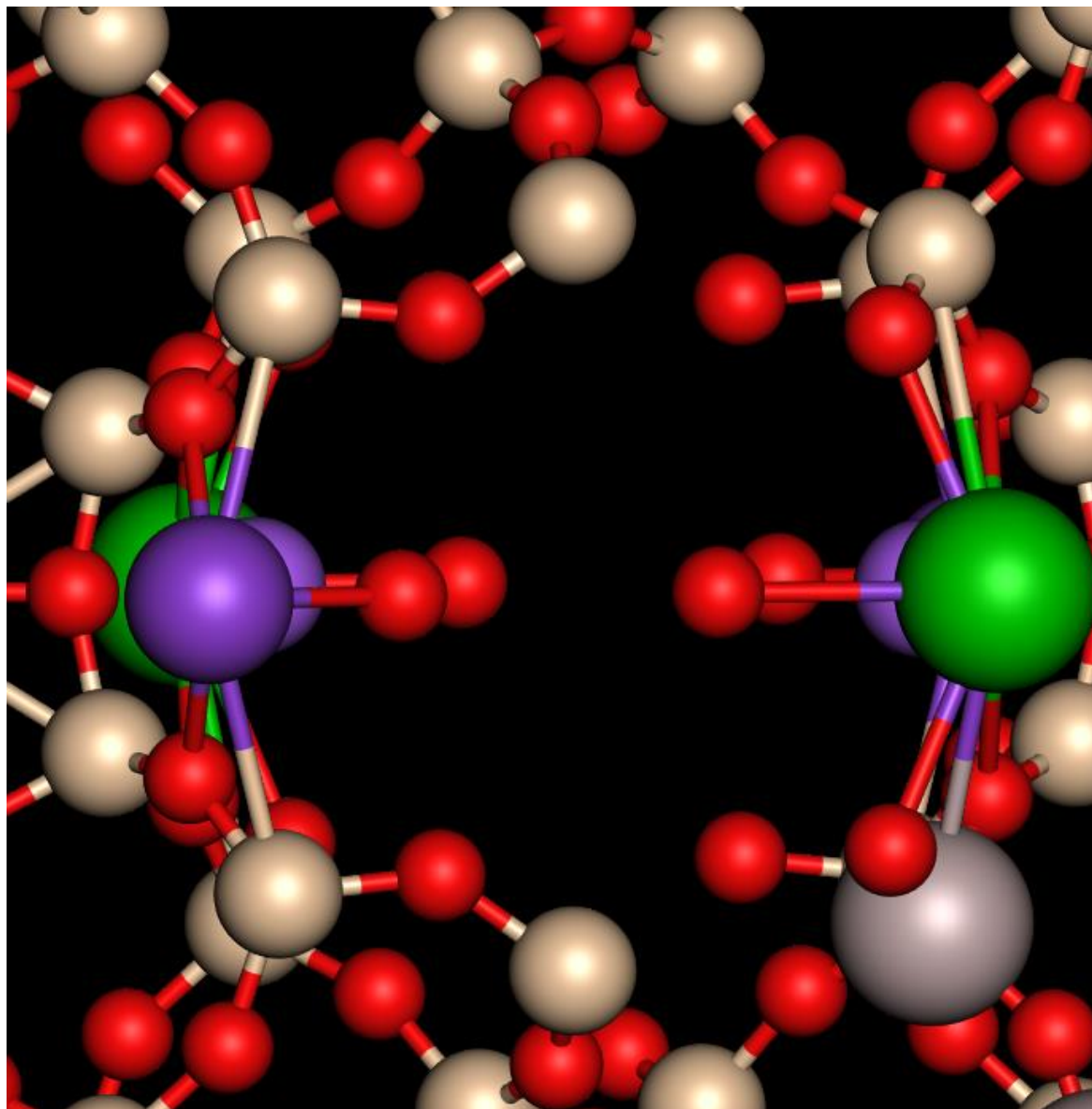


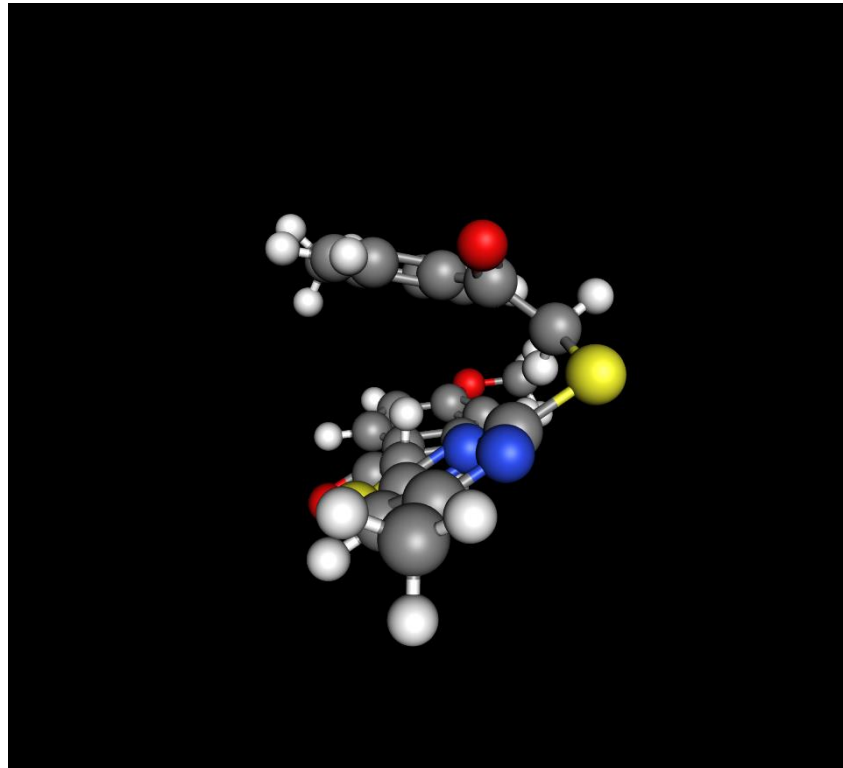
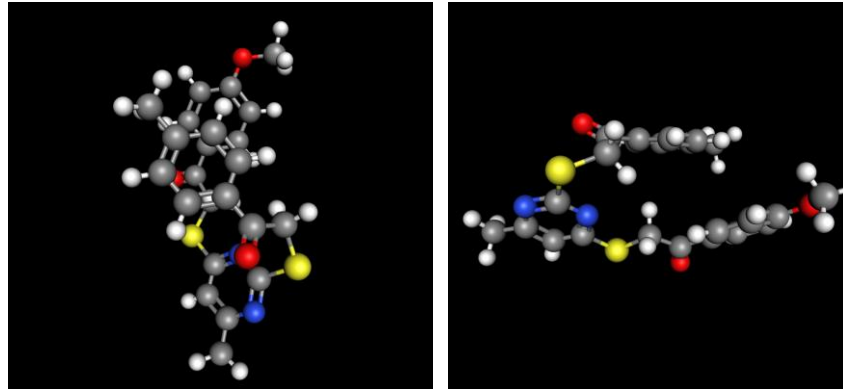


Clinoptilolite

- $(\text{Na, K, Ca})_{2-3}\text{Al}_3(\text{Al, Si})_2\text{Si}_{13}\text{O}_{36}\cdot 12\text{H}_2\text{O}$
- Natural zeolite with a microporous mineral arranged in a tetrahedra of silica and alumina.
- Due to its complex formula sodium (Na), potassium (K), and calcium (Ca) can be substituted to create different mineral structures. The structure shown on the right uses Clinoptilolite-K, a potassium-based model which has increased pore spaces when compared to Ca or Na.







Silica Aerogel

- $C_{23}H_{22}N_2O_3S_2$
- Aerogel is a man-made mineral that is 95% air, there are different types of aerogels, including carbon, but here we focus on silica aerogel due to its availability.
- Pore spaces in aerogel are created due to the folded structure as well as the cyclohexane bonds formed when combined to form the full compound.



Rowleyite

- $[\text{Na}(\text{NH}_4, \text{K})_9\text{Cl}_4][\text{V}^{5+, 4+}_2(\text{P}, \text{As})\text{O}_8]_6 \cdot n[\text{H}_2\text{O}, \text{Na}, \text{NH}_4, \text{K}, \text{Cl}]$
- Rowleyite is a newly discovered mineral in the Rowley Mine in Maricopa County, Arizona.
- Rowleyite belongs to polyoxometalate (POM) group of chemical compounds, but because it has V_4O_{16} , it more specifically belongs to the subclass polyoxovanadate.
- The mineral features a double cage structure which then connects to the vanadate structures creating a complex network of pore spaces, but also areas of channel like pore spaces.

