

## THE SYNTHESIS OF ZINC SILICATES AT 20°C AND ATMOSPHERIC PRESSURE

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**Abstract**—Zinc silicates were synthesized under conditions analogous to surficial weathering environments. The main product, regardless of conditions of precipitation or ageing, was shown by X-ray, i.r., electron microscopic and chemical evidence to be a 2:1 layered zinc silicate equivalent of stevensite. In the presence of aluminium, a 1:1 layered zinc silicate was formed as well, in confirmation of published work. The stability of the zinc silicate, in relation to carbonate, was favoured by the presence of aluminium in the lattice and silicic acid in the equilibrium solution. Zinc layer silicates were formed under conditions that generated orthorhombic zinc hydroxides and/or basic salts in the absence of silicon; the involvement of the brucitic zinc hydroxide ( $\alpha$ -form), as proposed by earlier workers, could not be supported. Crystalline zinc layer silicates were formed by the slow evolution of the initial gels. Such layer silicates, but not willemite or hemimorphite, could have an important role in the control of chemical reactions of zinc in soils.

### INTRODUCTION

Zinc silicate minerals such as willemite ( $Zn_2SiO_4$ ) and hemimorphite [ $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ ] and saucconite, with the generalized composition  $(Si,Al)_8(Al,Fe,Mg,Zn)_6O_{20}(OH)_4$ , are found in nature in the oxidation of some sulphide ore bodies. Laboratory studies by Roy and Mumpton (1956) and Esquevin (1960) have contributed to our knowledge of the formation and relative stability of such minerals. Roy and Mumpton's work was carried out at elevated temperatures (130–730°C) and pressures (34.5–276 bar) and showed that willemite and hemimorphite were more stable than saucconite which was only formed with difficulty. Two-layered zinc silicates (1:1) of the antigorite type were not formed. Their results suggested that willemite might not form below 250°C whereas pure saucconite was stable up to 210°C. Esquevin's work, mainly at 100°C and under atmospheric pressure, extended this study to conditions more applicable to the sub-aerial environment. He reported that hemimorphite, willemite and 2:1 layer silicates were formed but not the zinc equivalent of antigorite. Esquevin suggested that zinc added to soils may be fixed by the formation of willemite or hemimorphite.

In studies of the reactions of heavy metal cations with clays and alumina at 20°C, Tiller (1968a,b) has shown that the *adsorption* of either zinc or silicic acid by silicate clays will favour the removal of the other from solution. *Precipitation* of zinc in the presence of clay was also favoured by the presence of silicic acid. The possibility of a zinc silicate phase at clay edges or

existing separately could have important implications in the chemistry of zinc in soils and sediments.

The aim of these experiments was to study further the formation of zinc silicates but under conditions more appropriate to low temperature environments, especially soils. Experiments at higher temperatures were avoided because the advantage of higher reaction rates could be offset by the formation of compounds with a different stability field.

### MATERIALS AND METHODS

#### *General procedures*

Experiments were conducted in a constant temperature room at  $20 \pm 1^\circ\text{C}$ . Details of procedures are given later. Monomeric silicic acid was considered the appropriate source of silicon since it is the common form of silicon in soil solution (McKeague and Cline, 1963) and probably other weathering environments. This was prepared by passing potassium silicate solution of the required concentration through a  $H^+$ -saturated, strongly acidic cation exchange resin. All precipitations were carried out in polyethylene bottles or polypropylene tubes.

Dialysis was carried out using seamless cellulose tubing. The distilled water used for dialysis was changed regularly for several months, frequently at first, but less so later.

#### *X-ray diffraction*

X-ray diffraction analyses were carried out with a

5.73 cm dia. camera using Co K $\alpha$  radiation. The patterns obtained were measured and compared with reference standards (J.C.P.D.S., 1972). Visual comparisons were also made with standard photographs where possible. All samples were examined after drying at room temperature: many samples were also re-examined after heating at 110°C or higher, and some, after treatment with glycerol.

