The effect of mechanochemical treatments of sepiolite with CsCl on the calcination products

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Abstract Calcination of sepiolite and of two sepiolite/CsCl mixtures, unground and air-ground was investigated by thermo-XRD-analysis. At 200 °C sepiolite, neat, mixed or air-ground with CsCl lost interparticle and zeolitic water. The framework of sepiolite persisted during the dehydration but became defected, mainly in the air-ground mixture, less in the unground mixture and little in the neat clay. At 500 °C, with the loss of bound water, the neat clay was folded and transformed into sepiolite anhydride. In sepiolite/CsCl mixtures the dehydrated variety persisted but the degree of crystal-imperfection increased in the air-ground mixture more than in the unground mixture. At 700 °C the neat clay remained crystallized, but the CsCl mixtures became amorphous. Some crystalline dehydrated sepiolite or sepiolite anhydride persisted in the unground and air-ground CsCl mixtures, respectively. At 850 °C, the neat clay crystallized into protoenstatite with some enstatite and clinoenstatite. The amorphous fraction of sepiolite in the unground sepiolite/CsCl mixtures crystallized into pollucite and forsterite and the crystalline fraction was transformed into enstatite, protoenstatite, and clinoenstatite. In the air-ground mixture, the amorphous phase was transformed into pollucite with some forsterite and the crystalline fraction into enstatite.

Keywords Cesium chloride · Clinoenstatite · Enstatite · Forsterite · Mechanochemistry of sepiolite · Pollucite · Protoenstatite · Thermo-XRD-analysis

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Introduction

The use of different earths (e.g. fuller earths) for cleaning clothes or for pharmaceutical and medical purposes as well as for cosmetic purposes is known from ancient times [1]. From recent geological surveys, it is known that the clay fraction of most earths mentioned by Greek historians or quoted in Egyptian medical papyri or Sumerian lists is calcium montmorillonite. However, in many of these earths sepiolite or palygorskite is the principal clay fraction. For these applications, the earth was ground and in many cases also thermally treated. In order to provide special properties to the clay, different inorganic or organic additives were ground together with the earth.

Mechanochemical interactions of clay minerals with alkali halides were widely investigated in our laboratory (see e.g. [2–13]). Cesium is unique among the alkalis. Due to its large size the polarizing power and hydration abilities are weak. Cs^+ breaks water structure, enriching the system with monomeric water molecules. Recently, our attention has been focused on the mechanochemical reactions of sepiolite with several alkali halides and it has been found that the effect of CsCl differed from that of the other salts.

Most clay minerals have a layer structure [14, 15] and during mechanochemical treatments with alkali halides they delaminate [3–9]. Sepiolite and palygorskite are unique. In their structure, there is a repeated inversion of the tetrahedral-octahedral-tetrahedral (TOT) layer. As a result of this inversion, they have intraparticle tunnels and interparticle channels [16]. The two minerals differ in the frequency of inversion, sepiolite having wider tunnels.

Grinding and thermal treatments of sepiolite are applied in different industries [17]. Calcination of sepiolite has been widely investigated, and most investigators claim that clinoenstatite is the principal thermal product [18].

In 'wet-grinding', few drops of water are added to the system to keep it moist during the process. In 'air grinding', the process is carried out at ambient atmosphere without adding water [12, 13]. The purpose of this study is to find the effect of the mechanochemical treatment and that of CsCl on the calcination products. In this study, air-ground neat sepiolite, unground sepiolite/CsCl mixture and air-ground mixture were heated at 200, 500, 700 and 850 °C, respectively, and the thermal products were determined by X-ray.

Experimental

Materials

Sepiolite used in this study was from Vallecas (Spain), supplied by Ward's Natural Science Establishment. The mineral was crushed and ground manually in an agate mortar and sieved to 100 mesh. Cesium chloride was of a Suprapur grade, supplied by Merck.

Methods

Three different samples were prepared. Sample *a* is air-ground neat sepiolite. For comparison, samples of unground and wet-ground neat sepiolite were also prepared. Sample *b* is a thoroughly mixed unground mixture of 100 mg sepiolite (previously ground for 3 min) and 200 mg CsCl. Sample *c* is a mixture of 100 mg sepiolite and 200 mg CsCl manually ground in ambient air. The ground mixture is termed '*air-ground*'. Manual grinding of samples *a* and *c* was carried out in an agate mortar for 3 min.