Figure 4

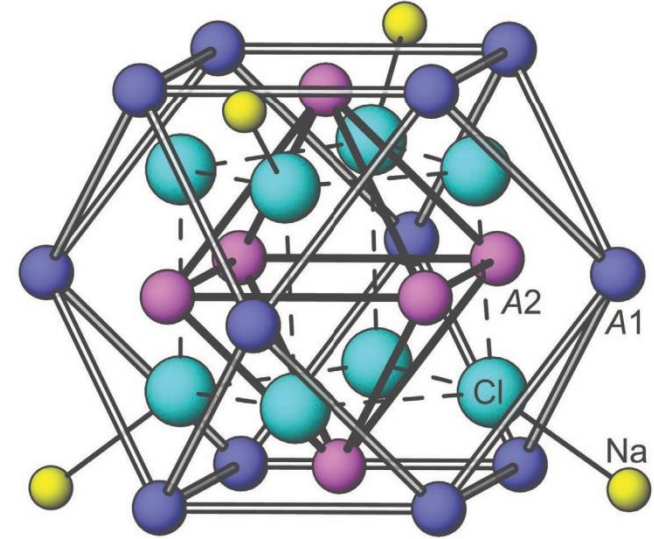
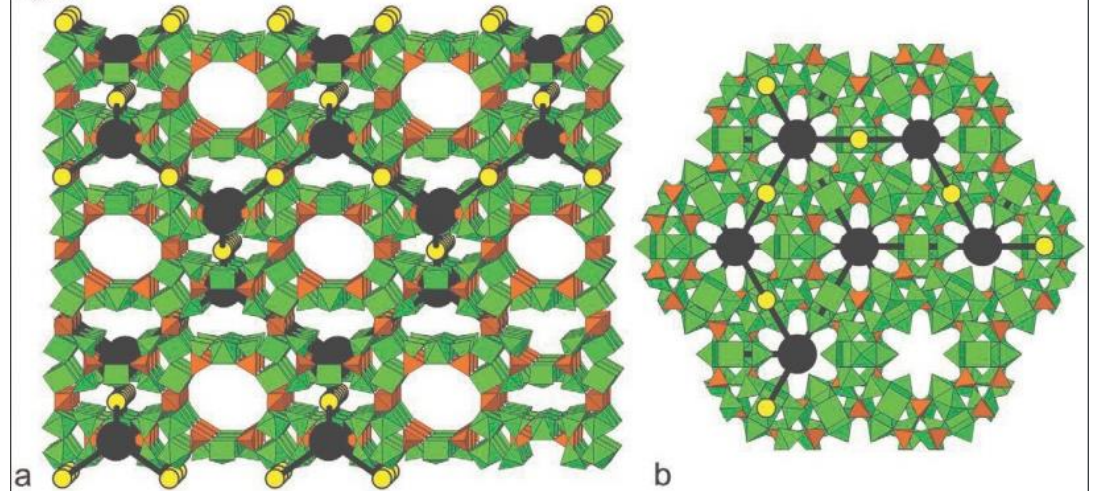
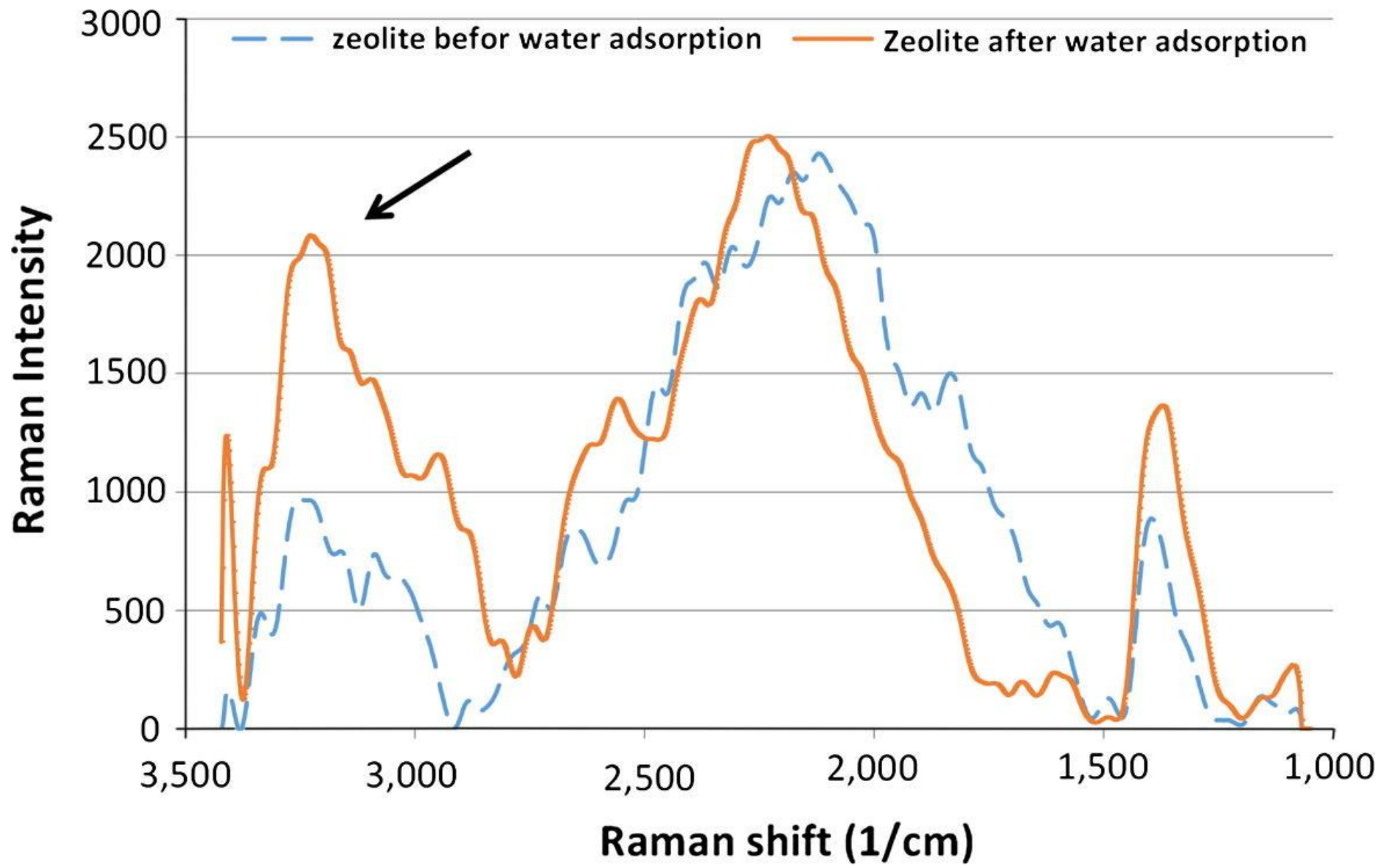
