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# Hydrothermal synthesis (200 °C) of Co–kaolinite and Al–Co–serpentine

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ABSTRACT

In the systems $CoO–Al_2O_3–SiO_2–H_2O$ and $CoO–Al_2O_3–SiO_2–HCl–H_2O$, at initial pH between 5.5 and 8.1 and temperature of 200 °C, kaolinite is unstable and the following phases form through a dissolution-precipitation process: a) kaolinite and Co-bearing kaolinite; b) Al–Co–serpentine; and c) poorly crystalline phases. Identification of the several phases was carried out from a combination of X-ray diffraction and transmission/analytical electron microscopy.

Co–kaolinite shows variable morphologies: a) Platy lath-shaped particles with very low Co content; b) Spherical particles, with relatively constant Co contents (in the order of 0.10 apfu); c) Kaolinite stacks with very variable Co contents (up to 0.25 apfu). Analytical data indicate that the presence of $Co(OH)_2$ in the system favors the dissolution process as well as serpentine formation but it leads to the parallel formation of abundant poorly crystalline phases. The Co-content in kaolinite increased as a function of the $Co(OH)_2/CoCl_2$ ratio in the initial systems, and it is reflected by a parallel increase of the *b*-cell parameter of kaolinite. The average composition of the coexisting Al–Co–serpentine is: $(Al_{1.20}Fe_{0.11}Co_{1.27})(Si_{1.64}Al_{0.36})O_5(OH,Cl)_2$, with Cl contents in the order of 0.14 apfu.

The assemblage Co–kaolinite+Al–Co–serpentine, which appears to be stable at 200 °C, has not been described in natural environments, probably because it requires unusual Al- and Co-rich chemical systems.

## 1. Introduction

It is rare for minerals of the kaolinite group (kaolinite, dickite, nacrite and halloysite) to contain appreciable amounts of elements other than Si and Al. Nevertheless, $Fe^{3+}$ has been found in natural kaolinites (e.g. Herbillon et al. 1976; Mestdagh et al. 1980; Cuttler, 1981; Stone and Torres Sánchez, 1988; Delineau et al. 1994; Gaite et al. 1997; Balan et al., 1999). In addition, Cr-rich kaolinites have been described occasionally (e.g. Brookins, 1973; Maksimovic and Brindley, 1980; Maksimovic et al. 1981; Singh and Gilkes, 1991; Mosser et al. 1993). Maximum amounts of ionic substitutions (Fe=0.44 apfu (atoms per formula unit for $O_5(OH)_4$); Cr=0.56 apfu) have been described for halloysites (Newman and Brown, 1987). It appears that the type of foreign cations present in the kaolinite structure mainly depends on the bulk-rock composition, whereas the amount of substitution is controlled by the structure, the disordered varieties accepting higher amounts of substitutions (Brindley et al. 1986).

Kaolinites with appreciable Fe contents have also been synthesized (e.g. Angel et al. 1975; Petit and Decarreau, 1990; Iriarte et al. 2005). Minor data exists, however, about the presence of isomorphous substitutions of other cations (Cu, Ga, etc) for $Al^{VI}$ in kaolinites (e.g. Angel et al. 1975; Meads and Malden, 1975; Petit et al. 1995; Martin et al. 1998) but we are unaware of previous work on the synthesis of kaolinites containing appreciable amounts of Co.

The present work is a part of a more extensive study designed to investigate the rate of incorporation of trace elements in kaolinite and the influence of such substitutions on the kaolinite structure and morphology. From the work of Meads and Malden (1975), incorporation of transition metal ions in kaolinite is considered to provide light on the genesis conditions, especially in lateritic soils and hydrothermal alterations. The incorporation of trace elements in kaolinite could have, in addition, important environmental implications, since it could control the migration of pollutants at surficial conditions (Balan et al. 2002).

Previous results (Bentabol et al., 2006, 2007) indicated that Mg and Ni enter easily into the kaolinite structure reaching up to 0.56 and 0.59 apfu, respectively. We present in this paper the results obtained from a set of hydrothermal reactions designed to favor Co–kaolinite formation.

## 2. Experimental

As in previous experiments, we have used, as starting material, poorly crystalline kaolinite from Georgia (standard KGa-2, from the Clay Mineral Society Source Clays Repository), after an intense grinding. Details of the grinding method have been previously described (Bentabol et al., 2006). Transmission electron microscopy

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**Table 1**
Reactions studied

| | | Time |
|---|---|---|
| Reaction Z: 1Kln+0.6 $CoCl_2$ | | |
| | Z-1 | 1 day |
| | Z-15 | 15 days |
| | Z-30 | 30 days |
| Reaction ZM: 1Kln+0.3 $CoCl_2$+0.3 $Co(OH)_2$ | | |
| | ZM-1 | 1 day |
| | ZM-15 | 15 days |
| | ZM-30 | 30 days |
| Reaction ZT: 1Kln+0.6 $Co(OH)_2$ | | |
| | ZT-1 | 1 day |
| | ZT-15 | 15 days |
| | ZT-30 | 30 days |

(TEM) observations and granulometric analyses indicated that grinding led to amorphization of a high fraction of kaolinite, as deduced from the presence of a broad diffraction band between 20 and 30°2$\theta$, and to the formation of rounded particles with an average size of <0.5 µm (González Jesús et al. 2000). The impurities detected by X-ray diffraction (XRD) and transmission/analytical electron microscopy (TEM/AEM) consist of abundant grains of anatase and minor Fe oxide.

