

86. *Hydrothermal Chemistry of Silicates. Part XII.** *Synthetic Strontium Aluminosilicates.*

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The hydrothermal crystallisation of hydrous gels of composition $\text{SrO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ ($1 \leq n \leq 9$) has been studied between 110° and 450° . The species produced have been characterised and examined by *X*-ray and electron diffraction, differential thermal analysis, and thermogravimetric analysis, and through their optical and sorptive properties.

The crystals produced include the orthorhombic and hexagonal polymorphs of strontium feldspar, a strontium mica, a near-chabazite, and two unidentified strontium zeolites, all in good yield. Two other unidentified species were produced in good yield, together with montmorillonite, boehmite, cancrinite, gmelinite, analcite, mordenite, and heulandite in smaller or irreproducible yield. The excess of silica crystallised as cristobalite at the higher temperatures. Possible reasons for the irreproducible appearance of various crystalline phases are discussed.

VERY few studies have been made of the hydrothermal synthesis of strontium silicates and aluminosilicates. Carlson and Wells¹ investigated the reaction of silica gel with aqueous strontium hydroxide up to 300° . They produced two anhydrous and seven hydrated silicates. Different forms of silica gel yielded different products, and the excess of silica was converted into cristobalite. The action of strontium and barium hydroxide solution on vitreous silica has also been investigated by Corwin *et al.*² The reaction yielded strontium or barium silicate and, in the case of $\text{Sr}(\text{OH})_2$, β -cristobalite which transformed rapidly into α -cristobalite. Hydrothermal crystallisations often yield species also found in sintering or pyrolytic reactions. Phase equilibria of strontium aluminosilicates have been studied by Dear³ and Sorrel.⁴ Besides three silicates and four aluminates, a strontium anorthite was observed, and its hexagonal polymorph, as well as two phases of compositions $2\text{SrO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$ and $6\text{SrO}, 9\text{Al}_2\text{O}_3, 2\text{SiO}_2$. The versatility of the hydrothermal method, and the possibility of preparing new synthetic aluminosilicates, led us to examine the growth of compounds from aqueous gels containing strontia, alumina, and silica in alkaline conditions. The crystallisation fields of various phases were defined, although these cannot necessarily be identified with thermodynamic stability boundaries, since metastable species frequently appear. In previous investigations some crystallisation fields of calcium aluminosilicates have been examined,^{5,6} and in a future paper an account will be given of an analogous study of barium aluminosilicates together with a comparison of occurrences of some of the calcium, strontium, and barium phases of similar type.

EXPERIMENTAL

The reagents used were recrystallised strontium hydroxide octahydrate, aluminium hydroxide gel freshly prepared by the action of ice-cold distilled water on lightly amalgamated aluminium foil,⁷ and "Syton 2X," a stable sol of silica (30% by wt.) in water. The aqueous gels were prepared by mixing together the strontium hydroxide and the aluminium hydroxide gel with a little water in a mortar. The silica sol was then added from a graduated pipette and

* Part XI, *J.*, 1963, 434.

¹ Carlson and Wells, *J. Res. Nat. Bur. Stand.*, 1953, **51**, 73.

² Corwin, Yalman, Edwards, and Shaw, *J. Phys. Chem.*, 1957, **61**, 1437; Corwin, Yalman, Edwards, and Owen, *ibid.*, p. 939.

³ Dear, *Bull. Virg. Polytech. Inst., Eng. Expt. Station*, Series 117, 1957, **50**, No. 6.

⁴ Sorrel, *Amer. Min.*, 1962, **47**, 291.

⁵ Ames and Sand, *Amer. Min.*, 1958, **43**, 476; Goldsmith and Ehlers, *J. Geol.*, 1952, **60**, 386; Ehlers, *ibid.*, 1953, **61**, 223; Flint, McMurdie, and Wells, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 13.

⁶ Barrer and Denny, *J.*, 1961, 983.

⁷ Weiser and Milligan, *Chem. Rev.*, 1939, **25**, 1.

mixed in. The resultant suspension was transferred to a stoppered conical flask with the remainder of the water and stirred for about an hour. 7 ml., containing 0.5 g. (dry wt.) of oxides, were measured into each autoclave.

The autoclaves, of stainless steel, had an internal capacity of 14 ml. Below 300° they were heated in air-ovens thermostatically controlled to $\pm 3^\circ$. Between 300° and 450° a copper-block electric furnace (referred to previously⁶) was employed, the temperature of which was maintained within $\pm 1^\circ$. After the chosen reaction time the autoclaves were air-cooled or water-quenched, and the reaction products were filtered off, washed, and dried at 105°. The pH of the cold mother-liquor, as given in Table 2 (figures in parentheses), was measured to the nearest 0.5 unit. The products were then variously examined and characterised. The methods employed included optical examination in the polarising microscope or Vickers projection microscope, X-ray powder photography, electron-diffraction or electron microscopy, and differential thermal analysis and thermogravimetry (in both cases with a heating rate of 10° per min). Sorption studies were made in some instances, with a volumetric sorption apparatus, and for certain crystals infrared spectra were obtained on an Infracord 137E spectrophotometer for Nujol mulls between sodium chloride plates.

RESULTS

In order to facilitate the presentation of results each species produced was designated as indicated in Table 1, column 1. The identity, yield and reproducibility of formation of the crystals, as determined by optical and X-ray methods are also given in this Table. A "major" yield implies that, in the best case, the species in question forms the greater part of the solid products. The Table demonstrates that with strontium, as with calcium,⁶ a rich variety of aluminosilicates can be formed, among which zeolites are prominent.

The products obtained from gels of anhydrous oxide compositions $\text{SrO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ ($1 < n < 9$) are shown in Table 2. For each value of n the temperature was varied between 110° and 450°, and the duration of the experiments from a few hours to several weeks. In general, the lower the temperature and the larger the value of n , the longer was the time required for crystallisation. Thus, for $n > 5$ the gels were amorphous after 3 weeks at 200°,

TABLE 1.
The synthetic Sr-aluminosilicate phases.

Symbol	Species	Yield	Reproducibility
Sr-B	Montmorillonite	Minor	V. poor
Sr-C	Orthorhombic polymorph of Sr-feldspar	100%	V. good
Sr-D	Sr-zeolite	100%	Good
Sr-E	Boehmite	Minor	V. poor
Sr-F	Gmelinite	Major	Nil
Sr-G	Near-chabazite	Major	Good
Sr-H	α -Cristobalite	Major	Good
Sr-I	Analcite	Major	Nil
Sr-J	Cancrinite	V. minor	Nil
Sr-K	Unidentified	Major	Fair
Sr-L	Mica	Major	Good
Sr-M	Mordenite	Minor	V. poor
Sr-N	Unidentified	Major	Good
Sr-P	Hexagonal polymorph of Sr-feldspar	Major	Good
Sr-Q	Sr-zeolite	100%	Good
Sr-R	Heulandite	Major	Nil
Sr-S	Unidentified	V. minor	Poor
Sr-T	Unidentified	V. minor	Poor
Sr-W*	Monoclinic feldspar	100%	—
Sr-X	Uncrystallised gel	—	—

* Produced by a sintering reaction.

TABLE 2.
Experimental results.*

435°	$\text{SrO}, \text{Al}_2\text{O}_3, 0.87\text{SiO}_2$			$0.77\text{SrO}, \text{Al}_2\text{O}_3, \text{SiO}_2$		$\text{SrO}, 2\text{Al}_2\text{O}_3, 2\text{SiO}_2$					250°		
	20h	3d	7d	410°	25h	5d	455°	17h	20h	63h		4d	4d
m C	m C	sm C		m C	m C		gd C	gd C	gd P	gd P	gd C		gd P
gd N	gd N	f N		f N	gd N		gd L	gd L	gd L	tr L	gd L		gd L
SrCO_3 (>10.5)	SrCO_3 (10.0)	(10.0)		(>10.5)	SrCO_3 (>10.5)		(5.0)	(6.0)	(5.5)	(7.0)	(7.0)		(7.0)

TABLE 2. (Continued.)

