Concentration of Simple Aldehydes by Sulfite-Containing Double-Layer Hydroxide Minerals: Implications for Biopoesis

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Dedicated to our great teacher and friend *Albert Eschenmoser* on the occasion of his 75th birthday. We hope that our joint exploration of mineral assistance '*In der Welt von Gestern*' will carry over also into the '*Brave New World*'.

Environmental conditions play an important role in conceptual studies of prebiotically relevant chemical reactions that could have led to functional biomolecules. The necessary source compounds are likely to have been present in dilute solution, raising the question of how to achieve selective concentration and to reach activation. With the assumption of an initial 'RNA World', the questions of production, concentration, and interaction of aldehydes and aldehyde phosphates, potential precursors of sugar phosphates, come into the foreground. As a possible concentration process for simple, uncharged aldehydes, we investigated their adduct formation with sulfite ion bound in the interlayer of positively charged expanding-sheet-structure double-layer hydroxide minerals. Minerals of this type, initially with chloride as interlayer counter anion, have previously been shown to induce concentration and subsequent aldolization of aldehyde phosphates to form tetrose, pentose, and hexose phosphates. The reversible uptake of the simple aldehydes formaldehyde, glycolaldehyde, and glyceraldehyde by adduct formation with the immobilized sulfite ions is characterized by equilibrium constants of $K = 1.5$, 9, and 11, respectively. This translates into an observable uptake at concentrations exceeding 50 mM.

Introduction. – One of the favored conceptual pathways toward the emergence of an 'RNA World' leads through the formation of glycolaldehyde, its phosphorylation and aldolization to form sugar phosphates. The seminal work of *Eschenmoser* and coworkers has included the synthesis of glycolaldehyde phosphate [1] [2], its aldomerization to a variety of tetrose, pentose, and hexose phosphates [3], and the demonstration of the base-pairing properties of nucleic acids (formally) derived from some of these sugar phosphates. Specifically, oligonucleotides based on pentose 2,4-diphosphates are strong and selective pairing systems [4]. More recently, an even simpler oligonucleotide pairing system based on threose 2,3-diphosphate was discovered [5].

To play a role in biopoesis, such molecules would have to arise by abiotic, environmentally plausible processes that decrease entropy by concentrating, combining, and organizing the reactants. Processes have been demonstrated that are capable of formation and phosphorylation of simple aldehydes, in some cases under conditions that could possibly prevail in nature. One such scheme is associated with the formation and reactivity of oxiranecarbonitrile, which, on ring opening with phosphate anions in aqueous solution, forms glycolaldehyde phosphate cyanohydrin and converts to glycolaldehyde phosphate in the presence of formaldehyde [1]. However, the environmental plausibility of this model reaction leaves some questions open. One concerns the synthesis of oxiranecarbonitrile in the Earth's early, unobservable atmosphere, or as a proxy, the interstellar cloud medium. Initial experiments aimed at detection of rotational transition lines of oxiranecarbonitrile in the interstellar medium indicate that its abundance in the space plasma is lower than that detectable by the technique used [6]; the search is currently continued with more sensitive detectors. It is possible, however, that oxiranecarbonitrile, as a compound with low vapor pressure upon formation (photochemically or by ion-molecule reactions), condenses out on solid grains at the low kinetic temperature in the molecular cloud medium, *ca.* 10–50 K. Hence, it would be of interest to search for oxiranecarbonitrile or its reaction products in comets and carbonaceous meteorites that are thought to be aggregates of interstellar dust particles.

Another environmental constraint that has yet to be addressed in model experiments involving formation of glycolaldehyde phosphate and glyceraldehyde 2-phosphate from oxiranecarbonitrile is the requirement for high phosphate and formaldehyde concentrations. Such experiments required *ca.* 2M water-soluble orthophosphate and 0.3M formaldehyde concentration at pH 10.5 for glycolaldehyde phosphate and 4M formaldehyde concentration for glyceraldehyde phosphate formation [1]. In Nature, orthophosphate solubility is very limited by the ubiquitous presence of Ca^{2+} and Mg^{2+} ions[1]).

