The mechanism and kinetics of rehydroxylation in calcined clay minerals as a key to a new method of archaeological dating (RHX-Clay).

Popular science summary

Manufacturing of fired-clay ceramics is the one of oldest human activities and some fired-clay objects, such as “Venus of Dolní Věstonice” from Czech Republic, date back to almost 30,000 years ago. Ceramics production from a clay have always accompanied the development of every civilization. No surprise, therefore, that ceramics has become one of the most important archaeological objects and dating a fired clay is now the major tool in modern archaeology. Unfortunately, all available dating methods, including the broadly-applied ^{13}C dating, have limitations that often hamper determination of correct ages. However, beside radioactive decay, there is another phenomena that is common to all fired-clay ceramics, which can possibly be used as an internal clock. This is the ceramics’ mass gain caused by slow, time-dependent regain of OH groups, removed by firing from the clay minerals present in raw ceramic material during production.

Clay minerals are one of the most abundant mineral groups on the Earth's surface and the most important component of raw clay used in manufacturing ceramics. The clay minerals’ structure contains OH groups, which are lost at increased temperature, e.g. during firing, in a process called dehydroxylation. When the ceramics is cooled, the structure of clay minerals starts to slowly regain OH groups using moisture from ambient environment, in a process reverse to dehydroxylation - rehydroxylation. Detailed mechanisms of rehydroxylation remain unclear in ancient ceramics that are complex mixtures of clay minerals and other components. Nevertheless, as was recently shown, mass gain coming from rehydroxylation in fired-clay ceramics is proportional to the time elapsed since firing. Based on that relationship, a new dating method for archaeological artifacts was proposed and named Rehydroxylation dating (RHX dating). However, after initial success, many gaps in RHX dating have been identified. Nowadays, a general agreement in RHX dating community is that further development of the method is not possible without understanding the basic mechanisms controlling rehydroxylation in fired-clay artifacts. The structure and susceptibility to rehydroxylation of each individual clay mineral component control key properties of ceramics, including rehydroxylation behavior. The further development of the RHX dating, therefore, requires involving clay mineralogists with methodology, experience, and interpretations coming from decades of development in their field.

The project aims at finding kinetics and mechanisms of rehydroxylation in clay minerals commonly forming raw clay materials used in ceramics manufacturing by detailed investigation of simple cases involving pure, monomineralic clays and model ceramics. Samples will be characterized in their natural, dehydroxylated, and rehydroxylated states by multiple techniques involving X-ray diffraction, thermogravimetric analysis, infrared spectroscopy, and nuclear magnetic resonance. In addition, *in-situ* dehydroxylation and rehydroxylation experiments will be performed by using our unique, custom-made setup. Experimental results will be supplemented with molecular modeling of the studied structures and reactions, to provide a comprehensive picture of processes occurring during the removal and regain of OH groups in clay minerals. A new technique for measuring the rate of rehydroxylation will be proposed and tested. The project will bring procedures, kinetic models, and structural relationships directly applicable to RHX dating, hoping to make a leap in the development of RHX dating.