$\text{SrO}, \text{Al}_2\text{O}_3, 5\text{SiO}_2$																
435°	22h	3d	7d	380°	24h	2d	5d	7d	12d	340°	20h	3d	7d			
	m C	gd C	f C		sm P	gd P	gd C	gd P	gd C		tr P	sm P	m Q			
	sm P	gd H	gd H		(7-0)	(7-0)	(7-5)	(7-0)	(7-0)		(6-0)	(7-0)	(7-0)			
	sm H	(7-0)	(7-5)													
295°	2d	5d	21d	250°	3d	8d	15d	205°	2d	5d	21d					
	sm C	gd C	gd C		X	m P	m P		X	X	X					
	(7-0)	(5-5)	(7-0)		(-)	(-)	(7-0)		(8-5)	(7-0)	(7-0)					
200°	3d	8d	22d	110°	48d											
	X	X	X		sm G											
	(-)	(-)	(10-5)		(10-0)											
$\text{SrO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$																
435°	22h	3d	7d	410°	24h	3d	6d	380°	25h	3d	7d	340°	20h	3d	7d	
	m P	gd C	f C		m P	gd C	gd C		X	sm P	m C		X	tr P	gd Q	
	gd H	gd H	gd H		m C	f H	gd H		(7-0)	sm C	f H		(7-0)	(7-0)	(7-0)	
	(7-0)	(7-0)	(7-5)		sm H	(7-0)	(7-0)			sm H	(7-0)					
$\text{SrO}, \text{Al}_2\text{O}_3, 8\text{SiO}_2$																
300°	3d	8d	16d	250°	3d	8d	15d	20d	27d							
	X	m C	gd K		X	X	X	gd Q	X							
	(7-0)	(7-0)	(7-0)		(7-0)	(7-5)	(8-0)	(7-0)	(7-5)							
200°	6d	16d	20d	150°	6d	16d	110°	62d	105d							
	X	X	X		X	X		tr G	X							
	(7-0)	(6-5)	(7-0)		(7-0)	(6-5)		(>10-5)	(>10-5)							
$\text{SrO}, \text{Al}_2\text{O}_3, 7\text{SiO}_2$																
435°	21h	3d	7d	380°	24h	2d	3d	3d	4d	7d	10d					
	m P	gd C	gd C		X	gd D	gd D	m P	m P	sm P	f C					
	tr H	f P	vg H		(7-0)	sm P	m P	sm D	tr C	(7-0)	vg H					
	(7-0)	f H	(7-0)			(7-0)	(7-0)	(7-0)	sm H		(8-0)					
									sm D							
									(7-5)							
340°	16h	2d	4d	7d	8d	11d	300°	36h	3d	5d	6d	9d	12d	13d	15d	23d
	X	X	sm D	X	gd D	gd D		X	X	m C	sm C	sm C	m C	sm C	m C	f C
	(6-0)	(7-0)	sm Q	(6-0)	gd Q	gd Q		(6-5)	(7-0)	gd M	(7-5)	(7-0)	m Q	(7-0)	(7-0)	(8-0)
			(7-0)		(7-0)	(7-0)				(8-0)						
250°	36h	6d	19d	200°	36h	6d	20d	150°	6d	20d						
	X	X	m C		X	X	X		X	X						
	(7-0)	(6-5)	(7-0)		(7-0)	(7-5)	(7-0)		(8-5)	(8-0)						
$\text{SrO}, \text{Al}_2\text{O}_3, 8\text{SiO}_2$																
435°	3d	5d	8d	410°	24h	3d	6d	400°	27h	4d	8d					
	gd P	gd P	gd P		sm P	m P	m P		m P	gd K	m P					
	vg H	sm C	sm C		sm H	gd H	m C		gd H	(7-0)	m C					
	(7-0)	(7-0)	(7-0)		(7-0)	(7-0)	gd H		(6-5)		gd H					
							(7-0)				(7-0)					
380°	22h	2d	3d	4d	7d	8d	15d	340°	2d	4d	7d					
	X	gd D	sm P	m D	gd D	gd P	vg H		X	gd Q	gd Q					
	(7-0)	(7-5)	(7-0)	m P	gd H	gd H	gd C		(7-0)	(7-0)	(7-0)					
				sm H	tr P	(7-5)	(7-0)									
				(7-0)	(7-0)											
300°	5d	9d	12d	15d	280°	4d	8d	14d	250°	4d	4d	12d	19d	21d		
	X	X	m C	m C		sm C	m Q	sm C		vg I	X	X	X	m Q		
	(8-0)	(7-5)	(7-0)	sm Q		(7-0)	(7-0)	gd H		(brown)	(7-0)	(7-0)	(7-0)	(7-0)		
				(7-0)				(7-0)		(10-5)						
200°	8d	14d	19d	22d	150°	8d	19d	110°	62d							
	X	X	X	X		X	X		X							
	(7-0)	(8-5)	sm J	(8-5)		(8-5)	sm J		(>10-5)							
$\text{SrO}, \text{Al}_2\text{O}_3, 9\text{SiO}_2$																
435°	25h	4d	8d	380°	24h	3a	3d	5d	6d	10d	10d	10d	10d	10d	12d(2)	
	m P	m P	vg H		X	X	gd D	gd D	tr D	gd H	gd D	m D	m D	gd H		
	tr H	m H	(7-0)		(7-0)	(7-0)	(4-0)	m H	(7-0)	sm C	m H	m H	m H	sm D		
	(7-0)	(7-0)					(7-0)	(7-0)		(7-0)	(7-0)	(5-0)	(6-0)	(8-5)		
340°	17h	2d	3d(2)	4d	6d	7d	10d	12d	300°	11d	21d(2)	23d				
	X	X	X	tr Q	sm D	X	gd D	sm D		m C	m Q	gd Q				
	(7-0)	(8-0)	(7-0)	(8-0)	(7-0)	(7-0)	(8-5)	(8-0)		gd Q	(8-0)	(8-0)				
										(7-0)						
250°	20d	21d	23d	23d(2)	27d	200°	11d	21d	150°	21d	110°	62d				
	X	X	m R	X	X		X	X		X	X	X				
	(8-5)	(7-0)	(8-5)	(8-0)	(9-0)		(8-0)	(7-5)		(8-0)		(>10-5)				
$1-6\text{SrO}, \text{Al}_2\text{O}_3, 9\text{SiO}_2$																
250°	20d	23d	27d		300°	4d	8d	21d	250°	4d	12d	21d	200°	7d	29d	
	gd D	gd D	gd Q			X	X	gd Q		X	X	X		X	X	
	(8-5)	gd M	(10-0)			(7-0)	(7-0)	(7-0)		(7-0)	(7-0)	(7-0)		(7-0)	(7-0)	
			(9-0)													

* Yields: vg = very good; gd = good; m = moderate; f = fair; sm = some; tr = trace.

while at 250° with $n = 8$ it still required three weeks to effect any crystallisation. For low $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratios, however, crystallisation sometimes occurred within 24 hr.

The crystallisation fields of a number of the species of Table 1 are summarised in Fig. 1a and b. Some of the species, such as Sr-paracelsian (Sr-C), hexagonal $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Sr-P), and a new zeolite (Sr-Q), occurred over a wide range of conditions, whereas others including an unidentified phase (Sr-N), a chabazite-like phase (Sr-G), and a second new zeolite Sr-D were found in much more limited and relatively sharply defined regions of the field.