Direct sources of formaldehyde and glycolaldehyde exist in nature, but the molecules are in such cases not activated for phosphorylation. Formaldehyde is one of the most common molecules formed by plasma reactions in the interstellar cloud medium and is correspondingly abundant in comets [10]. It would also be expected to form electrochemically in the aurora and in silent electric discharges in an atmosphere consisting largely of carbon dioxide and water vapor. Such an atmosphere, containing also molecular nitrogen and small amounts of reducing compounds such as carbon monoxide and methane, is thought to have characterized the primordial Earth [11]. In his studies on the formation of biologically important molecules in electric-discharge reactions in such model atmospheres, *Löb* [12] found small amounts of glycolaldehyde among the products[2]). Hence, it does not seem improbable that the crucial requirement for dimerization of formaldehyde could be satisfied in the Archean environment.

Selective concentration would seem to be of primary importance in biopoesis, since all production mechanisms realistically proposed for source molecules appear to give quite low yields. Further dilution in the ocean would prevent intermolecular reactions and rather favor destruction by hydrolysis. Plausible concentration mechanisms include phase separation such as freezing, where the water is efficiently separated as ice with negligible solubility for any solutes. This has been shown to efficiently concentrate organic molecules such as HCN in a small volume of interstitial liquid [15]. Unless it is combined with other selection processes, a limiting factor in the freeze-out model is the

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[1]) In contrast, linear and cyclic phosphates are highly soluble, *e.g.*, *meta*-triphosphate and amidotriphosphate, which are shown to be effective phosphorylation reagents in reactions of interest in biopoesis [7–9].

[2]) Quite effective production of glycolaldehyde was found by reacting C-atoms (produced by electric discharge) with H_2O [13]. Glycolaldehyde was very recently observed in the interstellar space [14].

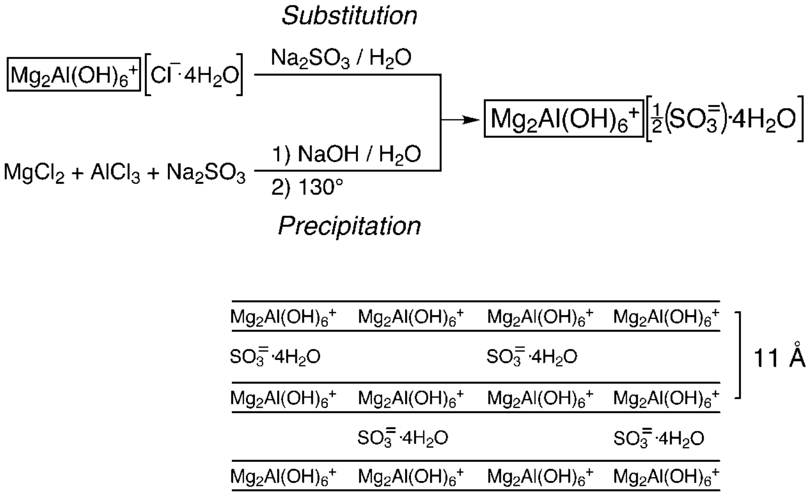
lack of selectivity from a mixture of different compounds in the eutectic solution. A lipid surface film on the hydrosphere, such as suggested by *Mendeleev* [16] could provide effective concentration of lipophilic compounds into an extended two-dimensional reaction medium. For hydrophilic compounds such as aldehydes, the petroleum-film model would, however, not be applicable.

