Materials Research, Vol. 7, No. 2, 359-361, 2004.

Thermal Decomposition of Illite

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Received: March 21, 2003; Revised: October 4, 2003

The effect of heat treatment on illite in air at temperatures ranging from 750 to 1150 °C was studied using the Mössbauer effect in ^{57}Fe. The dependence of the Mössbauer parameters and relative percentage of the radiation absorption area was measured as a function of the firing temperature. The onset of thermal structural decomposition occurred at 800 °C. With rising temperature, the formation of hematite (Fe_2O_3) increased at the expense of the silicate mineral.

Keywords: *Illite,Thermal decomposition, Mössbauer Spectroscopy*

1. Introduction

Kaolinite and Illite are the clay minerals most commonly used for structural clay products in the traditional ceramic industry. Illite is probably the world's most widespread clay mineral, especially in the temperature latitudes and on the ocean floor[1].

Illites are sheet silicates with low iron content. Their composition is quite variable and strongly dependent on their origin. Their structural family is 2:1 and they are normally dioctahedral. i.e., an octahedral sheet is sandwiched between two tetrahedral sheets of SiO_2. The octahedral cations are surrounded by four oxygens and two hydroxyls in a trans- or cis- configuration. The octahedral sites are occupied by Mg^{+2}, Fe^{+2}, Fe^{+3}, Al^{+3}, etc. and are assigned by M1 if they are in the trans- position or by M2 if they are in the cis-position.

Although much work has been done on the thermal decomposition of sheet silicates in general, little has been published on illite in particular. Most of the studies on sheet silicates have been confined to biotites and micas. The thermal decomposition of muscovites and biotites has has been studied by infrared spectroscopy[2]. Mössbauer spectroscopy is extensively used by mineralogists, geologist and physicist to analyze clay minerals. The Mössbauer spectra of illites reported on in the literature have proved quite variable and strongly dependent on geological and geochemical parameters[4,5,6]. The objective of this work is to study the thermal decomposition of illite as a function of the temperature, using Mössbauer spectroscopy.

2. Experimental Procedure

Illite samples from the ceramic industry of the state of Rio Grande do Norte (Brazil) were collected directly at the plant and heat treated at different temperatures in air. The raw material was milled for eight h in a planetary ball milling machine to a fine powder (10 μm). After heat treatment, the samples were mounted in an acrylic sample holder and the Mössbauer spectra recorded at room temperature. The ^{57}Fe Mössbauer spectra were obtained in a transmission geometry, using a conventional constant acceleration spectrometer operating in triangular wave mode with a ^{57}Co source in a Rhodium matrix at room temperature. The spectrometer was calibrated with a 25 mm thick α-Fe foil.

3. Results

Figures 1 shows the differential thermal analysis curves. The clay shows endothermic bands at 110 to 140 °C corresponding to water loss. The curve shows an endothermic reaction occurring between 470 and 580 °C caused by dehydroxilation of the octahedral sheet (constitutive wa-

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Articles presented at the XV CBECIMAT, Natal - RN, November de 2002.

ter). The hydroxyl groups of the tetrahedral sheet are gradually removed up to 850 °C. An exothermic peak resulting from crystal reformation (spinel phase) then appears between 850 and 920 °C. It can also be inferred that the endothermic peaks at 1110 - 1150 °C are due to the formation of mullite and cristobalite phase. The existence of both endothermic and exothermic peaks is congruous with the results of reference[7].

The Mössbauer spectrum of the untreated sample, which is shown in Fig. 2, was fitted using a least squares procedure with the sum of four Lorentz-shaped doublets corresponding to the quadrupolar splitting of Fe^{+2} and Fe^{+3} in the two M1 and M2 sites[4]. The two most intense central doublets are ascribed to Fe^{+3} in the M1 and M2 sites. The two right shifted doublets are attributed to Fe^{+2} in the same coordination sites (M1 and M2).

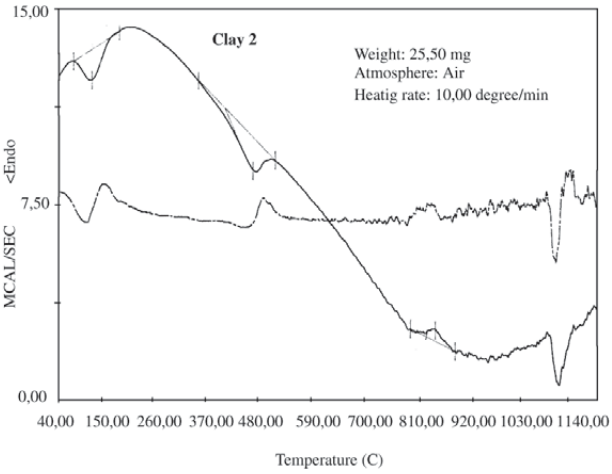

Figure 1. differential thermal analysis curves of the untreated sample.

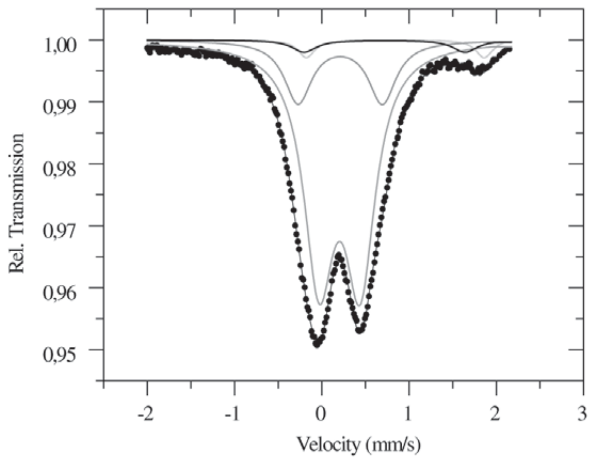

Figure 2. Mössbauer spectrum of untreated sample.