Strontium Zeolites.—Seven zeolites were synthesised (Table 1) which were representative

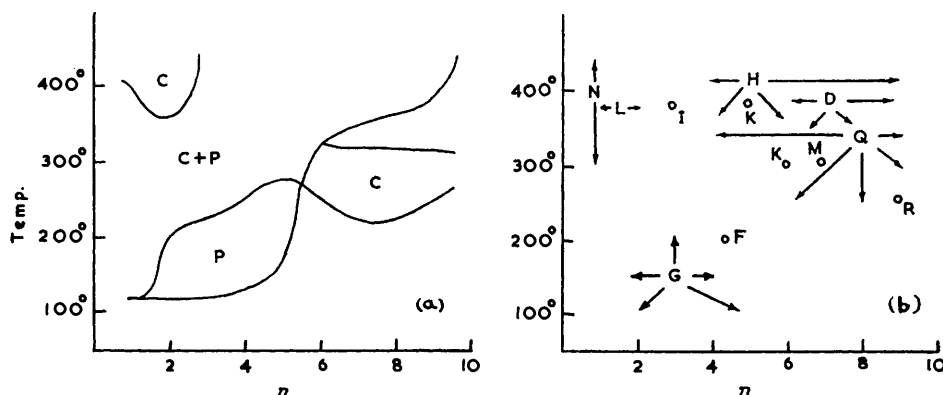
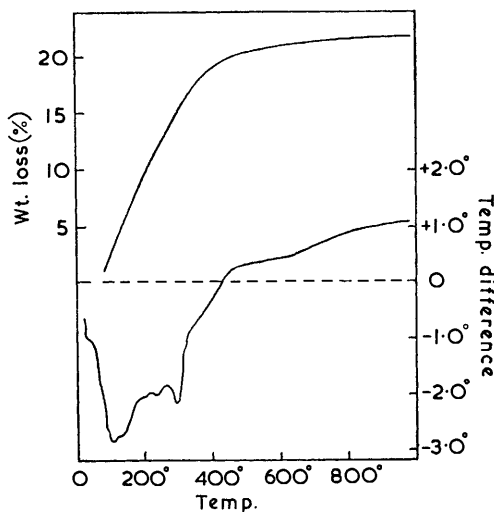


FIG. 1. Crystallisation fields of some strontium aluminosilicates. For key to reference letters see Table 1. The crystallisation fields in Figs. 1a and b occur together, but have been drawn in the separate diagrams for clarity in presentation.

FIG. 2. D.t.a. and thermogravimetric analysis of species Sr-G.



of several zeolite groups. In addition, two of these appeared to be new species. The characteristics of the synthetic compounds are given below.

Sr-G (*near-chabazite*). This compound crystallised reproducibly and in good yield at temperatures below 200° from aqueous gels of oxide composition $\text{SrO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ where $2 \leq n \leq 4$. It was often mixed with some unchanged gel, and sometimes contained strontium carbonate which could be removed by washing with dilute hydrochloric acid. The characteristic habit was spherulitic (Plate 1a) and the X -ray powder pattern was closely similar to that of natural chabazite (Table 3). The pattern was indexed to give a hexagonal unit cell with $a = 13.67 \text{ \AA}$ and $c = 15.49 \text{ \AA}$. A sample gave a weight loss of 21.8% on thermogravimetric

TABLE 3.
X-Ray patterns for zeolitic species.

Sr-G		Natural Chabazite		Sr-G		Natural Chabazite		Sr-F		Natural gmelinite		Sr-F		Natural gmelinite	
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
9.43	m	9.47	s	2.91	s	2.91	s	11.91	ms	11.94	s	2.93	ms	2.93	s
6.80	m	6.93	mw	2.82	vw	—	vs	9.40	w	9.42	w	2.87	m	2.86	s
5.54	m	5.55	m	2.78	vw	—	—	7.65	vw	7.70	ms	2.675	ms	2.700	s
5.12	m	5.02	m	2.74	vw	—	—	6.93	vw	6.91	ms	2.608	s	2.605	m
4.48	vw	—	—	2.54	m	2.59	m	5.95	vw	5.91	w	—	—	2.520	w
4.37	vw	—	—	2.28	mw	2.30	m	5.54	vw	5.55	vw	2.302	m	2.323	w
4.30	ms	4.32	s	2.09	mw	2.08	m	5.14	w	5.14	mw	2.091	ms	2.092	ms
3.95	m	3.89	ms	—	—	1.87	m	4.99	s	5.05	ms	2.050	vw	2.060	vw
3.68	w	3.57	ms	1.81	mw	1.80	s	—	—	4.64	vw	1.947	vw	1.949	w
3.21	w	3.34	ms	1.71	mw	1.72	ms	4.53	mw	4.50	m	1.912	vw	1.914	w
3.12	m	3.16	mw	—	—	1.65	m	—	—	4.41	vw	—	—	1.877	w
2.95	vw	—	—	—	—	1.56	m	4.32	m	4.32	m	—	—	1.843	w
								4.12	s	4.11	vs	1.801	m	1.815	m
								3.98	m	3.97	vw	—	—	1.793	w
								3.89	vw	3.87	vw	1.727	s	1.724	m
								3.54	mw	—	—	1.694	w	1.700	w
								3.46	ms	3.45	ms	—	—	1.683	mw
								3.32	w	3.31	w	1.658	w	1.653	vw
								3.19	w	3.24	s	1.640	w	1.634	vw
								2.99	s	2.98	s	1.599	vw	1.600	w

Sr-I		Sr-I (brown)		Sr-I		Sr-I (brown)		Sr-M		Natural mordenite		Sr-M		Natural mordenite	
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
5.60	s	5.60	s	1.757	ms	1.739	s	13.56	mw	13.56	m	3.23	s(b)	3.22	s(b)
4.87	mw	4.85	m	1.719	vw	1.712	mw	9.10	m	9.04	ms	3.04	mw	2.98	vw
3.68	vw	3.66	w	1.695	vw	1.695	m	6.63	m	6.60	m	2.92	s(b)	2.90	ms
3.44	vs	3.43	vs	—	—	1.660	vw	6.43	w	6.41	mw	—	—	2.75	w
2.93	s	2.917	s	—	—	1.612	w	6.07	vw	6.08	w	2.69	mw	2.703	w
2.806	vw	2.796	w	1.596	mw	1.592	m	5.86	m	5.80	mw	—	—	2.642	w
2.691	m	2.686	ms	—	—	1.457	mw	—	—	5.11	vw	2.563	ms	2.569	mw
2.509	m	2.500	m	1.415	ms	1.410	m	4.76	mw	4.66	vw	2.523	ms	2.529	m
2.423	m	2.421	mw	—	—	1.367	vw	4.55	m	4.53	m	—	—	2.46	w(b)
2.227	m	2.219	m	1.360	ms	1.353	m	4.32	vw	4.26	vw	—	—	2.44	w(b)
—	—	2.165	vw	—	—	1.304	w	4.18	m	4.14	vw	2.182	w	2.174	vw
1.906	ms	1.899	ms	—	—	1.281	w	4.00	ms	4.00	s	2.090	w	2.102	w
—	—	1.863	m	—	—	1.258	w	3.84	vw	3.84	vw	1.886	w	1.887	m
								3.76	w	3.77	w	1.821	w	1.818	w
								3.64	w	3.63	vw	1.798	vw	1.796	w
								3.48	s	3.49	vs	1.705	vw	1.710	vw
								3.40	ms	3.41	s	1.638	vw	1.626	vw

Heulandite *		Sr-R		Clinoptilolite ¹⁸		Heulandite *		Sr-R		Clinoptilolite ¹⁸	
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
9.0	s	9.04	m	8.96	vs	3.29	vw	3.33	w	3.33	w
7.9	m	7.99	m	7.94	m	3.16	m	3.18	mw	3.18	w
6.78	m	—	—	6.80	w	—	—	3.13	mw	—	—
—	—	—	—	5.98	vw	—	—	3.09	vw	—	—
—	—	5.28	mw	—	—	2.96	s	2.97	ms	2.98	s
5.09	m	5.12	ms	5.13	m	2.80	m	2.80	m	2.81	m
4.64	w	4.66	w	4.65	w	—	—	2.74	m	2.74	w
4.33	vw	4.37	w	4.35	w	—	—	2.67	vw	2.68	vw
3.96	vs	3.98	vs	3.97	vs	2.53	vw	—	—	2.54	w
—	—	3.92	w	—	—	2.42	vw	—	—	2.44	w
—	—	3.84	vw	—	—	2.35	vw	—	—	2.36	vw
3.70	vw	3.73	vw	3.72	w	—	—	2.28	vw	—	—
3.54	vw	3.58	mw	3.55	w	1.96	vw	1.96	vw	1.96	w
—	—	3.44	w	—	—	—	—	1.83	vw	1.83	vw
3.40	m	3.41	w	3.43	m	—	—	—	—	—	—