#### *Infra-red spectroscopy*

Infra-red spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer using KBr discs of the samples after drying at 50°C. The discs were pressed (440 bar) under vacuum.

## RESULTS

#### *Preliminary experiments*

In preliminary experiments, zinc was precipitated during a period of about 20 min in solutions containing  $1.85 \times 10^{-3}$  molar silicic acid, by neutralization of zinc chloride with dilute sodium hydroxide solution. The pH of precipitation was varied but not maintained constant. The reactants varied in Si/Zn molar ratio from 0.67 to 3.00: the products were stored in suspension for periods from 2 to 40 days. All products were amorphous to X-rays and formless under the electron microscope.

#### *Experiments with controlled conditions of precipitation and ageing*

(a) *Aged for 10–12 weeks.* Zinc compounds were precipitated over a period of about 2 hr by adding zinc chloride solution to about 1 litre of solution containing approximately  $2 \times 10^{-3}$  molar silicic acid and the required electrolyte. The reactants were well stirred during precipitation and the pH maintained constant by addition of the appropriate base. Aluminium was introduced as aluminate in sodium hydroxide solution when required. Precipitates were aged, either as precipitated or after dialysis against distilled water. In the former case, the appropriate pH was maintained constant. Experimental conditions included variable Si/Zn ratio (0.64–1.20), pH (6.5–9.0), and electrolyte (M NaCl, 0.05 M CaCl<sub>2</sub>, 0.01 M CaCl<sub>2</sub>, or none), addition of Al and the two methods of ageing.

Most products prepared by precipitation in the presence of low or no added electrolyte and aged without dialysis are effectively amorphous to X-rays although a few weak reflections are present, which are associated with layer silicates. The electron microscope showed that all samples consist mainly of formless material; some dialyzed, aluminium-free samples also contain

many well defined platelets ( $0.2 \mu\text{m} \times 0.5 \mu\text{m} \times 10\text{--}20 \text{ \AA}$ ). These are presumed to be due to a zinc carbonate phase, probably subcrystalline hydrozincite ( $2\text{ZnCO}_3 \cdot 2\text{Zn(OH)}_2$ ), because of the i.r. spectra. Infra-red data also showed that all products regardless of experimental conditions are incipient 2:1 layer silicates (see later).

(b) *Aged for at least 1 yr.* Most of the products referred to under (a) above were permitted to age for much longer periods, some as long as 7 yr. For confirmation additional experiments were performed under sterile conditions using autoclaved, filtered solutions to minimize the possibility that bacterial products might affect the evolution of crystalline products. This precaution did not affect the results.

#### *X-ray diffraction data*

The ageing of precipitates for 1 yr at 20°C resulted in well defined diffraction patterns of broad lines. The patterns became a little more distinct on further ageing of precipitates up to 2 yr but there was no further change up to 7 yr, apart from some sharpening of the hydrozincite lines when present. An example of the kind of pattern obtained is shown in Fig. 1. The minerals identified in the various products together with the corresponding experimental conditions are summarized in Table 1. Examples of the X-ray diffraction data are given in Table 2.

The aluminium-free products consisted mainly of a 2:1 layer silicate, the intensity of the diffraction pattern being favoured by higher pH conditions and lower electrolyte concentration during precipitation and by ageing without dialysis. Hydrozincite was also produced, especially when the products were dialyzed.

The products containing aluminium consisted of the 2:1 layer silicate and a second mineral with a spacing at about 7.4 Å which could only be assigned to a 1:1 layer silicate. Willemite was not identified in any products: hemimorphite occurred in only one.

The diffraction band at 12 Å in the pattern of both air-dried samples, collapsed to 11 Å on heating the sample at 110°C, and irreversibly to 10 Å at 300°C. No pattern remained after the samples were heated at 500°C. On treatment with glycerol, the pattern of the type sample, S14/3, sharpened a little but there was no swelling.