Ionic charge provides a good means for selectively sorbing reactant molecules on or in surface-active minerals such as positively charged double-layer hydroxide (DLH) minerals. In expanding sheet-structure minerals of this kind, high anion concentrations of typically 10M can be reached in a practically two-dimensional aqueous interlayer with a thickness of one or a few hydrated molecules. Phosphate ions, particularly polynuclear species, are exceptionally well-suited for this purpose. Cyclotriphosphate (CTP) has been shown by *Etaix* and *Orgel* [7] to be an effective phosphorylation agent, and *Kolb et al.* used it for phosphorylation of glycolate [8]. To achieve the necessary concentration and reactivity, the anion was sorbed together with CTP into the interlayer of hydrotalcite, a DLH mineral. *Krishnamurthy et al.* demonstrated facile phosphorylation of glycolaldehyde in dilute aqueous solution with amidotriphosphate, formed from CTP and NH_3 [9]. *Yamagata et al.* showed that hydrothermal steam condensate, emanating from volcanic magma, is a source of highly soluble polynuclear phosphates [17]. *Arrhenius et al.* demonstrated efficient thermal condensation of phosphate ion in protonated minerals to form linear phosphates up to twelve residues in length [18]. The phosphate species produced in both of these processes are readily concentrated from dilute (*ca.* 10 mM) solution by the positively charged DLH minerals, that, upon substitution with activated phosphate species, form hydrated, solid phosphorylation agents. Such mineral-assisted reactions could be imagined to have participated in biopoesis. Minerals offer plausible solutions to the problems of selection and concentration of anionic compounds, and protection against hydrolytic destruction. DLH Minerals also provide a reaction space for aldolization of glycolaldehyde 2-phosphate and glyceraldehyde 2-phosphate to form *rac*-tetrose 2,4-diphosphates, *rac*-pentose 2,4-diphosphates, and *rac*-hexose 2,4,6-triphosphates [19][20]. Specific minerals do kinetically favor different sugar phosphate diastereoisomers, such as ribose 2,4-diphosphate [20]. However, the synthesis of pentose phosphates requires the interaction of an odd-carbon aldehyde, glyceraldehyde or formaldehyde, the latter more significant from a geochemical point of view. The question then arises how formaldehyde in dilute aqueous solution can be brought into high concentration in a reaction space that would permit condensation with glycolaldehyde phosphate to form triose and subsequently pentose phosphates. We considered the possibility of achieving concentration of uncharged aldehydes by adduct formation with sulfite or hydrogen sulfite ions sorbed in interlayers of DLH minerals. Such a system would seem appealing also from a geochemical point of view. Bisulfite ion is, besides water and carbon dioxide, a major component of condensates from volcanic gases, such as in Halemaumau, Hawaii, where it rises to 8% in solution [21]. Experiments were, therefore, undertaken to study the incorporation of sulfite in the aqueous interlayers of DLH-type minerals and to explore their potential for subsequent aldehyde adduct formation.

Results and Discussion. – 1. *Preparation of Sulfite-Containing DLH Minerals.* The mixed-valence double-layer hydroxide (DLH) minerals that were employed in this investigation consist of sheets of octahedrally coordinated OH^- ions surrounding the alternating divalent and trivalent small metal cations, normally in proportion 2:1. In this hexagonal-sheet arrangement, $[(M^{2+})_2M^{3+}(OH^-)_6]^+$ leads to an excess positive charge for each M^{3+} ion in the sheets, which thus repel each other and stratify the structure with alternating interlayers containing charge-compensating, exchangable, and hydrated anions. The anion/H_2O ratio is at ambient temperature and moisture saturation around 1/4, generating a quasi-two-dimensional diffusive anionic solution, bilaterally bounded by the positively charged metal-hydroxide sheets. Divalent ions in these minerals mostly involve Mg, Fe, Co, Ni, and Zn; the trivalent ion is most commonly Al, Fe, or Cr[3]).

For our investigations, we prepared a variety of DLHs, containing sulfite anions in the interlayer, by substitution of Cl^- ions with sulfite ions, or by direct precipitation of the amorphous mineral in the presence of sulfite ions, followed by annealing (*Scheme 1*). The preparation of sulfite-containing DLHs by substitution was achieved by treating aqueous suspensions of $[Mg_2Al(OH)_6] \cdot [Cl \cdot 4\,H_2O]$ (hydrotalcite chloride) under Ar at ambient temperature with an excess of aqueous Na_2SO_3 solutions.

Scheme 1. *Preparation of the Sulfite-Containing DLH Mineral Hydrotalcite Sulfite by Substitution and Precipitation* (top); *Schematic Representation of the Structure* (bottom). The positively charged metal-hydroxide sheets are separated by interlayers, hosting hydrated anions. The interplanar distance between two main metal-hydroxide sheets in the hydrotalcite sulfite is *ca.* 11 Å (*cf. Figs. 1* and *3*).



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[3]) These DLH minerals occur in various sedimentary and metasomatic environments in nature. Most abundant today are the $Mg^{2+}Al^{3+}$ (hydrotalcite) and $Mg^{2+}Fe^{3+}$ (ferriaurite) species with CO_3^{2-}, SO_4^{2-} and Cl^- as interlayer anions. Under pre-oxic Archean conditions, an abundance of the $Fe^{2+}Fe^{3+}$ mineral (green rust) is indicated by the widespread occurrence in the sedimentary-banded iron formations of magnetite ($FeO \cdot Fe_2O_3$), a low-temperature alteration product of green rust [22].