Sr-D				Sr-Q											
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int								
9.51	ms	3.48	s	2.712	mw	1.776	vw	9.66	w	3.48	w	2.374	vw	1.701	mw
7.09	vw	3.44	vw	2.644	mw	1.767	vw	7.89	vw	3.30	w	2.328	w	1.651	mw
6.96	vw	3.39	vw	2.580	vw	1.707	vw	6.96	mw	3.27	s	2.196	w	1.609	mw
6.63	ms	3.31	w	2.479	vw	1.652	vw	6.61	vw	3.14	w	2.146	w	1.586	mw
4.97	vw	3.26	vw	2.411	m	1.616	vw	6.30	w	3.10	ms	2.129	vw	1.568	vw
4.75	w	3.22	w	2.307	w	1.605	vw	5.88	vs	3.05	vs	2.095	w	1.527	w
4.65	vw	3.14	ms	1.996	w	1.580	vw	4.76	vs	2.95	vs	2.076	vw	1.497	vw
3.94	mw	3.06	ms	1.922	mw	1.484	w	4.65	s	2.93	ms	2.032	vw	1.475	vw
3.86	w	3.03	vw	1.866	m	1.425	mw	4.31	s	2.89	vw	2.000	m	1.465	vw
3.78	m	2.96	w	1.832	vw	1.361	vw	4.16	ms	2.788	mw	1.976	vw	1.455	vw
3.73	vw	2.93	w	1.807	vw	1.307	vw	4.06	w	2.738	mw	1.954	vw	1.427	w
3.68	w	2.89	m	1.781	vw	1.270	vw	3.94	ms	2.657	m	1.924	vw	1.396	w
3.54	s	—	—	—	—	—	—	3.76	mw	2.542	vw	1.894	ms	1.346	vw
								3.67	vw	2.454	w	1.828	vw	1.333	vw
								3.54	w	2.416	m	1.730	m	1.306	vw

* Koizumi and Kiriya, *J. Geol. Soc. Japan*, 1953, 59, 88.

analysis, and a differential thermal analysis (d.t.a.) trace similar to that obtained ⁸ for other natural and synthetic chabazites (Fig. 2). Although the sample used in the d.t.a. run became amorphous and did not show a recrystallisation exotherm at high temperatures, that used in the thermogravimetric analysis up to 1000° recrystallised to give the species Sr-P.

⁸ Barrer and Langley, *J.*, 1958, 3804, 3811, 3817.

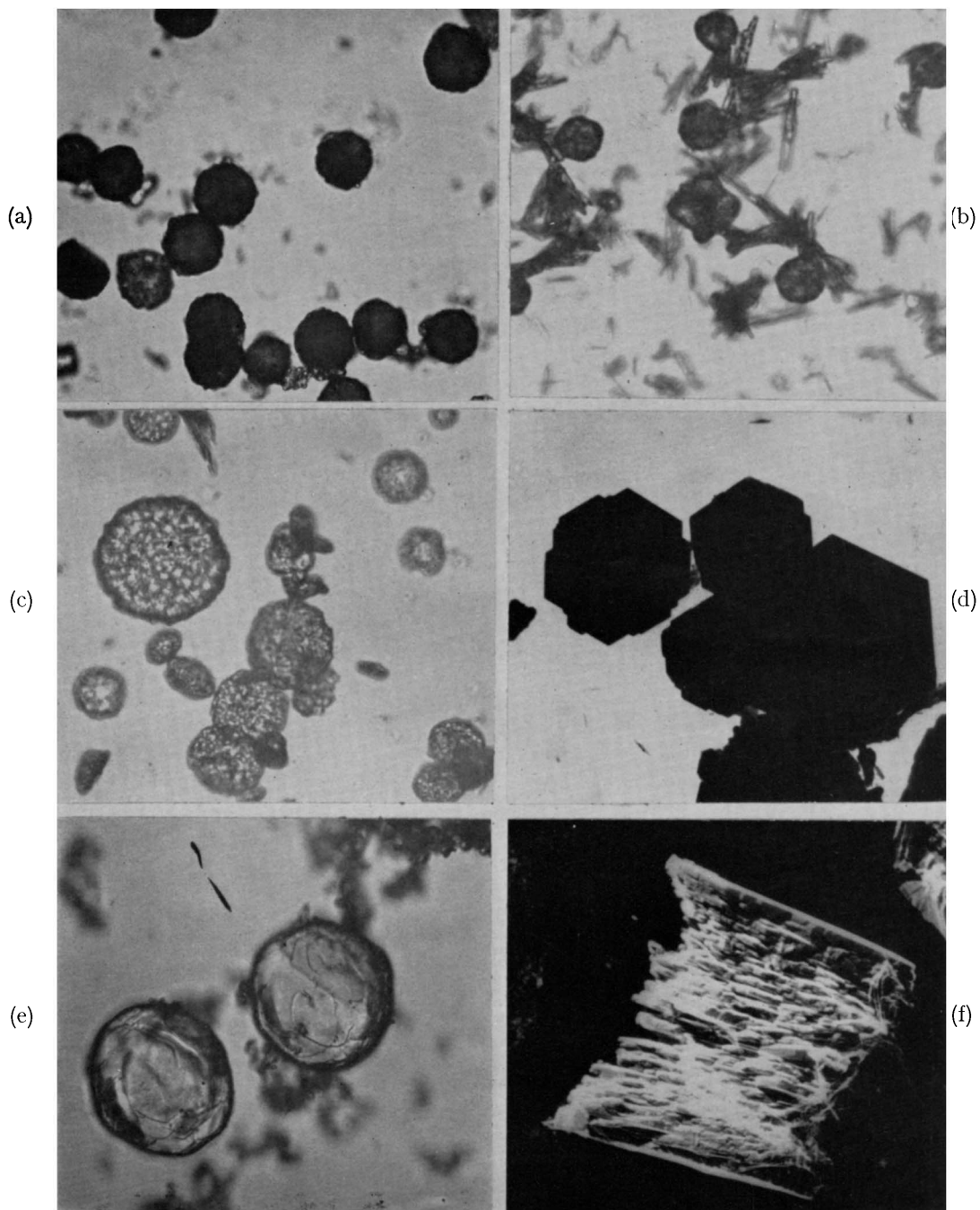


PLATE I. (a) Species Sr-G, 325 \times . (b) Spherules of Sr-I, with some laths of Sr-C, 650 \times . (c) Sr-F, 510 \times . (d) Sr-F, 2700 \times . (e) Sr-D, 385 \times . (f) Sr-D (replica), 3940 \times .

