value of M_s mentioned above and assuming that the density of the product is 4.1 g/cm^3 as taken from the x-ray data. No noticeable coercivity was found at room temperature, indicating that the product is magnetically soft.

Infrared absorption spectra of the product were studied by Perkin-Elmer 521 type spectrometer in the range of wave length 2.5–40μ. Continuous absorption and no characteristic absorption peak were observed throughout the range. The result is similar to that of pyrrhotite, but differs from that of pyrite and marcasite (pyrite and marcasite have several characteristic absorption peaks in the range 23–32μ).

The author wishes to express his cordial thanks to Dr. T. Katsurai for his valuable advice in regard to autoclaving and also for his kind interest in the preparation of this paper.

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THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

PREPARATION OF PURE ARAGONITE AND ITS TRANSFORMATION TO CALCITE

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INTRODUCTION

By varying the conditions of preparation different polymorphic modifications of calcium carbonate have been obtained in comparatively pure state. The methods suggested for the preparation of aragonite, the orthorhombic modification of calcium carbonate make use of

(1) the precipitation of calcium carbonate at or above 60° C., from a solution of calcium salt by alkali carbonate (Faivre, 1946; de Keyser, 1950; Wray and Daniels, 1957),

(2) passage of carbon dioxide through calcium hydroxide solution (Ievins *et al.*, 1955) or (3) removal of carbon dioxide from a solution of calcium bicarbonate (Kitano *et al.*, 1962).

In most of the methods suggested for the preparation of aragonite, some alkali or alkaline earth ion is introduced to suppress the formation of the undesirable phase. The tendency for the metastable phases of calcium carbonate to be precipitated from aqueous solution, is increased by raising the precipitation rate or by increasing the concentration of foreign substances like magnesium ion or calgon (Brooks *et al.*, 1950). The alkali or alkaline earth ion is difficult to wash off beyond the 0.001 per cent range. We now report a method for preparing highly crystalline aragonite by homogeneous precipitation of calcium carbonate from trichloroacetate medium. Aragonite obtained by this method has both phase and chemical purity. The transformation of aragonite to calcite has been studied by differential thermal analysis (DTA) and photomicrography with a hot stage.

EXPERIMENTAL METHODS

Preparation of aragonite. 0.1 M solution of calcium trichloroacetate was prepared by dissolving 10 g of A.R. calcium carbonate (B.D.H.) in an aqueous solution of 34 g Trichloroacetic acid (E. Merk). The slightly acidic solution was filtered and heated on a boiling water bath (97° C.) for about 8 hours, The crystals were filtered, washed thoroughly with distilled water, till free of chloride ions. They were dried first at room temperature and later at 100–110° C. for 3 hours.

X-ray analysis. Rich Seifert *x*-ray unit and copper Kα radiation were employed. The pattern was taken with Straumanis mounting in a 114.6 mm Phillips powder camera. The powder pattern was measured with a Carl Zeiss Jena glass scale and distances were estimated correct to 0.05 mm.

Differential thermal analysis. A manually operated instrument, employing chromel-Alumel thermocouples was used. A heating rate of 10–12° per minute was maintained by means of a 'Variac.'

Microscopy and photomicrography. Microscopic examinations were carried out under a Bausch and Lomb polarizing microscope. Effect of thermal treatment was followed under an Earnst Leitz Wetzlar photomicrograph equipped with a hot stage. The sample was heated at 5°/minute. The magnification employed was 600×.

EXPERIMENTAL RESULTS AND DISCUSSION

Higher temperatures and the presence of sodium, magnesium and strontium favour the formation of aragonite. Aragonite obtained in the presence of these ions will not be useful for a study of the energetics of its transformation to calcite, since even traces of impurities are known to affect crystal structure transformations. Consequently aragonite prepared by the homogeneous precipitation would prove to be the best for a study of the kinetics and mechanism of transformation, as the sample will be practically free of all mineral ions. Photomicrographs of the powder indicate an average crystallite size of 20μ, while the normal crystallite size obtained with other precipitation methods is $10–15\mu$.

X-ray data. An accurate determination of lattice constants of aragonite was necessary for a detailed study of the mechanism of its transformation to calcite. This required the complete powder pattern, particularly in the high angle region. The National Bureau of Standards (Swanson and Fuyat, 1954) reports only lines up to $d = 1.160$ Å. Hence a complete powder pattern of aragonite was not available except the very early data of Olshausen (1925). A fuller and more complete x-ray data are given in Table 1.

The lines were indexed by comparing the calculated and observed values of $\sin^2\theta$. The intensities reported in Table 1 are visual estimates only.