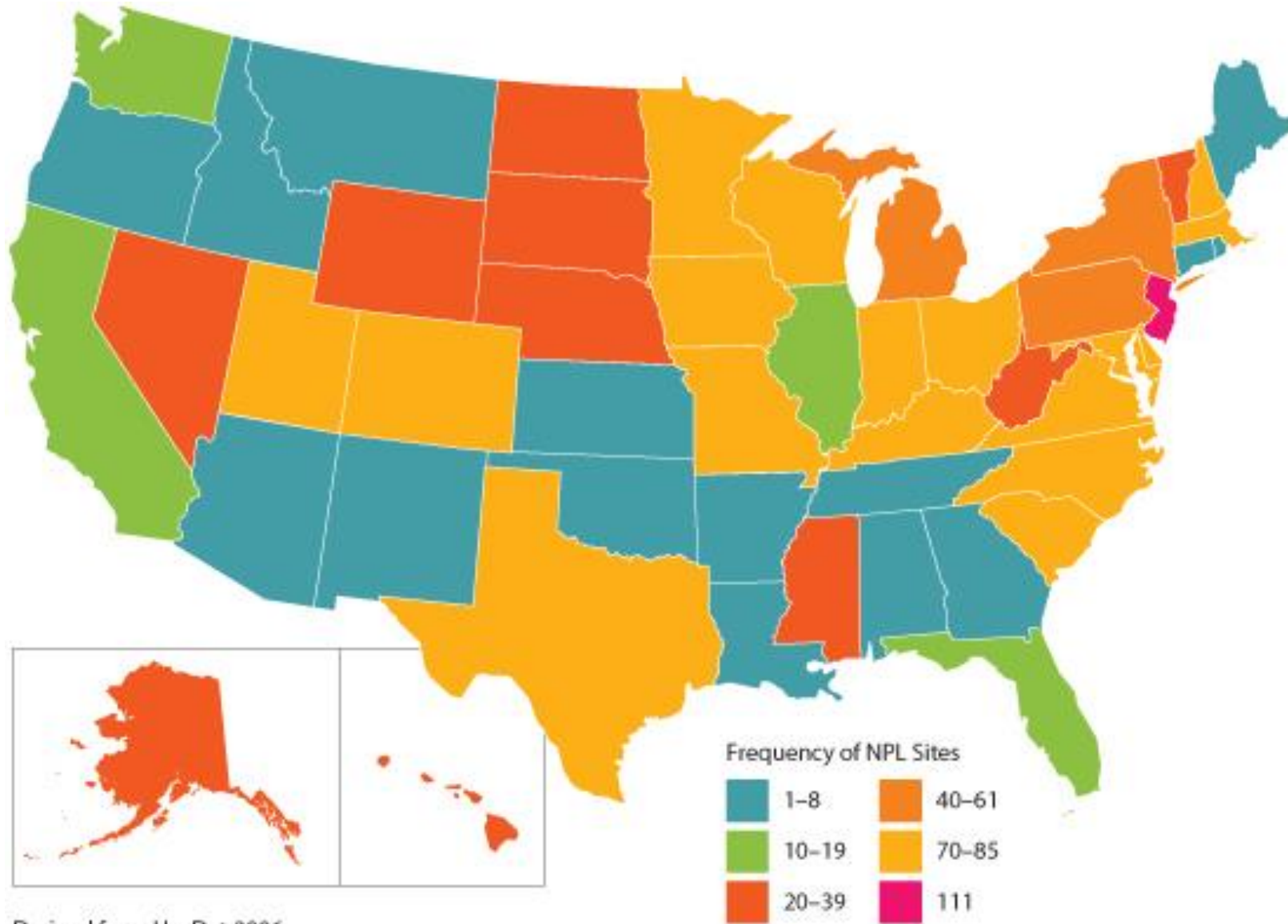