#### *Electron microscopy*

Many of the products examined under the electron microscope consist of more than one phase. The second phase is commonly amorphous. Sample S14/3 is representative of those products which appeared to consist of one phase under the electron microscope. As illustrated in Fig. 1, the micrographs show aggregates

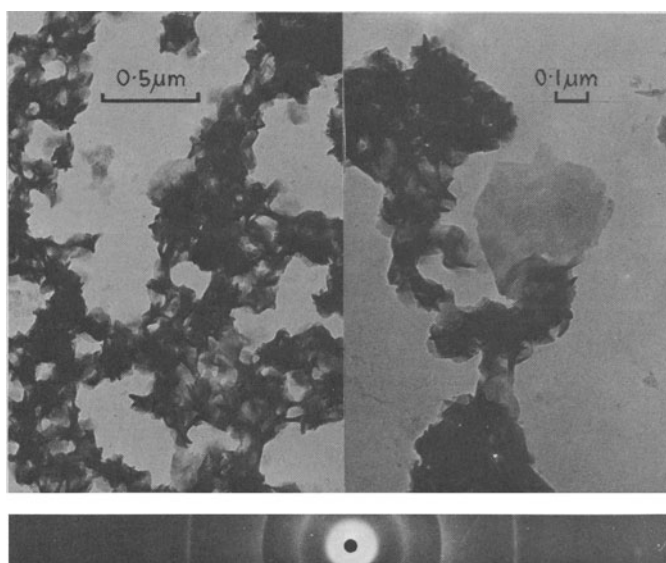


Fig. 1. Electron micrograph and X-ray diffraction of sample S14/3 after ageing 2 yr at 20°C.

Table 1. Mineral composition of products aged at least 1 yr at 20°C

Sample no.	Experimental conditions				Minerals present			
	pH	Precipitation Salt	Ageing Dialysis	No dialysis	2:1	1:1	Hydrozincite*	Hemimorphite
S3/1	7.5	M NaCl		*	M		T	
2	8.5	M NaCl		*	M		T	
3	7.5	0.05 M CaCl <sub>2</sub>		*	M		T	
4	8.5	0.05 M CaCl <sub>2</sub>		*	M		T	
5	7.5	None added		*	M		T	
6	8.5	None added		*	M		T	
7	7.5	0.01 M CaCl <sub>2</sub>		*	M		T	
8	8.5	0.01 M CaCl <sub>2</sub>		*	M		T	
S4/1	7.5	M NaCl	*		M		P	
2	8.5	M NaCl	*		M		P	
3	7.5	0.05 M CaCl <sub>2</sub>	*		M		P	
4	8.5	0.05 M CaCl <sub>2</sub>	*		M		P	
5	7.5	None added	*		M		P	
6	8.5	None added	*		M		P	
S6/1†	7.5	M NaCl	*		M	P		
2	7.5	M NaCl	*		M		P	
3†	8.5	M NaCl	*		M	P		
4	8.5	M NaCl	*		M		P	
5†	7.5	None added	*		M	P		
6	7.5	None added	*		M		P	
7†	8.5	None added	*		M	P		
8	8.5	None added	*		M		P	
S14/1	7.5	M NaCl		*	M			
2	7.5	M NaCl	*		M		T	P
3	7.5	None added		*	M			
4	7.5	None added	*		M		P	

\* Disordered.

† Aluminium included; Al/Zn  $\approx$  0.3.

M = main constituent, P = present, T = trace.

1:1 = A material with a spacing of  $\sim 7.4$  Å without lines of hydrozincite, hemimorphite, hydroxide or basic salts.

2:1 = A disordered trioctahedral montmorillonite (see text).

The Si/Zn ratio of reactants varied from 0.64 to 0.80 in this series of experiments.

Table 2. X-ray diffraction data of selected samples

Air dried		S6/3*		Oven dried (110°C)		S14/3† Air dried	
d(Å)		I	d(Å)	I	d(Å)	I	
12.1		100	11.1	40	12.3	100	
7.4		80	7.3	100			
4.7	} Band	60	4.7	} Band	4.7	} Band	
3.5			4.2				4.0
3.3‡	} Sharp spotty	60	3.6	} ↓			
2.63			2.63			2.68	
2.38	} Band	↓90	2.44		2.44	} Band	
			40				
1.53		90	1.53	80	1.55	80	
1.50		20	1.50	40			
1.32		20			1.34	20	

\* Contains Zn, Al and Si.