DTA. The differential thermogram (Fig. 1) shows a small but definite endothermic peak around 465° C., which is ascribed to the transformation of aragonite to calcite.

The sample on heating over a hot stage showed no perceptible change up to about 480° C. Thereafter the crystallites cracked to smaller bits but retained the original needle habit. A sample was heated at 600° C. for 4 hours and quenched. This on examination under a polarizing microscope showed no alteration in the morphology of the crystals, but showed symmetrical extinction.

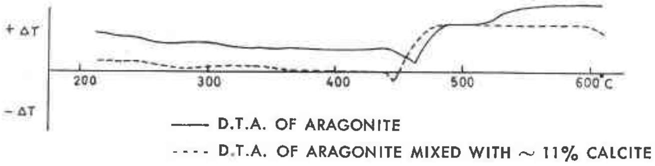

FIG. 1. Differential thermal analysis curves for pure aragonite and aragonite mixed with calcite.

The presence of small amounts of powdered calcite in aragonite is known to favour the transformation (Chaudron *et al.*, 1952). Aragonite mixed with about 11% finely powdered calcite shows the endothermic

Table 1. Powder *X*-Ray Crystallographic Data of Aragonite

Crystal system: Orthorhombic
Space group: D_{2h}^{16}—*Pmcn* (*Pnma*)(Bragg, 1924)
Lattice constants: $a = 4.957 \pm 0.007$ Å
$b = 7.976 \pm 0.007$ Å
$c = 5.740 \pm 0.006$ Å
Density 2.93 ± 0.01 g/c.c. (*x*-ray)

hkl	d in Å	I/I₀	hkl	d in Å	I/I₀	hkl	d in Å		I/I₀
111	3.395	100	312	1.409	7	254	0.9806		4
021	3.273	50	242		4	235			6
				1.365			0.9694		
			331			433			
002	2.869	3							
			060	1.329	3	006	0.9577		3
012	2 700	45							
200	2.478	35							
			332	1.262	6	315	0.9363		4
031	2.408	15							
112	2.372	40	400	1.240	10	026	0.9299		2
						371			
130	2.342	30	134	1.225	5		0.9251		3
						182			
			243						
022	2.328	5		1.205	7	460	0.9051		2
			062						
211	2.188	10	153	1.190	6	461	0.8951		2
			162						
220	2.104	20		1.172	8	372	0.8914		3
			260						
						532			
221	1.976	70	421	1.160	4		0.8838		2
						083			
			412						
041	1.880	35		1.126	5	513	0.8747		2
			234						
132	1.814	25	170	1.110	2	462	0.8638		5
113	1.742	25	063	1.091	2	373	0.8415	α_1	8
							0.8410	α_2	
231	1.728	15	163	1.066	2	551	0.8330	α_1	8
							0.8330	α_2	
311	1.558	5	440	1.052	2	514	0.8114	α_1	8
							0.8112	α_2	
232	1.535	3	135						
				1.031	12	292	0.8014	α_1	7
			413				0.8015	α_2	
241	1.499	5	334	1.005	10				
151	1.468	8	045	0.9930	5				

peak in DTA round about 445° C., nearly 20° below that of pure aragonite. It is probable that the presence of calcite is one of the factors responsible for the wide variations in the temperatures reported for the transformation of natural samples of aragonite (Faust, 1949, 1950; Gruver, 1950).

ACKNOWLEDGMENTS

The authors thank professors A. R. Vasudeva Murphy and M.R.A. Rao for their interest and encouragement. One of the (S.R.Y.) thanks the Council of Scientific and Industrial Researh (India) for financial support.

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THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

CRYSTALLOGRAPHIC DATA FOR Er_2SiO_5 AND Y_2SiO_5[1]

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Recent phase equilibria investigations of rare-earth oxide–silicon dioxide systems and their compounds have been the subject of studies by Warshaw and Roy (1961) and Toropov *et al.* (1961). Of specific interest to this paper are the compounds Er_2SiO_5 and Y_2SiO_5, data for which were reported by both sets of authors. However, a comparison of the powder *x*-ray diffration data for these two compounds as given by Warshaw and Roy with that given by Toropov *et al.* for the identical compounds are not in agreement.

Recently, we have synthesized single crystals of Er_2SiO_5 and Y_2SiO_5 by solution growth from a molten $Li_2O \cdot 2MoO_3$ solvent at approximately 1100° C. Spectrochemical analyses of the erbium compound showed only significant quantities of erbium and silicon with less than 0.1% Mo present. Confirmation of the formula was obtained by solid state synthesis of these compounds. This was accomplished by physically mixing powders

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.