Figure 6

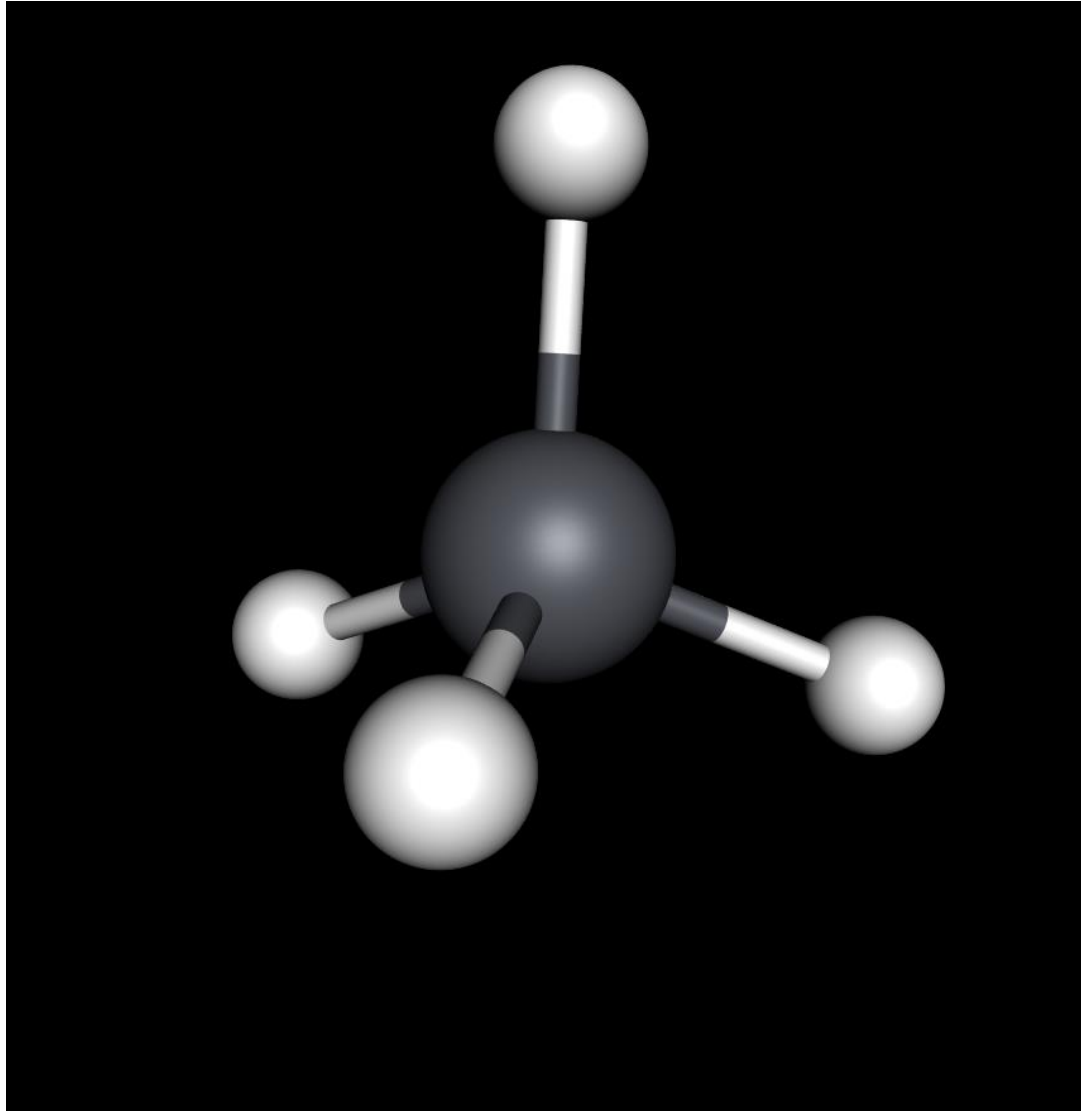






Derived from HazDat 2006





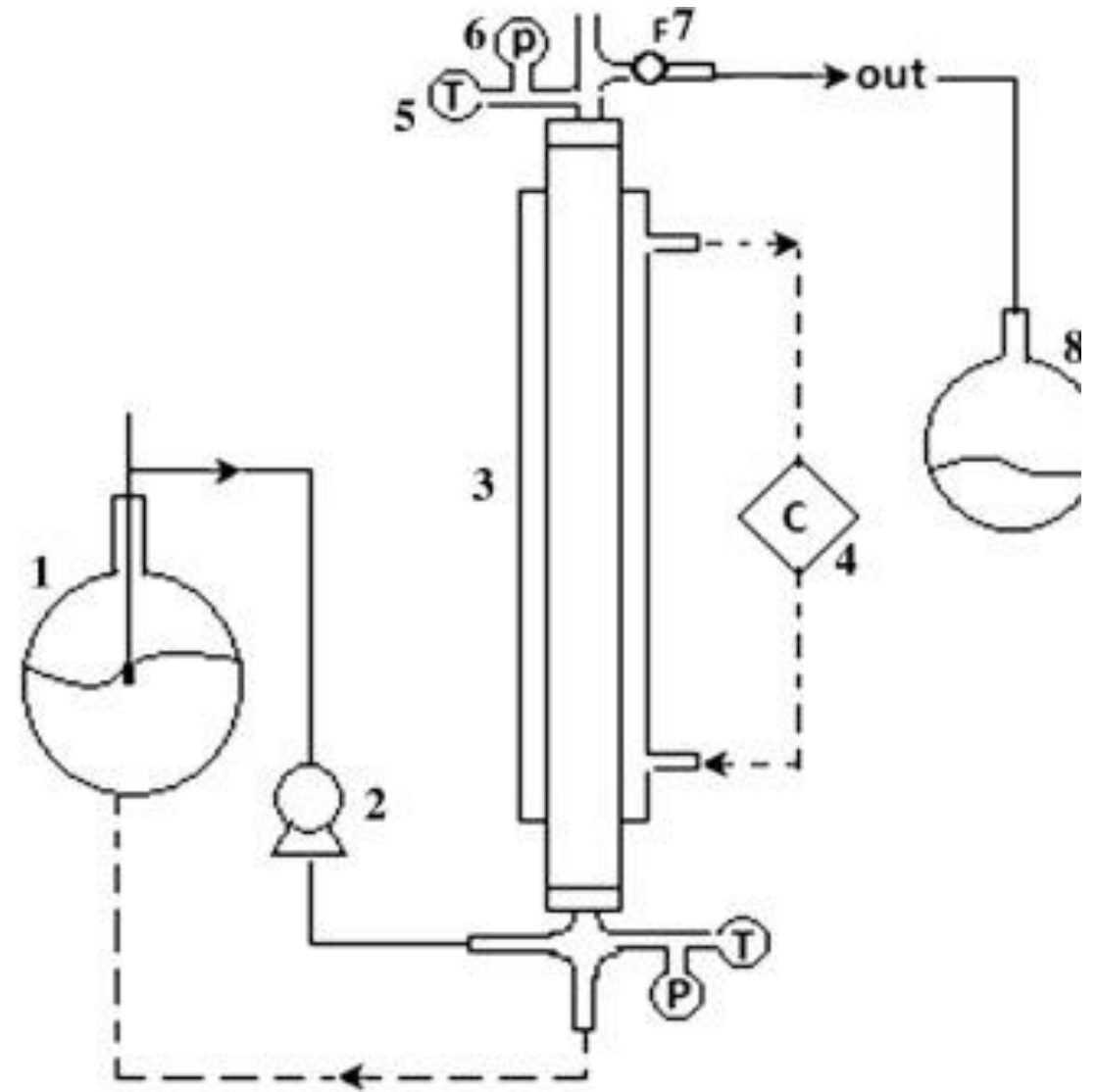
Lead

- Currently microporous minerals are being explored for the removal of petroleum byproducts from solution, but there is potential for them to be used to remove contaminants from water such as lead.
- Knowledge of lead can be traced to 4,000 BC
- Lead mining was done by the Phoenicians as early as 2,000 BC.
- Lead poisoning has been described by many scholars including Hippocrates but did not recognize the etiology.
- In our current century, the advent of leaded paints and gasoline have passed, but their effects are still felt.
- The Center for Disease Control reports that around 24 million homes still contain leaded paint.



Lead Experiments

- In order to test the effectiveness of microporous minerals a flow-through model will be implemented.
- The basic model is a lead contaminated water solution which flows into a cylinder with one of the minerals. On the other end of the cylinder there is a beaker that will collect the water.
- This model will be done at different time intervals to test the effectiveness of the mineral.



General overview

- Overall, during this summer research stint I've completed several models of microporous minerals.
- Collected mineral samples Raman, Fourier-transform infrared spectroscopy (FTIR), and X-Ray diffraction.
- We chose lead as a contaminant due to its affect on American society.
- For future study we hope to run flow-through models with lead.



Acknowledgments

- Undergraduate Research Center
- Dr. Aaron Celestian, Mineral Curator at the Natural History Museum
- Elizabeth Boyd and Elisa Ruiz for assistance in obtaining mineral samples