† Contains Zn and Si.

‡ Probably due to quartz contamination.

↓ Indicates direction of decreasing intensity within band.

of fine grained platy particles, similar in appearance to some montmorillonites. These aggregates could not be dispersed ultrasonically.

#### Infra-red spectroscopy

The aluminium-free products are characterized by absorption peaks at 990, 660, 460 and 300  $\text{cm}^{-1}$  with shoulders at about 900 and 400  $\text{cm}^{-1}$ . Infra-red patterns of these materials also contained other peaks due to basic zinc carbonates. The products containing aluminium have main absorption peaks at 1000, 560 and about 450  $\text{cm}^{-1}$ , but not at 300 or 660  $\text{cm}^{-1}$ . The i.r. spectra were only marginally affected by conditions of precipitation such as pH and electrolyte. Examples of these spectra are shown in Fig. 2 and compared with those of saucanite, hemimorphite and hydrozincite. The spectra of S14/3 and S6/6 are quite similar to that of saucanite and other 2:1 layer silicates such as saponite and stevensite (not shown), but differ from those of non-layer zinc silicates, willemite (not shown) and hemimorphite. Infra-red spectra often confirmed the presence of zinc carbonates in many products, e.g. S6/6.

#### Chemical data

Most samples were not analyzed chemically because of the difficulty of interpretation of data obtained from mineral mixtures. The chemical composition is given (Table 3) for sample S14/3 because other data indicated that it consisted of a single phase. Chemical formulae were calculated on the basis of either 11 oxygen atoms or 4 silicon atoms. An amount of zinc in excess of the requirements of a 2:1 layer mineral is evident. This excess varies from about one-tenth to one-third of

the total zinc, depending on which basis the empirical formulae are calculated and on the role of excess zinc

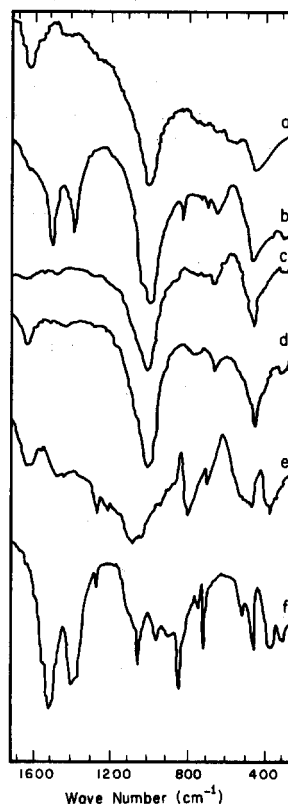


Fig. 2. Infra-red spectra of selected products and reference minerals: (a) S6/5 aged 1 yr; (b) S6/6 aged 1 yr; (c) S14/3 aged 2 yr; (d) saucanite; (e) hemimorphite; (f) hydrozincite. See Table 1 for details of products.

Table 3. Chemical composition of sample S14/3

	Analysis (% by weight)	Empirical formulae		
		Atoms/11 oxygens	Atoms/4 silicons	
ZnO	58.0	Zn	3.73	4.17
SiO <sub>2</sub>	41.1	Si	3.58	4.00
MgO	0.22	Mg	0.028	0.032
Al <sub>2</sub> O <sub>3</sub>	0.14	Al	0.014	0.016
CaO	0.38	Ca	0.035	0.040
Fe <sub>2</sub> O <sub>3</sub>	0.07	Fe	0.005	0.005
Total	99.91	O	11.00	12.30

Average of 2 analyses of Ca<sup>2+</sup>-saturated sample, after ignition at 1000°C.  
Analyses by J. T. Hutton, CSIRO, Adelaide.