The application of thermo-XRD-analysis in the study of clay minerals has been described [19]. The samples were heated at 200, 500, 700, and 850 °C, 3 h at each temperature and were cooled to room temperature in a desiccator. X-ray diffractograms were recorded at room temperature in the range 5.0–40.0 2θ by a Philips Automatic Powder Diffractometer (PW 1710) with a Cu-tube anode.

Results and discussion

Before the thermal treatment, sepiolite is hydrated. Interparticle water is adsorbed onto the external channels and intraparticle zeolitic and bound water is located inside the tunnels.

Sepiolite shows four thermal water evolution steps [17, 18]. In the first step (room temperature −250 °C), interparticle and zeolitic water escapes with almost no change in the sepiolite crystal [20]. The phase obtained at this stage is named *dehydrated sepiolite.* In the second step (250–430 °C), half of the *bound water* (water molecules bonded to Mg at the edges of the octahedral sheets inside the tunnels) is

lost. At this step, the crystal folds by rotation of the ribbons about an axis through the Si–O–Si corner bonds that link the ribbons [20–22]. The resulting phase is named *folded sepiolite*. In the third step (430–650 °C), the remaining bound water escapes together with partial dehydroxylation. The resulting phase with shorter *a* and *b* and longer *c* of the unit cell [23] is named *sepiolite anhydride*. In the fourth step (≥650 °C), the dehydroxylation of the clay occurs with the formation of amorphous *meta-sepiolite*. However, the latter immediately crystallizes into an enstatite variety.

Before the thermal treatment diffractograms of unground and air-ground neat sepiolite were similar, the latter showing the highest resolution.

Table 1 depicts representative reflection indices of sepiolite quoted from the literature [24], XRD spacings (in Å) and intensities (in %) in diffractograms of air-ground neat sepiolite (sample *a*), and of unground and air-ground sepiolite/CsCl mixtures (*b* and *c*, respectively) heated at 200 and 500 °C. Sepiolite/CsCl mixtures were diffracted in the presence of excess CsCl. 'Apparent intensities' were related to the most intense CsCl reflection (2.92 Å) and 'calculated intensities' to the most intense sepiolite reflection (12.00 Å).

Samples *a*, *b* and *c* heated at 200 °C

After 200 °C, dehydrated sepiolite was the principal component in each sample. Reflections with spacings similar to those recorded before the thermal treatment, appeared in diffractogram of thermal treated sample *a* indicating that the framework of sepiolite persisted the escape of zeolitic water.

Twelve reflections with spacings characteristic for sepiolite, appeared between 5.0–40.0 2θ in the diffractogram of the unground sepiolite/CsCl mixture heated at 200 °C, indicating that the sepiolite framework persisted the escape of zeolitic water from sample *b*. Calculated intensities of eight of the reflections were similar to the apparent intensities of the neat dehydrated sepiolite. The disappearance of characteristic reflections which appeared in the diffractogram of dehydrated sepiolite and the intensification of four reflections suggest that in the presence of CsCl dehydrated sepiolite contained more crystal imperfections than in its absence.

Only eight reflections with spacings characteristic for sepiolite, appeared in the diffractogram of the air-ground sepiolite/CsCl mixture heated at 200 °C, indicating that sepiolite framework of sample *c* survived the escape of zeolitic water. Calculated intensities of three of these reflections were similar to the apparent intensities of those of the neat dehydrated sepiolite, but four reflections intensified and one became weak suggesting that dehydrated sample *c* was the most disrupted among these three samples.

Table 1 Representative XRD reflection indices (h,k,l) quoted from the literature [24], spacings (Å) and peak intensities (int, %) in diffractograms of air-ground neat Vallecas sepiolite and of sepiolite/CsCl mixtures unground and air-ground after heating at 200 and 500 °C

