

High-temperature XRD investigations of phase transformation in mineralogy: examples for clay used in ceramics and phosphate minerals

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1. Introduction

High-temperature X-ray diffraction is a technique used to determine the mineralogy of a sample at various, non-ambient, temperatures. It allows the measurement and visualisation of dehydration and oxidation processes, phase transformations (Wahl *et al.*, 1961; Montanari, 2004; Zampori *et al.*, 2012), reaction processes and crystallite growth (Natter *et al.*, 2001). The approach was tested on two distinct materials, i.e. raw clays used for ceramic production and phosphate minerals. Four clay samples from Westerwald (Germany) were chosen: a Fe-rich illite clay, a red, a yellow and a white clay. In addition, two natural phosphate samples were selected: alluaudite [$\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$] from Townsite, Pringle, South Dakota, USA (sample TOW-01; Hatert, 2002), and triphylite [$\text{LiFe}^{2+}(\text{PO}_4)$] from Palermo pegmatite, New Hampshire, USA. Mineral transformation and vitrification processes were followed from 30 to 1250°C.

2. Methods

The *in situ* HT-XRD experiments were performed with a Bruker D8 Advance Eco instrument equipped with a Linxeye XE detector and a modular temperature chamber (MTC). Each powdered sample was placed directly on a platinum rhodium (PtRh) alloy strip combined with a thermocouple. XRD patterns were recorded in the 8-70° 2θ range with a step width of 0.02°. Samples were heated with a rate of 30°C/min and were kept at the desired temperature for 5 minutes before analysis. Each sample was first analysed at room temperature and then heated at 300, 600, 900, 1100, 1150, 1200 and 1250°C. Mineral proportions were then quantified using Topas software.

3. Results

The difference between the white, yellow and red clays lies in the temperature of appearance and the abundance of some minerals (Fig. 1). The white clay does not contain any Fe-bearing minerals. It is composed of kaolinite, illite, quartz and rutile. The red and yellow clay contain either hematite or goethite, respectively. During the heating process, the first mineral transformation observed in Fe-bearing clays is the dehydration of goethite to hematite occurring between 30 and 300°C. The second transformation, observed in all studied clays, is related to the dehydroxylation of kaolinite into metakaolin (amorphous) between 300 and 600°C. At 1100°C, the illite totally disappeared and a large amount of mullite is formed. At higher temperature cristobalite is formed at 1100°C for the red clay and at 1200°C for the yellow clay but it is not observed in the white clay. Fe-rich illite clay, used for its good vitrification properties at low temperature is different from the three other samples. It is less

stable, resulting in a lower dehydroxylation temperature (between 600 and 900°C). At higher temperature spinel was observed from 1100°C in this sample.

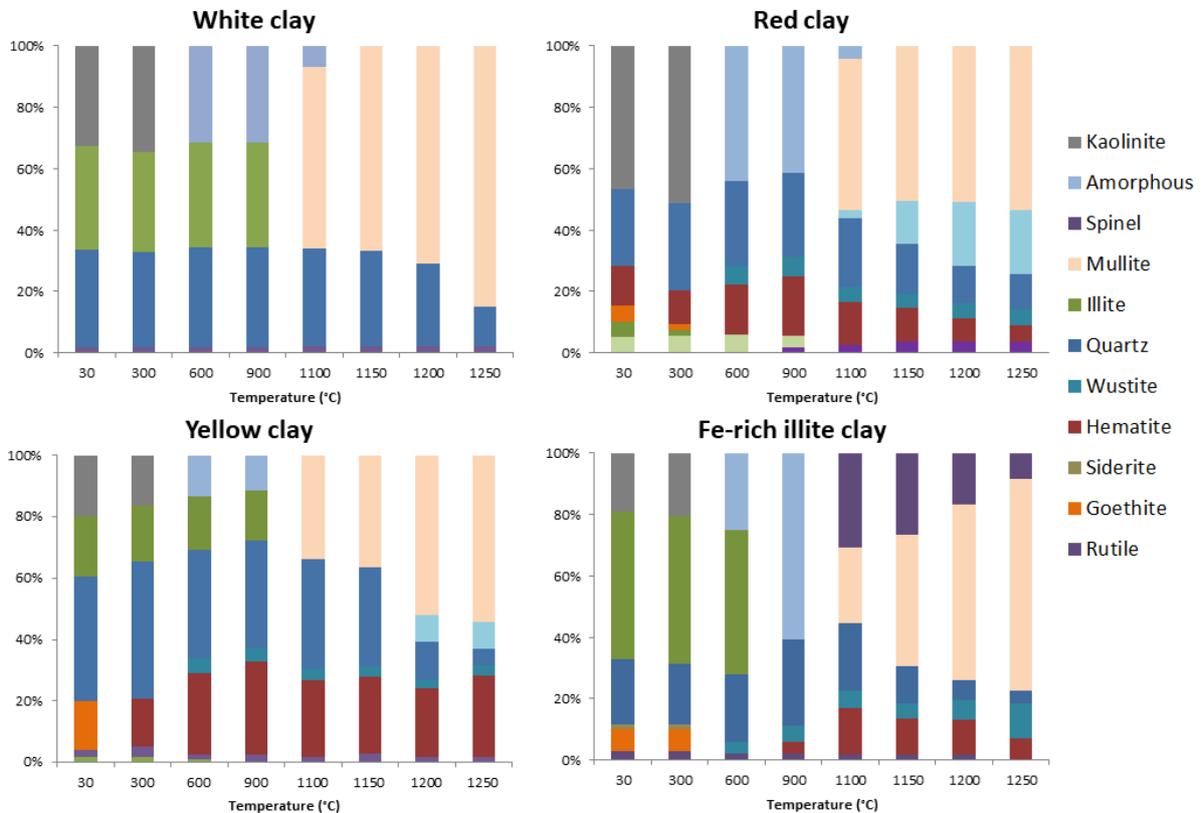


Figure 1 : Evolution of mineral proportions of clay samples with temperature

Heating experiments on phosphates are currently being processed. They will allow to shed some light on the variation of unit-cell parameters of alluaudite- and triphylite-type phosphates over heating. Moreover, accurate determination of phosphate proportions at different temperatures will help us to better understand the stability features of these minerals.

4. References

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