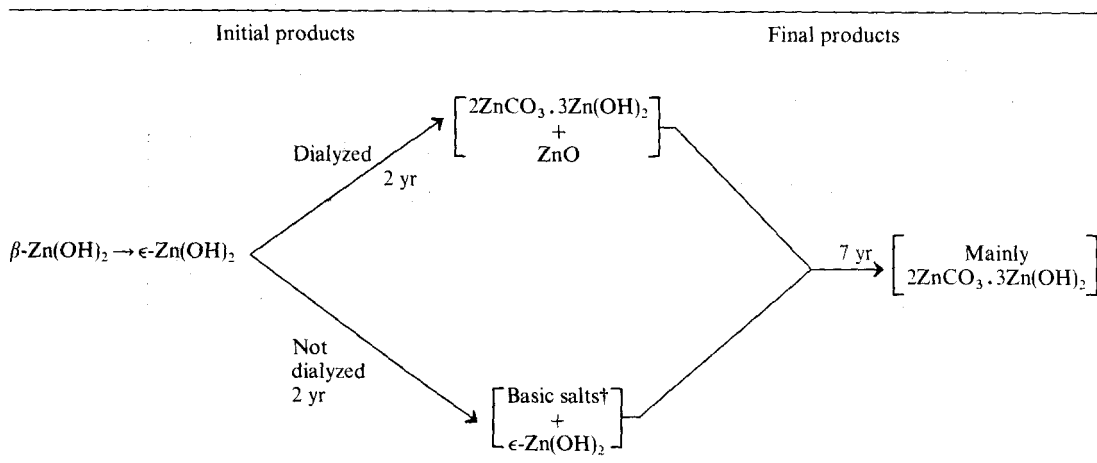
in balancing the resultant charge. Some of this excess zinc may occur as a brucite-like interlayer. This hypothetical zinc hydroxide interlayer cannot be very extensive because the 12.3 Å line collapsed to 11.1 Å when the sample was heated at 105°C. However, caution needs to be exercised in any analogy with natural chlorites because of the low stability of zinc hydroxide (see later). It is proposed that the 2:1 layer silicate of most products is analogous to a partially chloritized stevensite in which the brucite layer covers up to 40 per cent of the theoretical maximum interlayer area. Sample S14/3 has a net charge of about 7 m-equiv/100 g.

\* Determined by J. Holt, Division of Soils, CSIRO, Adelaide.

The surface areas\* of selected samples were determined by N<sub>2</sub> adsorption using a continuous flow method. Values of 223, 105 and 158 m<sup>2</sup>/g were obtained for samples S6/7, S6/8 and S14/3, respectively. The surface area of S14/3 is consistent with the size of particles seen under the electron microscope, assuming that one phase is present.

(c) *Synthesis of silicon-free zinc compounds.* Zinc compounds were prepared and aged under conditions identical to those of the S14 samples (Table 1) but in the absence of silicic acid. The initial precipitate in the presence of M NaCl was 4Zn(OH)<sub>2</sub> · ZnCl<sub>2</sub> plus an unidentified basic salt. Insufficient material was available for analysis of the corresponding aged product. The results for products prepared in the absence of added electrolyte are summarized in Table 4. These initial

Table 4. Evolution of silicon-free products\*



\* Samples S14/3 and 4 (Table 1) were produced under identical conditions; but including silicon. No electrolyte was added. Air dried at room temperature.

† Consists of unidentified salts containing carbonate (shown by i.r.) and some 4Zn(OH)<sub>2</sub> · ZnCl<sub>2</sub>.

products were not analyzed but later precipitations under similar conditions always produced  $\beta$ -Zn(OH)<sub>2</sub> in addition to a small amount of an unidentified basic salt in some samples. This  $\beta$ -Zn(OH)<sub>2</sub> was transformed into the  $\epsilon$ -form within several days at 20°C. Both hydroxides decomposed to ZnO on heating overnight at 110°C. The ease of this conversion may be a function of the degree of crystallinity. The transition from  $\beta$ -Zn(OH)<sub>2</sub> to  $\epsilon$ -Zn(OH)<sub>2</sub> to ZnO on ageing or heating is consistent with their relative stability (Fricke and Hüttig, 1944). Hydrozincite is the final end product for both ageing conditions.