Works Cited

- Ambrozova, P., Kynicky, J., Urubek, T., and Nguyen, V.D., 2017, Synthesis and Modification of Clinoptilolite: *Molecules* (Basel, Switzerland), v. 22, doi:[10.3390/molecules22071107](https://doi.org/10.3390/molecules22071107).
- Ceci, A., Rhee, Y., Kierans, M., Hillier, S., Pendlowski, H., Gray, N., Persiani, A., and Gadd, G., 2014, Transformation of vanadinite (Pb₅(VO₄)₃Cl) by fungi: *Environmental Microbiology*, v. 17, doi:[10.1111/1462-2920.12612](https://doi.org/10.1111/1462-2920.12612).
- Jones, R.R., Hooper, D.C., Zhang, L., Wolverson, D., and Valev, V.K., 2019, Raman Techniques: Fundamentals and Frontiers: *Nanoscale Research Letters*, v. 14, doi:[10.1186/s11671-019-3039-2](https://doi.org/10.1186/s11671-019-3039-2).
- Kampf, A.R., Cooper, M.A., Nash, B.P., Cerling, T.E., Marty, J., Hummer, D.R., Celestian, A.J., Rose, T.P., and Trebisky, T.J., 2017, Rowleyite, [Na(NH₄,K)₉Cl₄][V₂₅₊,4+(P,As)₈O₈]_{6-n}[H₂O,Na,NH₄,K,Cl], a new mineral with a microporous framework structure: *American Mineralogist*, v. 102, p. 1037–1044, doi:[10.2138/am-2017-5977](https://doi.org/10.2138/am-2017-5977).
- Li, Y., Bai, P., Yan, Y., Yan, W., Shi, W., and Xu, R., 2018, Removal of Zn²⁺, Pb²⁺, Cd²⁺, and Cu²⁺ from aqueous solution by synthetic clinoptilolite: *Microporous and Mesoporous Materials*, v. 273, doi:[10.1016/j.micromeso.2018.07.010](https://doi.org/10.1016/j.micromeso.2018.07.010).
- Markiv, T., Sobol, K., Franus, M., and Franus, W., 2016, Mechanical and durability properties of concretes incorporating natural zeolite: *Archives of Civil and Mechanical Engineering*, v. 16, p. 554–562, doi:[10.1016/j.acme.2016.03.013](https://doi.org/10.1016/j.acme.2016.03.013).
- Mintova, S., Jaber, M., and Valtchev, V., 2015, Nanosized microporous crystals: emerging applications: *Chemical Society Reviews*, v. 44, p. 7207–7233, doi:[10.1039/C5CS00210A](https://doi.org/10.1039/C5CS00210A).
- Naber, J.E., de Jong, K.P., Stork, W.H.J., Kuipers, H.P.C.E., and Post, M.F.M., 1994, Industrial applications of zeolite catalysis, *in* Weitkamp, J., Karge, H.G., Pfeifer, H., and Hölderich, W. eds., *Studies in Surface Science and Catalysis*, Elsevier, Zeolites and Related Microporous Materials: State of the Art 1994 - Proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, 17-22 July 1994, v. 84, p. 2197–2219, doi:[10.1016/S0167-2991\(08\)63783-0](https://doi.org/10.1016/S0167-2991(08)63783-0).
- Pan, L., Wang, Z., Yang, Q., and Huang, R., 2018, Efficient Removal of Lead, Copper and Cadmium Ions from Water by a Porous Calcium Alginate/Graphene Oxide Composite Aerogel: *Nanomaterials*, v. 8, doi:[10.3390/nano8110957](https://doi.org/10.3390/nano8110957).
- Queen, W.L., Hwu, S.-J., and Reighard, S., 2010, Salt-Templated Mesoporous Solids Comprised of Interlinked Polyoxovanadate Clusters: *Inorganic Chemistry*, v. 49, p. 1316–1318, doi:[10.1021/ic902283g](https://doi.org/10.1021/ic902283g).
- Ritz, M., Zdrávková, J., and Valášková, M., 2014, Vibrational spectroscopy of acid treated vermiculites: *Vibrational Spectroscopy*, v. 70, p. 63–69, doi:[10.1016/j.vibspec.2013.11.007](https://doi.org/10.1016/j.vibspec.2013.11.007).
- Solimani, A., and Abbasi, M., 2008, Silica Aerogel; Synthesis, Properties and Characterization: *Journal of Materials Processing Technology*, v. 199, p. 10–26, doi:[10.1016/j.jmatprotec.2007.10.060](https://doi.org/10.1016/j.jmatprotec.2007.10.060).
- Štandeker, S., Novak, Z., and Knez, Ž., 2007, Adsorption of toxic organic compounds from water with hydrophobic silica aerogels: *Journal of Colloid and Interface Science*, v. 310, p. 362–368, doi:[10.1016/j.jcis.2007.02.021](https://doi.org/10.1016/j.jcis.2007.02.021).
- Stylianou, M.A., Hadjiconstantinou, M.P., Inglezakis, V.J., Moustakas, K.G., and Loizidou, M.D., 2007, Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column: *Journal of Hazardous Materials*, v. 143, p. 575–581, doi:[10.1016/j.jhazmat.2006.09.096](https://doi.org/10.1016/j.jhazmat.2006.09.096).
- Sullivan, E.J., Hunter, D.B., and Bowman, R.S., 1998, Fourier Transform Raman Spectroscopy of Sorbed HDTMA and the Mechanism of Chromate Sorption to Surfactant-Modified Clinoptilolite: *Environmental Science & Technology*, v. 32, p. 1948–1955, doi:[10.1021/es9708981](https://doi.org/10.1021/es9708981).
- Wang, S., and Peng, Y., 2010, Natural zeolites as effective adsorbents in water and wastewater treatment: *Chemical Engineering Journal*, v. 156, p. 11–24, doi:[10.1016/j.cej.2009.10.029](https://doi.org/10.1016/j.cej.2009.10.029).