h,k,l	Thermally treated at 200 °C								Thermally treated at 500 °C							
	Vallecas sepiolite		Vallecas sepiolite/CsCl mixtures						Vallecas sepiolite		Vallecas sepiolite/CsCl mixtures					
	Neat, air-ground		Unground			Air-ground			Neat, air-ground		Unground			Air-ground		
	Å	Int (%)	Å	Appar. int (%)	Calcul. Int (%)	Å	Appar. int (%)	Calcul. Int (%)	Å	Appar. int (%)	Å	Appar. int (%)	Calcul. Int (%)	Å	Appar. int (%)	Calcul. Int (%)
1,1,0	12.00	100	11.98	49	100	12.01	40	100	12.01	38	12.10	22	100	12.10	17	100
									10.10	44						
														9.36	14	–
														8.49	1	–
									8.10	47						
1,3,0	7.51	4	7.45	4	8	7.51	2	5			7.43	2	9	7.27	2	12
									5.88	3						
0,1,1	5.18	1							5.18	29						
1,5,0	5.03	2	5.03	1	2	5.02	2	5	5.00	24	5.01	1	5	4.99	2	12
									4.68	22						
0,3,1	4.52	9	4.50	4	8	4.54	3	8			4.48	3	14	4.55	3	18
									4.41	100						
1,3,1	4.32	13	4.30	6	12				4.33	72	4.32	6	27			
									4.06	9						
									3.90	20						
0,5,1	3.76	8	3.74	4	8				3.79	21	3.75	3	14	3.73	3	18
2,4,1	3.55	3	3.53	2	4				3.48	11						
4,0,0	3.35	9	3.34	7	14	3.34	7	18	3.34	11	3.34	5	23	3.33	6	35
									3.26	25						
3,3,1	3.19	7	3.19	6	12	3.20	5	13			3,20	4	18	3.21	4	24
2,6,1	3.04	2	3.03	4	8				3.12	28						
									2.99	14						
CsCl			**2.92**	**100**	–	**2.92**	**100**	–			**2.92**	**100**	–	**2.92**	**100**	–
0,10,0	2.69	2	2.69	1	2	2.69	2	5	2.70	9	2.70	1	5	2.70	2	12
1,9,1	2.56	9	2.55	4	8	2.56	2	5	2.56	21	2.56	3	14	2.55	1	6
									2.51	19						

Appar., apparent intensity is related to the most intense reflection of CsCl (at 2.92 Å)

Calcul., calculated intensity is related to the most intense reflection of sepiolite (at 12.00 Å, 110 reflection)

Reflection spacings and indices of CsCl are given in bold entries

Samples *a*, *b* and *c* heated at 500 °C

A reflection at 12.00 Å with 38% intensity appeared in the diffractogram of neat sepiolite after heating at 500 °C. In diffractograms of hydrated or dehydrated sepiolite, the intensity of this peak was 100.0%. The fading at 500 °C and the disappearance of several peaks which had appeared before the thermal treatment, suggested that a crystallographic transformation occurred with the escape of bound water. However, the appearance of this peak at 500 °C indicated that small amounts of dehydrated sepiolite retained. Eight reflections which appeared in the diffractogram of dehydrated sepiolite appeared also after heating at 500 °C but were highly intensified. This intensification together with the appearance of 11 new peaks, indicate the appearance of new phases, folded sepiolite and sepiolite anhydride [22, 23]. It should be noted that a new peak at 4.41 Å had an intensity of 100%.

Diffractogram of unground sepiolite/CsCl mixtures (sample *b*) heated at 500 °C differed from that of heated neat sepiolite at this temperature. Three reflections at 7.50, 4.50 and 3.20 Å occurred in both diffractograms at 200 °C but at 500 °C they were detected only in that of sample *b*. Six reflections appeared in both diffractograms but were

Table 2 Representative XRD reflection indices (h,k,l), spacings (Å) and peak intensities (int, %) in diffractograms of enstatite, protoenstatite, clinoenstatite, pollucite and forsterite quoted from the literature [24] and spacings and intensities in diffractograms of air-ground neat Vallecas sepiolite and of unground and air-ground sepiolite/CsCl mixtures thermally treated at 850 °C