## DISCUSSION

### *Layer silicates*

The characteristic reflections of 2:1 layer silicates were amongst the first to be detected as products achieved sufficient order to give rudimentary X-ray diffraction patterns. These were observed after the products were aged for about three months but only for those samples which were precipitated in solutions of low electrolyte content and not dialyzed. The X-ray patterns are well defined after ageing of the precipitates for 12 months but the definition improved somewhat on further ageing. These 2:1 zinc layer silicates have the surface area, crystal morphology, i.r. spectra and X-ray diffraction pattern of disordered trioctahedral montmorillonite. Because of the excess zinc present, the low net charge, and swelling characteristics, it is further proposed that this main product is analogous to a partially chloritized stevensite.

In the pure zinc-silicon system, the 2:1 layer silicate (or its precursor as shown by i.r.) is the only silicate mineral present over a large range of conditions including pH (6.5–9.0), concentration and kind of electrolyte, Si/Zn ratio of reactants (0.64–1.20) and different ageing conditions. Some factors did, however, marginally affect crystallinity of products. This is in contrast with the results of Esquevin (1960) who found that the minerals formed at 100°C depend strongly on pH and electrolyte. He produced mainly 2:1 silicate or hemimorphite, depending on the presence or absence of electrolyte. Willemite also formed at lower pH values. His experimental conditions of both pH and electrolyte were more associated with the rate of release of silicon from the glass walls of the container in relation to the rate of zinc added, rather than associated with conditions of precipitation and ageing. The experimental approach of Esquevin would favour the initial formation of precipitates of lower Si/Zn ratio, i.e. precursors of hemimorphite. Such phases would be emphasized eventually because of the greater opportunity for the evolution of crystalline products.

The non-formation of 1:1 layer silicates in the pure Zn-Si system, as shown by Roy and Roy (1954) and Esquevin (1960), was confirmed by our experiments at 20°C.

The X-ray patterns of products containing aluminium had, in addition, a reflection at about 7.4 Å that does not arise from 2:1 layer silicates, or from hemimorphite, hydrozincite or other basic salts. This peak is ascribed to a 1:1 layer silicate, which may be similar to zinc berthierine synthesized by Esquevin (1960). Diffraction data for the latter samples were not available for comparison. The X-ray evidence also shows that in the presence of aluminium, the diffraction band at 12 Å is weaker, and the (060) reflection occurs at 1.53 Å, compared with 1.55 Å for the aluminium-free 2:1 silicate. The adjacent reflection at 1.50 Å is presumed to be the (060) reflection of the 7.4 Å phase (see Table 2). These results are interpreted as being consistent with a mixture of two minerals, each of greater dioctahedral character than the aluminium-free 2:1 layer silicate mineral discussed above.

Infra-red spectra of these products show decreased absorption at 660 cm<sup>-1</sup> coupled with increased absorption at around 550 cm<sup>-1</sup> when aluminium was included. By analogy with the studies of Stubican and Roy (1961) on the substitution of Mg and Al in layer silicates, the i.r. results can be explained by the replacement of Al for Si in tetrahedral positions to produce saponite-like rather than stevensite-like compounds. It may also be possible that Al substitutes for Zn in the octahedral positions of a second phase. Appreciable substitution of Al in both tetrahedral and octahedral sites of one phase is unlikely although it has been reported in batavite (Brown, 1961).