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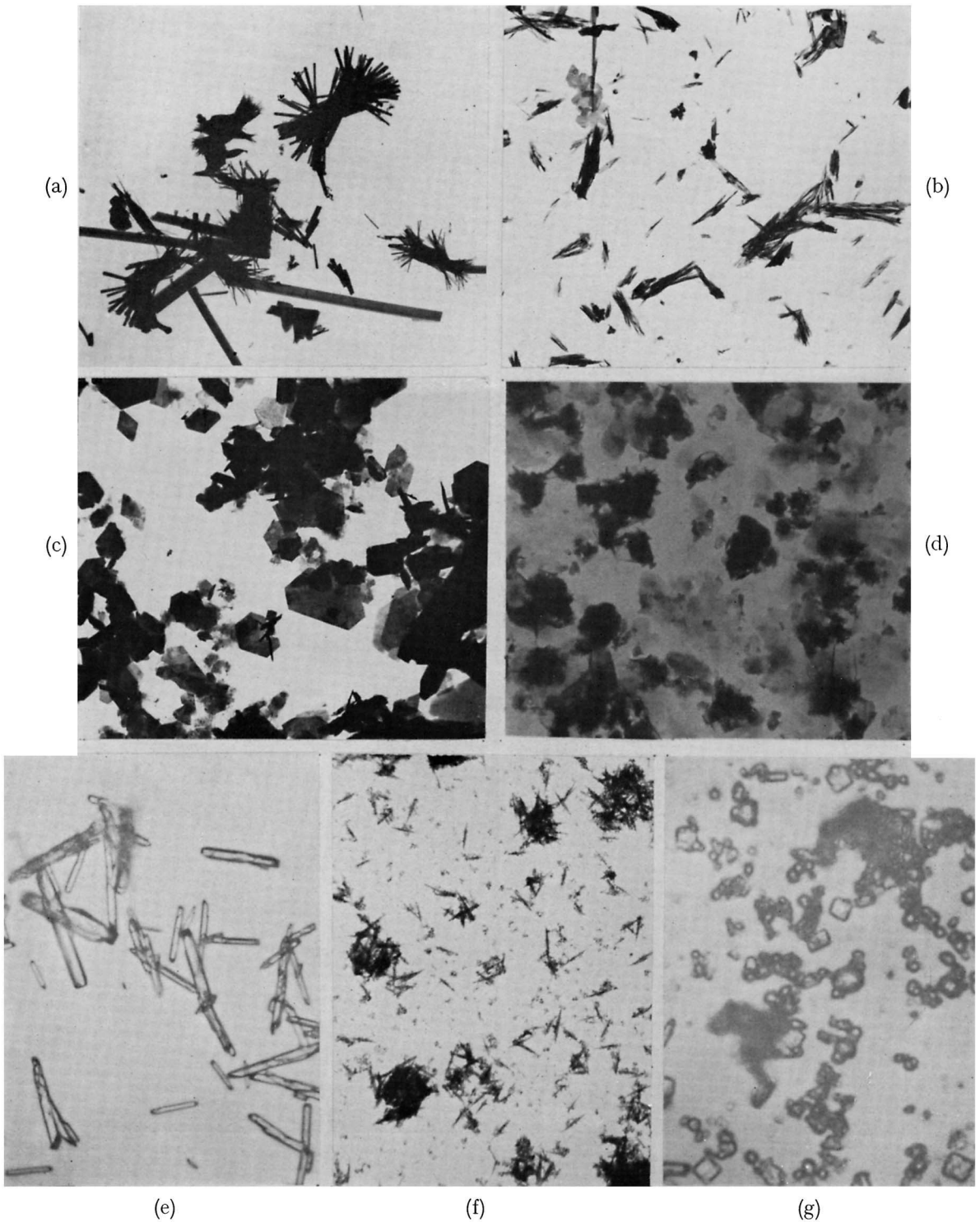


PLATE 2. (a) Species Sr-M, with some laths of Sr-C, 2700 \times . (b) Sr-Q, 2700 \times .
 (c) Sr-L, 2150 \times . (d) Sr-B, 8000 \times . (e) Sr-C, 540 \times . (f) Sr-P, 6000 \times .
 (g) Cuboid crystals of Sr-N, with some Sr-C, 380 \times .

Species similar to chabazite were also synthesised by the crystallisation of potassium aluminosilicate gels,⁹ but chabazite did not appear among crystallisation products of calcium aluminosilicate gels,⁸ or from gels of the other alkali metals.¹⁰⁻¹³

Sr-F (*gmelinite*). One well-crystallised sample of strontium gmelinite appeared, from an aqueous gel of composition $\text{SrO}, \text{Al}_2\text{O}_3, 4.4\text{SiO}_2$ treated at 205° for 6 days, but the preparation was not reproducible. The gmelinite was present as spherulitic aggregates of small hexagonal crystals (Plate 1c, d), and the X-ray powder diagram was in good agreement with that of a naturally occurring gmelinite (Table 3). The hexagonal unit cell was indexed to give $a = 13.80 \text{ \AA}$, $c = 10.01 \text{ \AA}$. At 90°K 1 g. of the hydrated zeolite, after outgassing, sorbed 55 c.c.³ of oxygen (at s.t.p.), and ignition gave a weight loss of 18.4%. The loss for a Sr-gmelinite of ideal composition $\text{SrO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 6\text{H}_2\text{O}$ would be 19.5%. In previous studies we have also grown gmelinites from sodium aluminosilicate gels,¹³ and from gels containing both Ca^{2+} and NMe_4^+ ions.⁶

Sr-I (*analcite*). In one preparation a strontium analcite was obtained in 50% yield, mixed with species Sr-C. The crystals were grown from an aqueous gel $\text{SrO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2$ at 380°. The crystal habit was spherulitic, with a few indications of crystal faces (Plate 1b), and the X-ray powder pattern was close to that of the natural mineral (Table 3). The cubic unit-cell edge was 13.74 Å, and falls in the correct position in the approximately linear relation between cation radius and unit cell volume for cubic analcites.¹⁴

The synthesis of Sr-analcite was, however, not reproducible, although on one other occasion a gel of composition $\text{SrO}, \text{Al}_2\text{O}_3, 8\text{SiO}_2$ yielded at 250° a magnetic, deep brown product, with the X-ray powder pattern of analcite and a cubic unit cell with $a = 13.69 \text{ \AA}$. This product was presumably formed by attack on the autoclave walls. Analcite, although difficult to prepare in the strontium field, is often a dominant phase when other cations are used. We have observed the formation of analcite-type species from gels containing Na, K, Rb, Cs, Tl, NH_4 , Ca, and Sr as cations.^{6, 9, 11-16}

Sr-M (*mordenite*). Two preparations of Sr-mordenite were effected, in both cases in admixture. One preparation in good yield also contained species Sr-C and was obtained from the aqueous gel $\text{SrO}, \text{Al}_2\text{O}_3, 7\text{SiO}_2$ at 300°. The other specimen was mixed with species Sr-D and formed from a gel $1.5\text{SrO}, \text{Al}_2\text{O}_3, 9\text{SiO}_2$ at 250°. The crystals showed the typical "wheat-sheaf" crystal habit of Plate 2a, and the X-ray powder pattern showed good agreement with that of the natural mineral (Table 3). Individual crystals were further identified by electron diffraction, and the *c*-centred orthorhombic unit cell had the dimensions $a = 18.13$, $b = 20.5$, and $c = 7.52 \text{ \AA}$.

In previous work, mordenite has been prepared from sodium and calcium aluminosilicate gels.^{6, 11, 17} Its preparation appears to be most readily accomplished from the sodium-containing gels.

Sr-R (*heulandite*). Only one sample was obtained of this zeolite. It crystallised moderately well from an aqueous gel of composition $\text{SrO}, \text{Al}_2\text{O}_3, 9\text{SiO}_2$, but lacked a distinctive crystal habit and was mixed with unchanged gel. The loss of water on ignition was 8.8%, to be compared with 14.6% for the strontium-form of the natural mineral, indicating a yield of about 60%. The distinction between heulandite and clinoptilolite is somewhat uncertain,^{18, 19} and the X-ray powder patterns of species Sr-R and the two natural zeolites are compared in Table 3. Species Sr-R is called a heulandite on the basis of the slightly closer resemblance of its powder pattern to that of heulandite.

Sr-D (*Sr-zeolite*). This zeolite crystallised well in the rather high-temperature range (for zeolitisation) of 340—400° from aqueous gels of composition $\text{SrO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ where $7 \leq n \leq 9$. The crystals were obtained in high yield and reproducibly. Several crystal habits were

⁹ Barrer and Baynham, *J.*, 1956, 2882.

¹⁰ Barrer and White, *J.*, 1951, 1267.

¹¹ Barrer and White, *J.*, 1952, 1561.

¹² Barrer and McCallum, *J.*, 1953, 4029.

¹³ Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.

¹⁴ Barrer, Baynham, and McCallum, *J.*, 1953, 4035.

¹⁵ Taylor, *J.*, 1949, 1253.

¹⁶ Barrer and Denny, *J.*, 1961, 971.

¹⁷ Barrer, *J.*, 1948, 2158.

¹⁸ Mason and Sand, *Amer. Min.*, 1960, 45, 341.