Enstatite [Mg₂(Si₂O₆)] Data from the literature			Protoenstatite [Mg₂(Si₂O₆)] Data from the literature			Clinoenstatite [Mg₂(Si₂O₆)] Data from the literature			Forsterite (Mg₂SiO₄) Data from the literature			Pollucite [CsAl(Si₂O₆)] Data from the literature			Thermally treated clay at 850 °C					
															Vallecas sepiolite Neat/air-ground		Vallecas sepiolite with CsCl Unground		Air-ground	
h,k,l	Å	Int (%)	h,k,l	Å	Int (%)	h,k,l	Å	Int (%)	h,k,l	Å	Int (%)	h,k,l	Å	Int (%)	Å	Appar. Int (%)	Å	Appar. Int (%)	Å	Appar. Int (%)
2,1,0	6.43	3	1,1,0	6.34	2	1,1,0	6.34	1							6.50	1				
												1,1,2	5.57	17					5.61	9
									0,2,0	5.10	28						5.09	9	5.12	3
																			4.56	5
0,2,0	4.48	10	0,2,0	4.46	5	0,2,0	4.41	9							4.46	13	4.40	25		
						0,1,1	4.29	8							4.25	16	4.24	32		
									0,2,1	3.89	73				3.79	14	3.88	61	3.90	7
									1,0,1	3.72	25									
						1,1,1	3.53	4				2,1,3	3.65	64	3.51	14	3.67	68	3.67	47
1,2,1	3.36	21	2,1,1	3.28	17	1,2,1	3.32	8				4,0,0	3.41	100	3.36	28	3.45	53	3.43	100
						0,2,1	3.29	30									3.28	100		
4,1,1	3.24	18	1,2,1	3.23	100										3.23	100	3.24	70		
2,2,1	3.20	100				2,2,0	3.17	47							3.18	41	3.17	89	3.18	6
																			3.06	2
			3,1,0	2.94	28	2,2,1	2.98	69							2.99	35	2.99	42		
6,1,0	2.90	62	1,3,0	2.84	2	3,1,0	2.88	100							2.89	51	2.87	79	2.88	5
			2,2,1	2.77	24				1,3,0	2.77	65	4,1,3	2.68	39			2.76	31	2.77	5
																	2.66	10	2.68	3
6,2,0	2.53	38	3,1,1	2.57	18	1,3,1	2.54	23	1,3,1	2.51	81				2.54	17	2.53	29	2.52	7
			1,3,1	2.51	7	0,3,1	2.52	19									2.51	35		
						0,0,2	2.46	35	1,1,2	2.46	100	4,4,0	2.41	30	2.46	11	2.46	45	2.46	8
																			2.42	19
			2,0,2	2.33	15				0,4,1	2.35	13								2.35	30
									1,2,2	2.27	43								2.27	3

weaker in that of sample **b**. On the other hand, diffractogram of sample **b** heated at 500 °C was similar to that of this sample heated at 200 °C. New reflections did not appear at 500 °C indicating that new phases were not formed. Most reflections intensified from 200 to 500 °C indicating an increase in crystal imperfections. To conclude, the principal component at 500 °C was disrupted dehydrated sepiolite.

The diffractogram of air-ground sepiolite/CsCl mixtures (sample **c**) heated at 500 °C also differed from that of the heated neat sepiolite and was similar to that of sample **c** heated at 200 °C. Reflections that appeared at 200 °C also appeared at 500 °C with a higher intensity indicating an increase in the crystal imperfections. Intensifications during heating from 200 to 500 °C were higher in sample **c** than in **b** suggesting that the air-ground sepiolite/CsCl mixture resulted in the most defected dehydrated sepiolite.

In addition to increasing crystal defects, the diffractogram of sample **c** heated at 500 °C showed two new peaks at 9.36 and 8.50 Å, suggesting the formation of small amounts of a new phase, probably a variety of folded sepiolite. These spacings differed from those of thermal treated sample **a** suggesting that this new phase differed from folded sepiolite of sample **a**.

Samples **a**, **b** and **c** heated at 700 °C

Diffractogram of neat sepiolite was similar to that recorded after heating the sample at 500 °C. Only the peak at 12.00 Å which is diagnostic for dehydrated sepiolite, became considerably weak as a result of further transformation of sepiolite to the folded and anhydrous varieties.

In the presence of CsCl, dehydroxylation and amorphization of the sepiolite was evident from the fading and disappearance of most characteristic sepiolite reflections in diffractograms of both samples. In both diffractograms, peaks of CsCl were very intense. In the diffractogram of the unground mixture, a weak reflection at 12.0 Å appeared suggesting the persistence of some crystalline dehydrated sepiolite. In that of the air-ground sepiolite/CsCl mixture a weak reflection at 8.5 Å was detected suggesting the presence of small amounts of crystalline sepiolite anhydride.