### *Zinc carbonates and other compounds*

Hydrozincite occurs with the layer silicates in many aluminium-free products, especially after the precipitates have been dialyzed and aged for extended periods. The formation of zinc silicate or carbonate compounds must depend on the concentration of silicic acid and bicarbonate ions in the system and the relative solubility of solid silicate and carbonate phases. Since carbon dioxide was not excluded in these experiments, dialysis tends to remove unreacted silicic acid without affecting the bicarbonate concentration, thus encouraging the formation of carbonates. The carbonate-free samples, S14/1 and S14/3, were associated with equilibrium solution concentrations of about  $7 \times 10^{-4}$  and  $3 \times 10^{-5}$  molar silicic acid, respectively. Accordingly the range of silicic acid concentrations found in natural soil solutions may suffice to inhibit the formation of zinc carbonate as a separate phase in normal soils.



Compounds containing carbonate never formed when aluminium was included regardless of whether the products were dialyzed or not. This inhibition of the formation of hydrozincite is probably the result of increased chemical stability associated with partial substitution of aluminium in lattice positions (see above).

Although Roy and Mumpton (1958) suggested that 200°C may be minimum temperature for the formation of willemite under hydrothermal conditions, it was produced by Esquevin (1960) at 100°C under atmospheric pressure. However, willemite was not detected in any of the products of this study at 20°C. It is therefore considered unlikely that willemite forms in soils or in other such low temperature weathering environments.

#### *Mechanism of formation of layer silicates*

Esquevin (1960) found in studies at 100°C that the conditions which favoured the precipitation of  $\epsilon$ -zinc hydroxide or basic salts in silicon-free systems, also favoured the production of hemimorphite when silicate was included. Similarly, willemite and layer silicates formed under conditions favouring the precipitation of the zinc oxide. He proposed, following the views of Caillère and Hénin (1961), that the initial formation of a zinc hydroxide with a brucitic structure [ $\alpha$ -Zn(OH)<sub>2</sub>], was essential for the synthesis of a layered zinc silicate. By their hypothesis, the relatively unstable  $\alpha$ -Zn(OH)<sub>2</sub>, which would have only a transitory existence in the absence of silicon, would be stabilized by silicate ions and lead to a 2:1 layer silicate. Thus the association of ZnO in the silicon-free products and the synthesis of layer silicates was seen in terms of  $\alpha$ -Zn(OH)<sub>2</sub>. By the same hypothesis conditions favouring the precipitation of orthorhombic zinc hydroxides ( $\epsilon$ - and  $\beta$ -) should yield hemimorphite (Esquevin, 1960).

In our experiments, the formation of layer silicate was associated with the formation of orthorhombic zinc hydroxide and/or basic salts in the silicon-free system. Products containing silicon were, however, amorphous to X-rays when first precipitated. Since  $\beta$ - and  $\epsilon$ -Zn(OH)<sub>2</sub> may be converted to ZnO by heating, or by ageing at 20°C, it seems possible that some of Esquevin's initial products at 100°C could also have been  $\beta$ -Zn(OH)<sub>2</sub> and not  $\alpha$ -Zn(OH)<sub>2</sub> as proposed. Interpretations based on initial products can be obscured by the fact that  $\beta$ -Zn(OH)<sub>2</sub> converts readily to the  $\epsilon$ -form, even at 20°C.

The transition from  $\beta$ -Zn(OH)<sub>2</sub>  $\rightarrow$   $\epsilon$ -Zn(OH)<sub>2</sub>  $\rightarrow$  2ZnCO<sub>3</sub>.3Zn(OH)<sub>2</sub> involves significant changes in unit cell dimensions and crystal symmetry. Accordingly, it seems reasonable that the initial precipitates with adsorbed silicic acid could evolve into

layer silicates in the same way and thus provide a mechanism for the formation of zinc silicates in soils. There is no evidence that the brucitic  $\alpha$ -Zn(OH)<sub>2</sub> is a necessary prerequisite for the formation of layer zinc silicates.

It has been established that 2:1 layer silicates can be formed under a range of conditions at 20°C from pure solutions, and also that silicon and zinc tend to be associated in the adsorbed state (Tiller, 1967). Within this framework, it seems likely that the template provided by natural alumino/silicate clays should enhance the formation of layer zinc silicates in low temperature weathering environments such as soils. The control of chemical reactions by such zinc silicates may, however, be difficult to assess because of indeterminate stability constants arising from ionic substitution, variable crystallinity and the presence of associated materials.