¹⁹ Mumpton, *ibid.*, p. 351.

observed, the two most characteristic being those shown in Plates 1e and f. Thermogravimetry showed a weight loss of 11.2% and the d.t.a. trace indicated the water to be zeolitic. On ignition, this species crystallised to give another, unidentified product the X-ray powder pattern of which is given in Table 4. The zeolite was a good sorbent, the uptake of oxygen at 90°K being 70 c.c.³ (s.t.p.) per g. of hydrated species Sr-D. The conditions of formation suggest that the zeolite is silica-rich.

Electron-diffraction patterns, taken from a lath in a sample the X-ray powder pattern of which showed only species Sr-D, indicated a body-centred, orthorhombic unit cell with $a = 18.5$, $b = 21.0$, and $c = 7.12$ Å, but because of the varying habit of the crystals of this species there was no certainty that this lath was the material Sr-D. The X-ray powder pattern (Table 3) could not be identified with that of any known zeolite so that material Sr-D appears to be a new species.

Sr-Q (Sr-zeolite). This species occurred quite widely (cf. Fig. 1) between 250° and 350° from gels with a high silica: alumina ratio, the optimum value being 8:1. It crystallised fairly reproducibly in high yield, normally as very small fibrous crystals (Plate 2b). The

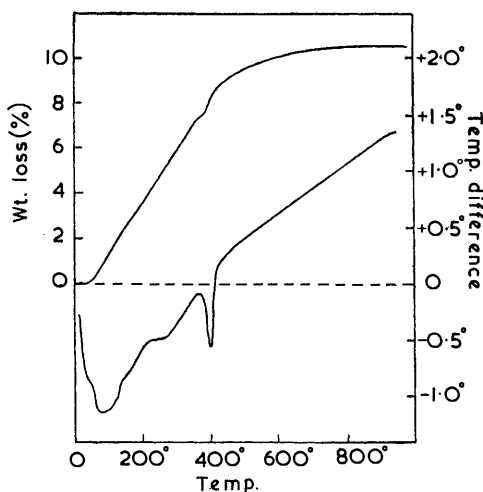


FIG. 3. D.t.a. and thermogravimetric analysis of species Sr-Q.

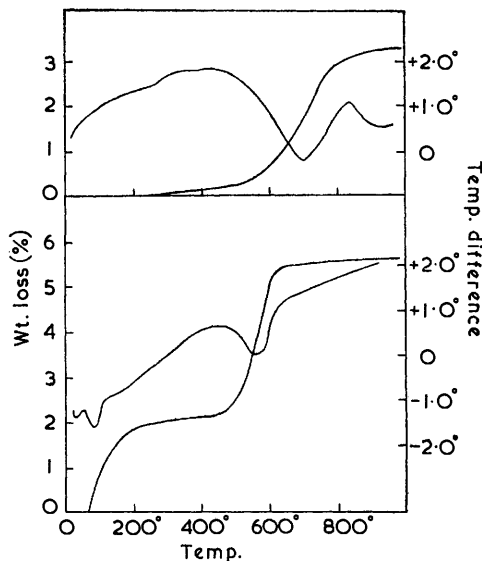


FIG. 4. D.t.a. and thermogravimetric analysis of two samples of species Sr-L.

results of thermogravimetry and differential thermal analysis are shown in Fig. 3. The weight loss is 10.5% and the compound is destroyed by 1000°. Since 90% of the weight loss occurs below 450° the water appears to be zeolitic. The distinctive peaks in the d.t.a. curve of Fig. 3 were observed with all the samples studied. The small, sharp peak at 400° is probably associated with the small kink in the thermogravimetric curve at this temperature. When the sample was heated only to 450° and was then cooled the X-ray powder pattern was unchanged, further supporting the view that the water lost was zeolitic. Material Sr-Q did not sorb oxygen at 90°K. The X-ray powder pattern (Table 3) could not be identified with that of any other mineral.

Layer Silicates.—Representatives of two important kinds of layer silicate were prepared: a Sr-mica and a Sr-montmorillonoid.

Sr-L (Sr-mica). When aqueous gels of composition $\text{SrO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ were crystallised for short periods at 380° the products contained many small hexagonal plates (Plate 2c) and gave an X-ray powder pattern very similar to that of a mica (Table 4). A gel with the theoretical composition of a strontium margarite ($\text{SrO}, 2\text{Al}_2\text{O}_3, 2\text{SiO}_2$) was heated at 455°, and runs of less than 3 days produced good yields of the mica, still mixed with either Sr-P or Sr-C. In addition to these major yields, some specimens of species Sr-C produced at 380° from aqueous gels of

TABLE 4.

X-Ray patterns of micaceous and unidentified species.

Sr-L															
Fresh sample		Ignited sample		Fresh sample		Ignited sample		Product from ignition of Sr-D							
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
9.85	vw	9.87	m	2.754	mw	2.766	vw	11.13	s	3.88	w	2.83	m	2.041	w
4.47	m	4.49	ms	2.582	s	2.604	ms	8.61	w	3.72	w	2.688	w	1.943	vvw
4.29	m	4.30	m	2.550	vs	2.568	vs	6.91	s	3.68	m	2.656	w	1.878	ms
3.84	mw	3.86	m	2.441	mw	2.460	w	6.66	w	3.65	w	2.626	w	1.726	m
3.46	m	3.47	mw	2.240	ms	2.253	ms	5.57	m	3.66	vs	2.494	w	1.665	vw
3.31	w	3.34	mw	2.190	w	2.212	w	5.49	s	3.54	m	2.450	vw	1.623	vw
3.27	mw	3.28	m	2.113	ms	2.130	ms	5.29	vw	3.19	w	2.318	w	1.592	vw
3.17	m	3.19	m	1.949	mw	1.964	m	4.97	w	3.13	w	2.302	mw	1.434	w
2.95	m	2.97	w	1.631	ms	1.638	ms	4.65	m	3.07	s	2.267	w	1.413	vw
2.93	m	2.93	mw	1.492	vs	1.504	s	4.31	m	2.92	s	2.159	vw	1.358	vw
2.90	mw	2.92	m	1.288	m	1.301	m	4.05	s	2.88	m				
—	—	2.89	mw												

Sr-N			Sr-N			Sr-N			Sr-S		Sr-T	
<i>hkl</i>	<i>d</i>	Int	<i>hkl</i>	<i>d</i>	Int	<i>hkl</i>	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
102	6.68	m	500,430	2.495	m	711,551	1.754	mw	5.81	m	6.10	s
112	5.89	m	414	2.397	w	526,109	1.742	m	4.57	m	4.69	w
003	5.30	mw	325	2.336	vw	209	1.697	vw	3.79	w	3.82	m
213	4.56	vs	424	2.276	m	536	1.666	mw	3.76	mw	3.31	w
213	3.84	u	503,433	2.258	mw	229	1.636	ms	3.60	mw	3.15	ms
204	3.33	m	405	2.222	m	714,554	1.612	ms	3.44	ms	2.706	m
303	3.28	ms	530	2.142	ms	626,447	1.580	ms	3.27	ms	2.206	m
005	3.166	ms	523,207	2.125	vs	810,740	1.549	vw	2.98	m		
330	2.940	vs	620	1.973	m	419	1.509	m	2.751	ms		
205	2.815	m	630	1.861	m	608	1.432	mw	2.407	m		
314,420	2.793	mw	631	1.847	mw	4,010	1.411	m	2.024	w		
215,421	2.751	s	614	1.818	ms	4,110	1.404	m	1.784	mw		
324	2.594	m	228	1.800	m	2,111	1.393	m	1.612	mw		
333	2.576	m	701	1.772	m	911	1.372					

composition $\text{SrO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$ were observed to contain a little material Sr-L, usually in amounts too small to be detected by X-ray methods.

