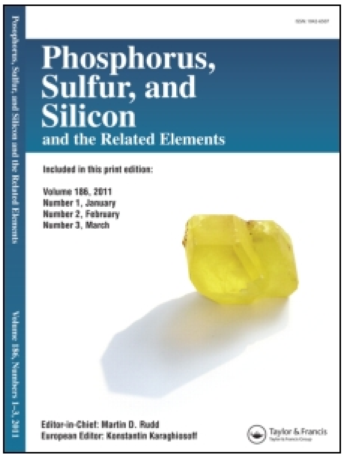

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PREPARATION AND CHARACTERIZATION OF THE CALCIUM POLYPHOSPHATE, TRÖMELITE

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Abstract The calcium polyphosphate, Trömelite, is prepared over a wide range of Ca/P ratios. Use of an acidic MCP as a raw material facilitates Trömelite formation. Quantitative ^{31}P NMR analysis of EDTA solutions show that Trömelite is initially formed as a hexapolyphosphate. Under tempering at 960°C, a relatively constant composition near 27% tripolyphosphate, 20% pentapolyphosphate, and 53% hexapolyphosphate is formed.

INTRODUCTION

The calcium polyphosphate, Trömelite, is formed as a single phase with an identifiable X-ray powder diffraction pattern over a wide range of Ca/P ratios in the $CaO-P_2O_5$ phase diagram.[1] Trömelite has been characterized variously by Ohashi and Van Wazer[2] as a pentapolyphosphate and by Thilo and coworkers[3] as a hexapolyphosphate. In this work, Trömelite is prepared and characterized in an attempt to better understand its synthesis and composition.

SYNTHESIS

Trömelite is prepared by heating compositions with an overall Ca/P mole ratio of approximately 0.6-0.8 to 960°C. The Ca/P ratios correspond to average polyphosphate chain lengths, $\bar{n}$, of about 4 to 9 in the final product. Unless otherwise stated, Trömelite was prepared from mixtures of monocalcium phosphate monohydrate (MCP), $Ca(H_2PO_4)_2*H_2O$, and dicalcium phosphate, $CaHPO_4$ (DCP). The formation of Trömelite is confirmed by X-ray powder diffraction (XRD). Synthesis depends on the MCP used; repeated attempts at preparing Trömelite were unsucessful when using MCP with a composition slightly more basic than theoretical (EM Science, MCP powder, Ca/P= 0.55). Reaction of basic MCP with either DCP or CaO did not yield Trömelite even after two weeks at 960°C. The use of acidic MCP (J.T. Baker, crystal MCP, Ca/P=0.48-0.50) resulted in conversion to Trömelite within a few hours. Trömelite is also prepared by heating $Ca_3H_2P_2O_7$ at 620°C.

CHARACTERIZATION

XRD patterns of Trömelite preparations usually indicate the presence of calcium pyrophosphate and calcium metaphosphate in addition to Trömelite. Among the various preparations, tions, no measurable shifts in 2θ values were observed for the Trömelite phase.

Trömelite samples are dissolved in EDTA solution at pH 7.0-7.5 over a two week period at ambient temperature. No hydrolysis is observed. EDTA solutions are analyzed for phosphate species distribution by quantitative ^{31}P NMR.[4]

Species analysis for Ca/P=0.70 (i.e. $\bar{n}$=5) indicates that hexapolyphosphate is formed initially (Table I). Upon

TABLE I Analysis of Dissolved Trömelite as a Function of Calcination Time; Ca/P= 0.70-0.71.

	Per Cent P_2O_5 as-						
Hours @ 960°C	Ortho n=1	Di 2	Tri 3	Tetra 4	Penta 5	Hexa 6	Meta high
1.5	4	6	7	0	7	68	8
20	3	7	6	0	14	65	5
123	8	8	19	0	15	29	21

tempering at 960°C, hexapolyphosphate undergoes some degree of disproportionation to tripoly-, pentapoly-, and metaphosphate until the composition stabilizes. An initial small weight loss but no appreciable shift in the XRD patterns are observed during the tempering.

Analysis of preparations with widely varying Ca/P ratios held at 960°C for 123 hr. are shown in Table II. Considering Trömelite as the collection of oligophosphates excluding pyrophosphate, it is a relatively constant composition near 27% tripolyphosphate, 20% pentapolyphosphate, and 53% hexapolyphosphate. Little to no tetrapolyphosphate or oligomers with $n \geq 7$ are present. Differences in overall Ca/P ratios of various preparations are balanced by the presence of calcium pyrophosphate and metaphosphate. A few percent of orthophosphate is also found.

TABLE II ^{31}P NMR Analysis of Dissolved Trömelite as a Function of the Ca/P Ratio.

		Per Cent P_2O_5 as-						
		Ortho	Di	Tri	Tetra	Penta	Hexa	Meta
Ca/P	$\bar{n}$	n=1	2	3	4	5	6	high
0.76	3.9	6	18	15	0	9	39	13
0.74	4.1	7	13	16	0	10	35	18
0.71	4.8	8	8	19	0	15	29	21
0.68	5.6	6	6	21	0	15	30	22
0.66	6.1	5	4	17	0	16	39	19
0.63	7.7	8	3	19	0	13	32	25
0.62	8.1	7	3	16	0	13	34	27
0.61	9.4	8	3	16	1	9	33	30

Trömelite is also formed by heating $Ca_3H_2(P_2O_7)_2$ at 620°C for 1 hr. This compound having Ca/P=0.75 corresponds to an average composition of the tetrapolyphosphate $Ca_3P_4O_{13}$ upon dehydration. Analysis of the Trömelite product shows it to be primarily tripoly-, hexapoly-, and metaphosphate. No tetrapolyphosphate is observed.

The phases formed in conversion of the orthophosphates to Trömelite was followed by XRD. At 300°C, the phases present included $CaHPO_4$, gamma-$Ca_2P_2O_7$, and an amorphous phase. The amount of amorphous phase was significantly larger for use of the acidic MCP. No $Ca_3H_2(P_2O_7)_2$ was observed by XRD at 240° or 300°C. By 420°C, the DCP has reacted and the amorphous phase has crystallized to delta-$Ca(PO_3)_2$. Delta-$Ca(PO_3)_2$ derived from the acidic MCP premix appears stable at 620°C while that formed from the basic MCP undergoes conversion to the beta form at this temperature. Trömelite is apparently formed by the reaction of delta-$Ca(PO_3)_2$ with gamma-$Ca_2P_2O_7$. Beta-$Ca(PO_3)_2$ is unreactive with $Ca_2P_2O_7$ even at 960°C for several days.

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