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**Résumé**—Des silicates de zinc ont été synthétisés dans des conditions analogues à celles de l'environnement superficiel naturel.

On a pu montrer, par diffraction X, i.r., microscopie électronique et analyse chimique que, quelles que soient les conditions de précipitation et de vieillissement, le produit principal est un phyllosilicate de zinc 2:1 équivalent à la stevensite.

En présence d'aluminium, un phyllosilicate de zinc 1:1 se forme, conformément aux travaux antérieurs. La stabilité du silicate de zinc par rapport au carbonate, est favorisée par la présence d'aluminium dans le réseau et d'acide silicique dans la solution à l'équilibre.

Les phyllosilicates de zinc se sont formés dans des conditions qui engendrent des hydroxydes de zinc orthorhombiques et/ou des sels basiques, en l'absence de silicium; l'intervention d'hydroxyde de zinc brucitique (forme  $\alpha$ ), proposée dans des travaux antérieurs, ne peut plus être avancée.

Les phyllosilicates de zinc cristallins se sont formés par évolution lente des gels initiaux. De tels phyllosilicates, mais non la willemite ou l'hémimorphite, pourraient jouer un rôle important dans le contrôle des réactions chimiques faisant intervenir le zinc dans les sols.

**Kurzreferat**—Zinksilikate wurden unter Bedingungen synthetisiert, die dem Verwitterungsmilieu an der Erdoberfläche analog sind. Unabhängig von den Fällungs- oder Alterungsbedingungen konnte röntgenographisch, infrarotspektroskopisch sowie elektronenmikroskopisch und chemisch als Hauptprodukt ein 2:1-Zinkschichtsilikat nachgewiesen werden, das dem Stevensit äquivalent ist. In Gegenwart von Aluminium wurde in Bestätigung veröffentlichter Arbeiten ebensowohl ein 1:1-Zinkschichtsilikat gebildet. Die Stabilität des Zinksilikates im Verhältnis zu Carbonat wurde durch die Gegenwart von Aluminium im Gitter und von Kieselsäure in der Gleichgewichtslösung begünstigt. Zinkschichtsilikate wurden unter Bedingungen gebildet, die in Abwesenheit von Silicium orthorhombische Zinkhydroxide und/oder basische Salze entstehen lassen. Die Beteiligung des brucitischen Zinkhydroxids ( $\alpha$ -Form), wie sie von früheren Autoren angenommen wurde, konnte nicht bestätigt werden. Kristalline Zinkschichtsilikate wurden durch langsame Entwicklung aus den ursprünglichen Gelen gebildet. Solche Schichtsilikate, jedoch nicht Willemit oder Hemimorphit, könnten eine wichtige Rolle bei der Kontrolle der chemischen Reaktionen von Zink in Böden spielen.

**Резюме**—Силикаты цинка синтезировались при условиях, аналогичных поверхностным погодным окружающим условиям. Несмотря на условия осаждения или старения, основной продукт, как показано рентгеновскими, инфракрасными лучами, электронным, микроскопическим и химическим способами, оказался 2:1 слоистым цинковым силикатом эквивалентным стивенситу. В присутствии алюминия образовался также 1:1 слоистый силикат цинка, в подтверждение опубликованной работы. Стабильность цинкового силиката в отношении к карбонатам улучшалась присутствием в сетке алюминия и кремневой кислоты в равновесном растворе. Слоистые силикаты цинка получались в условиях, которые образовали орторомбические цинковые гидроокиси и/или основные соли без присутствия кремния. Предполагаемое прежними работниками получение бруциновой гидроокиси цинка ( $\alpha$ -тип) не подтвердилось. Кристаллические слоистые силикаты цинка формировались медленной эволюцией исходных гелей. Такие слоистые силикаты, за исключением виллемита или гемиморфита, могут играть значительную роль при контроле химических реакций цинка в почвах.