Table 1 shows the hyperfine Mössbauer parameters and the relative absorption area (A(%)) of Fe^{+2} and Fe^{+3} in each site position. The absorption area was directly proportional to the amount of iron in the sample.

Figure 3 shows the Mössbauer spectra for the samples heat treated at temperatures between 750 and 1150 °C. The spectrum for the sample treated at 750 °C shows only two central doublets attributed to Fe^{+3}, indicating that Fe^{+2} was completely oxidized. The high value of the quadrupolar splitting at this temperature may have been caused by dehydroxilation of Fe^{+3} hydroxide and a variety of iron sites due to O^{-2} and trapped water molecules bringing about distortion in the lattice[3]. The Fe^{3+} components were assigned to configurations (a) and (b) for higher and lower Δ, respectively[3]. The (a) configuration was ascribed to the less symmetric $Fe^{3+}(O_5OH)$ coordination while the (b) configuration corresponded to the symmetric $Fe^{3+}(O_6)$ coordination. The samples heat treated at temperatures of 800 to 1150 °C also displayed Mössbauer spectra with the same two central doublets found in the sample treated at 750 °C. In addition, a sextet observed in all spectra was found to corre-

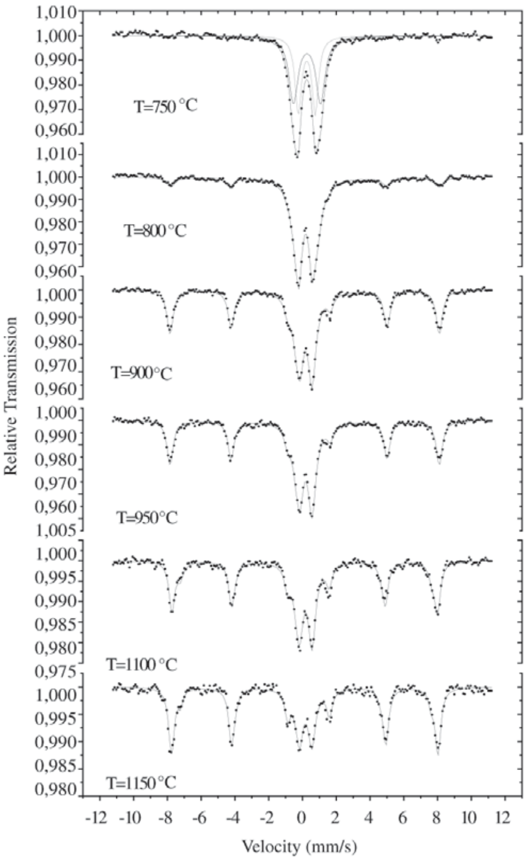

Figure 3. Mössbauer spectra of heat treated samples.

Table 1. Mössbauer parameters for untreated sample.

F.T(°C)	H (KOe)	Δ (mm/s)	δ (mm/s)	A (%)
750	-	1.60	0.26	55.3
	-	1.05	0.25	44.7
	-	1.21	0.21	52.1
800	-	0.75	0.18	32.8
	494	-0.10	0.25	15.1
	-	1.15	0.16	34.3
850	-	0.72	0.19	30.3
	494	-0.12	0.26	35.4
	-	0.90	0.14	33.0
900	-	0.68	0.21	22.1
	495	-0.12	0.26	44.9
	-	0.90	0.14	32.8
950	-	0.72	0.21	21.9
	495	-0.12	0.26	45.3
	-	0.88	0.14	22.8
1100	-	0.69	0.20	21.9
	462	-0.06	0.27	14.3
	489	-0.11	0.24	41.7
	-	0.86	0.16	13.1
1150	-	0.70	0.19	18.1
	460	-0.07	0.27	9.5
	490	-0.12	0.25	59.3

Table 2. Mössbauer parameters for Illite as a function of the firing temperature.

		δ (mm/s)	Δ (mm/s)	A (%)
Fe^{+3}	M1	0.21	0.96	18.6
	M2	0.20	0.47	74.9
Fe^{+2}		0.84	2.02	3.2
		0.72	1.84	3.3

spond to magnetic hyperfine splitting. A marked change was also observed in the samples' color, which started with orange at 800 °C and intensified to a bright red at 1150 °C. The sextet, with a hyperfine field of 495 kOe, was very well fitted with the hematite Mössbauer parameters. X-ray diffraction results published in the literature confirm the presence of Hematite at 1150 °C[9]. The low hyperfine fields 462 kOe and 489 kOe observed in samples fired at 1100 °C may be attributed to the small particle size. Similar values have been reported in the literature[8].

As can be seen from the above spectra, the absorption area of the hematite subspectra increased as the temperature rose to the detriment of the silicate subspectra absorption area, suggesting that the hematite thus formed was a product of the thermal decomposition of the silicate. Table 2 shows the Mössbauer parameters and relative absorption areas of the silicate and hematite subspectra.

The above results for illite are very different from those of the thermal decomposition of other sheet silicates reported in the literature. For example, a Mössbauer study of heat treatment in air of biotite showed no evidence of hematite formation below 900 °C[3], while another study reported hematite formation only at 980 °C[8].

4. Conclusions

We investigated the effect of heat treatment in air on illite. The results of this study led us to the following conclusions:

1. The changes in Mössbauer spectra were correlated with oxidation and dehydroxilation.
2. Onset of the dehydroxilation process began prior to the decomposition of the original silicate structure.
3. The magnetic pattern that appeared up to 800 °C was attributed to hematite.

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