Thermogravimetric and d.t.a. results for two samples containing species Sr-L are shown in Fig. 4. The calculated weight loss for a mica of composition $\text{SrAl}_2(\text{Al}_2\text{Si}_2\text{O}_{10})(\text{OH})_2$ is 4.0%. The weights lost above 400° by these two samples were 3.1% and 3.5%, respectively, indicating yields up to 80%. In each case the endothermic peak on the d.t.a. curve corresponds to the temperature of maximum rate of loss of weight and can be attributed to the loss of the hydroxyl groups. The difference in the peak temperatures of the two samples can be attributed to the small size of the mica crystals in the second sample.²⁰

The X-ray diffraction patterns of samples heated to 1000° showed a slight permanent expansion of the structure. This effect was also observed by Roy²¹ with natural mica at rather lower temperatures. A partial return towards the original dimensions was effected by treating an ignited sample hydrothermally with distilled water at 110° for 3 days. The infrared spectrum of the mica was also examined. The fresh samples gave a sharp moderately strong peak at 2.74 μ , as did a sample of natural margarite. This peak is characteristic of an inorganic OH group,²² and as expected was found to be absent or very weak in the infrared spectra of all the ignited samples.

When the crystals were examined by electron diffraction good patterns were obtained showing two-dimensional hexagonal symmetry. The best value for the repeat distance along the hexagonal *a*-axis was 5.12 Å.

Sr-B (*Sr-montmorillonoid*). Species Sr-B was observed only on one occasion, when an aqueous gel of composition $\text{SrO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2$ was held for one day at 405°. The main product was, however, species Sr-P, so that the occurrence of Sr-B could not be satisfactorily demonstrated by X-ray diffraction. However, in the electron microscope the characteristic, often filmy crystals of a montmorillonite were seen (Plate 2d), and the electron-diffraction pattern confirmed the presence of this clay mineral. Montmorillonoids may have occurred in minor yields in other preparations of short duration in this region of the crystallisation field, but, as noted above, could not be detected by X-ray diffraction alone.

Polymorphs of SrAl₂Si₂O₈.—These include Sr-paracelsian, hexagonal $\text{SrAl}_2\text{Si}_2\text{O}_8$, and a phase with some resemblance to anorthite. A monoclinic Sr-feldspar was also obtained in a sintering reaction. Some aspects of these compounds are described below.

²⁰ Yoder, 6th Nat. Conf. on Clays and Clay Minerals, 1959, p. 42.

²¹ Roy, *J. Amer. Ceram. Soc.*, 1949, **32**, 202.

²² Saksena, *Trans. Faraday Soc.*, 1961, **57**, 242.

Sr-C (Sr-paracelsian). Species Sr-C occurred very widely in the crystallisation field shown in Fig. 1. It was formed at 300°, and also above 370° from gels with SiO₂:Al₂O₃ ratios from 1:1 to 9:1. When this ratio was 1:1 or 2:1 this material was formed also at lower temperatures. The optimum yields were obtained from aqueous gels SrO,Al₂O₃,2SiO₂ at 380° or above, for runs lasting about 24 hr. In these conditions species Sr-C appeared as well-formed needle-like laths up to 25 μ in length (Plate 2e). When formed from other compositions of gel the yield and crystallinity were poorer and the material Sr-C was often mixed with other species. A study of Table 2 suggests that species Sr-P (see below) was sometimes the first product formed, but that in treatments of longer duration this species is converted into Sr-C. However, attempts to convert Sr-P into Sr-C by direct hydrothermal treatment were inconclusive.

Species Sr-C was unaffected by prolonged heating at 1050° and was inert towards thermogravimetry or differential thermal analysis. The X-ray powder pattern (Table 5) showed similarities to that of paracelsian, an orthorhombic barium mineral, and was indexed by comparison with Smith's data.²³ The unit cell, having $a = 8.91_0$, $b = 9.34_3$, and $c = 8.34_5$ Å, may be compared with that of paracelsian ($a = 9.076$, $b = 9.583$, and $c = 8.578$ Å). The smaller unit-cell dimensions of the strontium compound are in line with the smaller ionic radius of Sr²⁺ than of Ba²⁺. It is not clear why in the case of Sr²⁺ the orthorhombic phase should have replaced the monoclinic variety obtained in these laboratories with other cations in the parent gels.^{9,11,12,24} Moreover, monoclinic Sr-feldspar has been produced^{3,4} by high-temperature sintering reactions, and was also obtained in this work by sintering a sample containing mainly species Sr-P with a little of species Sr-C at 1250° for 14 days (Sr-W of Table 1). The X-ray powder pattern is given in Table 5.

Sr-P (hexagonal SrAl₂Si₂O₈). This polymorph is similar to that prepared hydrothermally from calcium gels⁶ and by sintering kaolin with strontium sulphate.⁴ It was formed from aqueous gels SrO,Al₂O₃, n SiO₂ for values of n from 1 upwards and at temperatures from 150° upwards, the temperatures of formation being progressively higher the greater the silica content (Fig. 1). For values of n other than 2 the crystallite contained other species or else non-crystalline gel. The optimum formation conditions were those when $n = 2$ or 3, at 200° for several days or for 15–20 hr. at 340°. Longer treatments tended to produce species Sr-C, particularly at higher temperatures. The crystals were always very small and of poorly defined habit (Plate 2f). The X-ray powder pattern was similar to those obtained for the corresponding calcium⁶ and barium²⁴ compounds, showing progressive displacement with increasing cation size. The hexagonal unit cell had $a = 5.19$ and $c = 7.59$ Å.

Sr-K (anorthite-type phase). Species Sr-K was obtained once, together with uncrystallised gel, from an aqueous gel SrO,Al₂O₃,6SiO₂ after 16 days at 300°. It also appeared twice in admixture with species Sr-P from aqueous gels of composition SrO,Al₂O₃,5SiO₂ at 380°. Although it was well crystallised, no distinctive habit of this species could be seen. A sample was ignited over a Meker burner for 24 hr., with no effect other than a slight sharpening of the X-ray pattern. This pattern (Table 5) had considerable similarities with that of Sr-anorthite, although in detail this resemblance was not close enough to identify species Sr-K as such. Nor could it be identified with any other mineral.

Other Crystalline Phases.—The remaining crystalline phases include a cancrinite, three unidentified species (Sr-N, Sr-S, and Sr-T), boehmite, and α-cristobalite. Of these, the occurrence of boehmite has been reported in several previous papers of this series,^{6,10,16} and it appears to be a normal by-product from alumina-rich gels. The other phases, however, have features of interest.

Sr-J (cancrinite). The feldspathoid, cancrinite, appeared in minor yield on two occasions from an aqueous gel SrO,Al₂O₃,8SiO₂ at 200° and 150°, respectively. It was in the form of black, magnetic particles which could be separated from unchanged gel with a magnet. It was identified by its X-ray powder pattern and was presumably formed by attack upon the walls of the autoclave. The formation was not reproducible and was not promoted by additions of small amounts of iron filings or ferrous or ferric chloride.

Sr-H (α-cristobalite). When the parent gel had a higher ratio of silica to alumina than was normal in the crystalline aluminosilicates produced, the excess of silica often crystallised at higher temperatures as α-cristobalite, in the form of small spherulites. This crystallisation was

²³ Smith, *Acta Cryst.*, 1953, **6**, 613.

²⁴ Barrer and Marshall, unpublished work.

TABLE 5.
X-Ray patterns of feldspathic species.