The reactions studied are summarized in Table 1. A solid/solution ratio = 1:15 was used in all the reactions, with solutions 0.16 M. The hydrothermal treatments were conducted in 50 $cm^3$ Teflon-lined reactors (Parr 4744), which were maintained at a constant temperature of 200 °C (±3 °C), with reaction times from 1 to 30 days.

After repeated washing, the solid products of the reactions were characterized by XRD, Fourier transform infrared spectroscopy (FTIR) and TEM/AEM. XRD patterns were obtained using a Philips X'Pert PRO MPD (Malaga University), with Cu$K\alpha$, radiation, at 35 mA y 45 kV, with a step size of 0.017° and counting time of 800 s. Randomly oriented XRD patterns were scanned between 2 and 65°2$\theta$.

FTIR spectra were recorded using KBr pellets (2% wt. sample) in a Nicolet spectrometer (20XB), in the range 4000–400 $cm^{-1}$. Resolution ranged from 1 to 8 $cm^{-1}$. 400 scans were accumulated to improve the signal to noise ratio in the spectra. The pellets were dried at 120 °C for 1 day before obtaining the spectra.

The TEM study was carried out using a Philips CM-20 microscope operated at 200 kV (CIC, University of Granada), fitted with an ultrathin window, solid-state Si(Li) detector for energy dispersive X-ray analysis (EDAX). Additional high-resolution images were obtained using a Jeol 3000 F, operated at 300 kV (University Complutense). The solid products were encased within an epoxy resin and then sliced. Microanalyses were obtained in STEM mode. Quantitative determinations used the thin-film approximation of Lorimer and Cliff (1976). Albite, spessartine and muscovite (Al), forsterite and annite (Mg and Fe), spessartine (Mn) and titanite (Ca and Ti) were used as standards.

## 3. Results

### 3.1. XRD

The solid phases identified by XRD in the products of the several reactions were: kaolinite and other kaolin-polytypes, serpentine and poorly crystalline phases (Fig. 1; Table 2). Only the products of the reaction ZT, for a short reaction time (1 day), show the presence of Co–

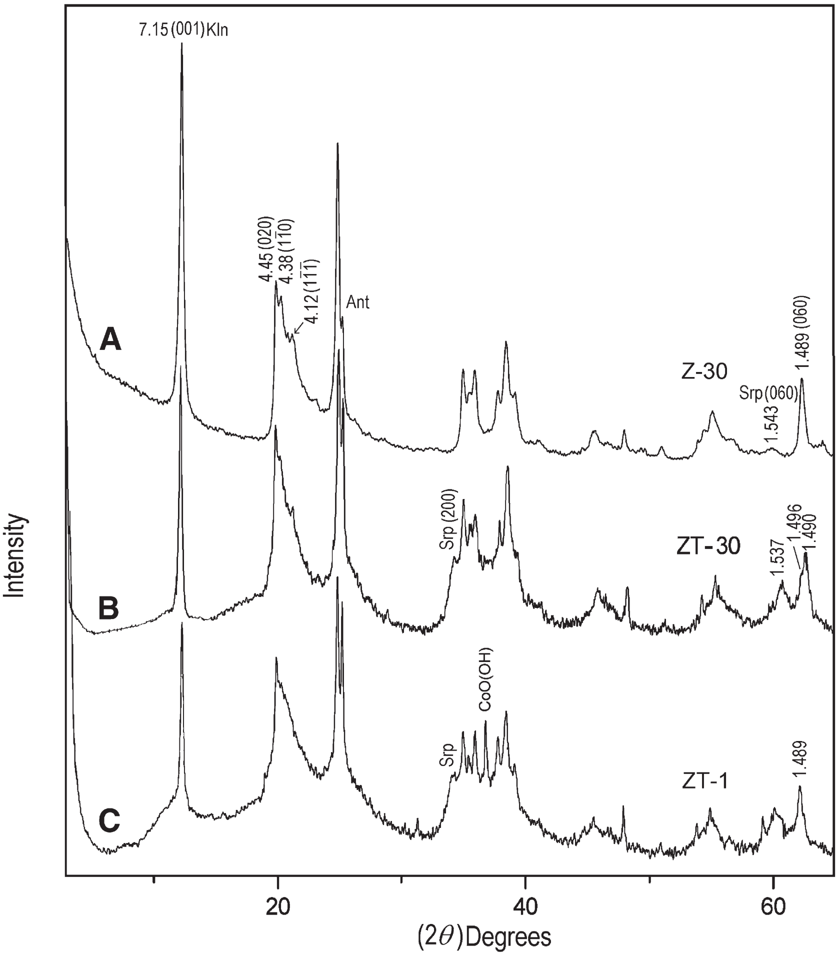

**Fig. 1.** Representative XRD patterns obtained from unoriented samples (range 2–65°2$\theta$) of the solid products of the hydrothermal reactions described in this work. Kln: Kaolinite; Srp: Serpentine; Ant: Anatase. Some kaolinite reflections have been indexed.