Samples **a**, **b** and **c** calcined at 850 °C

Table 2 depicts XRD reflection indices, spacings (in Å) and intensities (in %) in diffractograms of enstatite, protoenstatite clinoenstatite, forsterite and pollucite taken from the literature [24]. Reflection spacings and intensities in diffractograms of neat sepiolite (sample **a**) and of sepiolite/CsCl mixtures unground and air-ground (samples **b** and **c**, respectively) heated at 850 °C are also depicted in the table. X-ray diffractograms of four calcined samples are shown in Fig. 1.
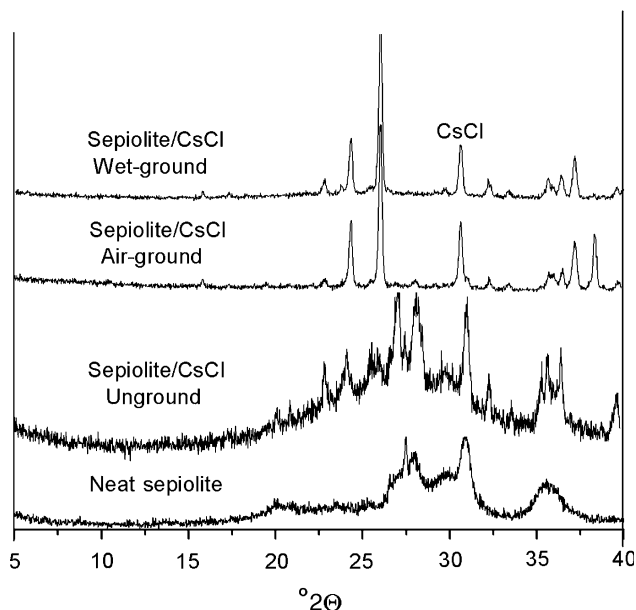

Fig. 1 From bottom to top, X-ray diffractograms of neat sepiolite (sample **a**), unground, air-ground and wet-ground sepiolite/CsCl mixtures (samples **b, c** and **d**, respectively), after thermal treatment at 850 °C

Based on data summarized in Table 2, it was concluded that during calcination at 850 °C neat Vallecas sepiolite was transformed into protoenstatite with some enstatite and clinoenstatite.

In the presence of CsCl with rising temperature, the dehydrated sepiolite became more and more disrupted. In contrast to the neat sepiolite, at 700 °C most of the clay was amorphous. At 850 °C, the calcination of the amorphous sepiolite/CsCl mixtures resulted in the crystallization of the cesium mineral pollucite and the magnesium mineral forsterite. Calcination of unground sepiolite/CsCl mixture resulted in considerable amounts of pollucite and forsterite from the amorphous phase and clinoenstatite with some enstatite and protoenstatite from the persisting dehydrated sepiolite. In the calcined air-ground sepiolite/CsCl mixture pollucite with some forsterite crystallized from the amorphous phase and small amounts of enstatite obtained from the persisting sepiolite anhydride.

Conclusions

Four thermal decomposition steps were identified during the thermo-XRD-analysis of neat sepiolite (sample **a**): (i) dehydrated sepiolite appeared with the escape of zeolitic water; (ii) folded sepiolite appeared with the escape of the first half of bound water; (iii) sepiolite anhydride appeared with the escape of the second half of bound water and (iv) three varieties of enstatite (enstatite, protoenstatite and

clinoenstatite) crystallized from amorphous meta-sepiolite formed during the dehydroxylation of the clay.

In the presence of CsCl, different reaction sequences occurred during the thermo-XRD-analysis which at 850 °C resulted in different calcination products. With the escape of zeolitic water, the unground mixture (sample **b**) gave disrupted dehydrated sepiolite. This phase persisted with the rise in temperature but became more disrupted and at 700 °C was amorphous. At 850 °C, the amorphous phase crystallized into pollucite and forsterite. Some dehydrated sepiolite persisted at 700 °C and at 850 °C was transformed to clinoenstatite, protoenstatite and enstatite.

With the escape of interparticle and zeolitic water from the air-ground CsCl mixture (sample **c**), highly disrupted dehydrated sepiolite was obtained. With the escape of the first half of bound water the degree of disruption of the dehydrated sepiolite increased and simultaneously small amounts of a new anhydride phase appeared which differed from the folded sepiolite of sample **a**. At 700 °C, the disrupted dehydrated sepiolite became amorphous and at 850 °C the amorphous phase crystallized into pollucite with some forsterite. Some crystalline sepiolite anhydride persisted at 700 °C which at 850 °C was transformed into enstatite and clinoenstatite.

In conclusion, mechanochemical treatment with CsCl has an effect on the calcination of sepiolite. Because of different reaction sequences during the thermal treatment, the calcination of samples **a**, **b** and **c** resulted in different products.

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