Sr-K		Sr-anorthite ^a		Sr-W		Sr-K		Sr-anorthite ^a		Sr-W	
<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int	<i>d</i>	Int
6.46	vw	6.44	35	6.48	ms	—	—	2.22	11	2.222	mw
—	—	5.77	11	5.79	w	—	—	—	—	2.203	vw
—	—	4.55	17	4.57	mw	—	—	2.19	13	2.191	vw
4.05	s	4.11	9	4.11	mw	2.160	m	2.16	9	2.158	m
3.95	vw	—	—	—	—	2.116	mw	—	—	2.112	vw
3.88	mw	—	—	3.77	w	—	—	2.10	7	2.095	vw
3.74	ms	3.75	40	3.74	s	—	—	—	—	2.070	vw
3.54	vw	3.58	20	3.59	w	—	—	2.06	11	2.057	vw
—	—	3.47	20	3.48	w	—	—	2.04	11	2.041	w
3.45	ms	3.43	70	3.44	vs	—	—	—	—	2.025	vw
—	—	3.27	100	3.26	vvs	1.94	mw(b)	1.965	3	1.961	ms
3.22	vs(b)	3.22	100	3.22	vvs	—	—	1.895	3	1.891	m
3.14	vw	—	—	—	—	—	—	1.872	7	1.867	w
2.95	vw	2.97	45	2.97	m	—	—	1.846	7	1.847	w
2.91	mw	2.89	25	2.885	mw	—	—	1.834	7	1.832	w
2.845	w	—	—	—	—	—	—	1.794	11	1.793	w
2.761	w	2.74	35	2.747	s	1.788	m	1.784	20	1.780	s
2.602	w	—	—	—	—	1.755	vw	1.744	7	1.739	w
2.53	mw(b)	2.55	65	2.552	s	1.715	w	—	—	1.715	vw
2.487	m	2.47	5	2.476	w	—	—	1.657	7	1.655	w
—	—	2.40	9	2.402	w	1.61	vw(b)	1.621	9	1.619	w
—	—	2.34	9	2.341	w	1.56	vw(b)	1.564	11	1.562	m
2.310	w	2.31	9	2.307	w	1.48	mw(b)	1.491	13	1.487	ms

Sr-C						Sr-P					
<i>hkl</i>	<i>d</i>	Int	<i>hkl</i>	<i>d</i>	Int	<i>hkl</i>	<i>d</i>	Int	<i>hkl</i>	<i>d</i>	Int
110	6.46	mw	040	2.338	ms	511	1.713	w	001	7.65	m
011	6.22	m	123	2.308	ms	052	1.703	w	100	4.49	vw
111	5.12	vw	213	2.291	vw	251	1.694	vw	101	3.875	vvs
002	4.17	m	400	2.227	vw	423	1.630	mw	002	3.80	vw
201	3.93	vs	141	2.180	ms	115,234	1.615	vvw	102	2.905	vs
121	3.71	s	401	2.151	ms	252	1.599	vvw	110	2.601	s
211	3.62	w	223	2.109	mw	080	1.557	m	200	2.252	w
112	3.50	s	411	2.101	mw	144	1.533	vvw	103	2.210	m
220	3.22	ms	004	2.088	m	153	1.520	mw	201	2.159	ms
022,030	3.11	mw	303	2.022	vw	433	1.516	mw	202	1.937	mw
202	3.045	w	241	2.007	w	—	1.483	w	004	1.901	m
122,130	2.940	m	114,142	1.986	mw	—	1.470	m	113	1.814	ms
031	2.920	ms	024	1.903	w	—	1.438	vw	211	1.659	m
212	2.895	ms	323,124	1.862	m	—	1.434	vw	212	1.551	m
310	2.830	w	150,340	1.833	m	—	1.417	w	114	1.531	m
311	2.681	m	422,430	1.812	mw	—	1.395	w	300	1.498	m
013	2.666	vw	341	1.794	w	—	1.388	mw	105	1.438	w
230	2.553	s	431	1.771	vw	—	1.340	w	213	1.409	vw
320	2.506	m	224	1.752	m	—	1.300	w	303	1.296	w
312	2.349	vw	—	—	—	—	—	—	222	1.229	vw
—	—	—	—	—	—	—	—	—	310	1.257	mw
—	—	—	—	—	—	—	—	—	222	1.229	vw
—	—	—	—	—	—	—	—	—	312	1.183	mw

common although the cristobalite is metastable with respect to quartz in the experimental temperature range. Its appearance is, nevertheless, in accord with previous studies which show that metastable cristobalite formation is favoured by a relatively low pH²⁵ and by the presence of alkaline earth cations.²

On the other hand, when the aqueous colloidal silica sol used in these experiments was treated alone at 380°, the product comprised mainly well-grown quartz crystals, although X-ray examination did reveal traces of α -cristobalite in the shortest run. The prior appearance of α -cristobalite may thus be an example of Ostwald's law of successive transformations, and the function of the alkaline-earth cations may be to delay or inhibit the subsequent transformation of the metastable cristobalite to the stable quartz.

Species Sr-N. This species was formed from aqueous gels with the ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ equal to unity (Table 2). Optimum temperatures of formation were above 400° although lesser yields were obtained down to 300°. All preparations of species Sr-N contained material Sr-C in varying amount. The compound crystallised as well-formed cuboid crystals up to 10 μ across (Plate 2g). Since species Sr-C was not affected when heated to 1000°, differential thermal and thermogravimetric analyses could successfully be made on species Sr-N containing Sr-C (Fig. 5). In the run illustrated in Fig. 5 a weight loss of about 3% occurred, mainly between 500° and 700°, and so may be attributed to hydroxyl-water. This inference was supported by the infrared spectrum of the mineral which before heating showed a sharp peak at 2.75 μ , characteristic of an OH group; in the spectrum of the ignited sample no trace of this peak remained.

²⁵ Corwin, Herzog, Owen, Yalman, and Swinnerton, *J. Amer. Chem. Soc.*, 1953, **75**, 3933.

The X-ray powder pattern (Table 4) was indexed to give a possible tetragonal unit cell with $a = 12.4_8$ and $c = 16.0_0$ Å. Species Sr-N was not a hydrogrossular, as might have been expected by analogy with parallel work on calcium aluminosilicates,⁹ nor could it be produced from aqueous gels of composition $\text{SrO}, \text{Al}_2\text{O}_3$ at comparable temperatures. The X-ray powder pattern was not identified with that of any other mineral.

Species Sr-S and Sr-T. Small amounts of these two unidentified compounds appeared in

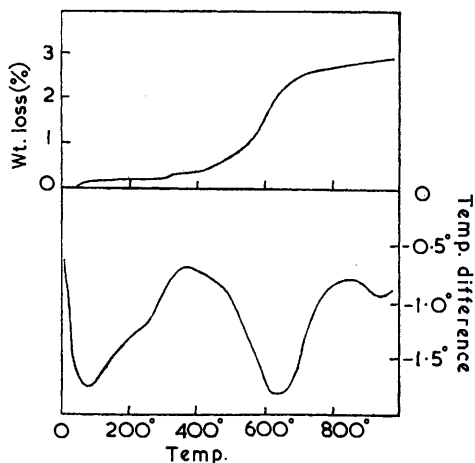


FIG. 5. D.t.a. and thermogravimetric analysis of species Sr-N.

the crystallisate from aqueous gels $\text{SrO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ (Table 2). Their presence was indicated by weak lines in the X-ray powder patterns which could not be attributed to the major species present (Table 4).

DISCUSSION

A feature of hydrothermal crystallisation from strontium aluminosilicate gels has been the lack of reproducibility among some of the preparations. Gels having the same composition would yield different products at the same temperature in successive runs, and often this behaviour bore no relation to the duration of the run. This was particularly noticeable in the case of the zeolites, four of which (gmelinite, analcite, mordenite, and heulandite) occurred once or twice only. This behaviour accords with a delicate balance in some circumstances between different possible nuclei, so that, even though the procedure was standardised as far as possible, slight changes in concentration or conditions locally within the autoclave, or for the gel as a whole, suffice to turn the course of crystallisation and hence change the compounds formed. It seems likely that some of the species obtained were metastable, and their occurrence could, as in the case of cristobalite, exemplify the Ostwald law of successive transformations. However, once formed, a metastable product can persist for a long time, and when removed from its mother-liquor may do so indefinitely.

A further interesting result is the formation of the zeolites Sr-D and Sr-Q at temperatures unusually high for zeolite formation. This is particularly true of the reproducible formation of species Sr-D at 380°. An analogous situation is the crystallisation of potassium near-phillipsite up to 400° and of K-analcite in good yield at 450°.⁹

A general comparison of trends in the hydrothermal synthesis of aluminosilicates of calcium, strontium, and barium will be made in connection with a study of part of the $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ crystallisation field

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