Afterwards, the minerals were repeatedly washed with deoxygenated H_2O, until iodometry of supernatant solutions indicated complete removal of the excess Na_2SO_3. By iodometric titration of such samples, typical values of 85–95% SO_3^{2-} incorporation (based on the original Cl^- contents) were determined. X-Ray powder-diffraction measurements (XRD) of wet samples showed the complete disappearance of the reflections of the Cl^- form at 8 Å and appearance of the reflections of the SO_3^{2-} form at 11 Å (*Fig. 1*)[4]). Practically complete exchange was shown also by X-ray fluorescence

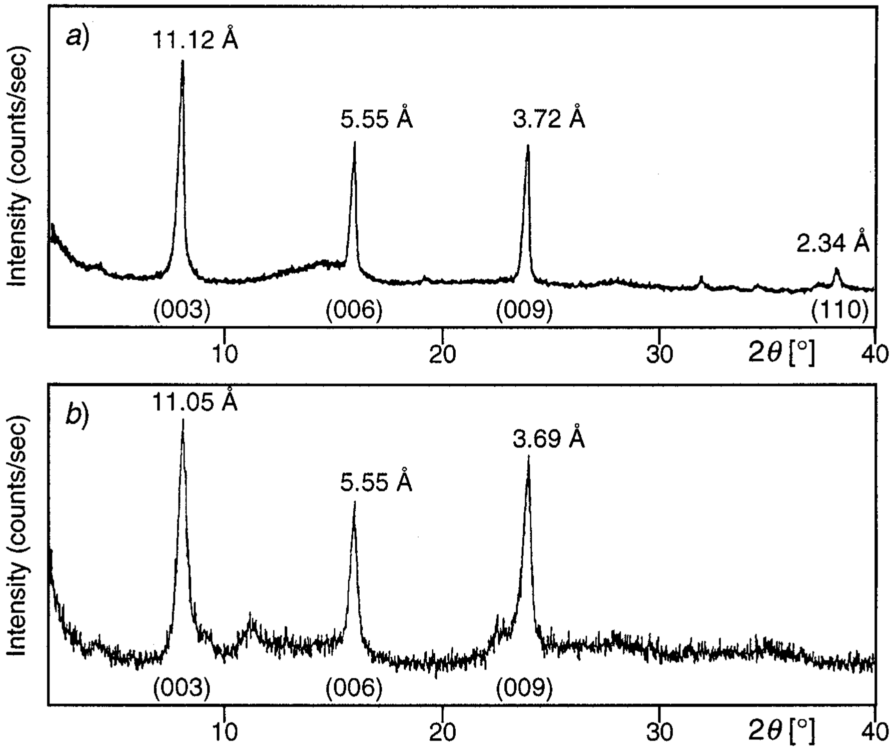

Fig. 1. *X-Ray powder diffractograms of the mixed-valence DLH mineral hydrotalcite sulfite* $[Mg_2Al(OH)_6]\cdot[\frac{1}{2}SO_3\cdot 4H_2O]$: a) *prepared by precipitation and* b) *by substitution.* Due to their plate-like habit, the microcrystals are mainly oriented on the basal plane (001), and consequently show an intense reflection (003) at 11.1 Å, and higher-order reflections (006) and (009) (the (001) and (002) reflections are normally forbidden but may appear as superstructure reflections). The interplanar distance of 11.1 Å for (003) represents the spacing of the double-layer units of the mineral structure (*Scheme 1*), each double layer consisting of the main metal-hydroxide sheet together with the aqueous interlayer. The interlayer constitutes a quasi-two-dimensional, concentrated (*ca.* 10M) aqueous solution of exchangeable anions. The main hydroxide sheet has a thickness of 4.7 Å, leaving 6.4 Å as the thickness of the interlayer solution, sensitive to the size and state of hydration of the interlayer anion, in this case SO_3^{2-}. The reflection from (110), normal to the basal plane, represents the mesh size, 2.34 Å, in the hexagonal net of the main metal-hydroxide sheet. The cell dimensions of this layer net are insensitive to the variations in the interlayer spacing (003) that are induced by variation in composition of the aqueous interlayer solution and normal to the basal plane.

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[4]) In a dry state, such minerals showed a contraction of the interlayer spacing from 11 to 8 Å, identical to that observed with the Cl^- form (*Fig. 3*).

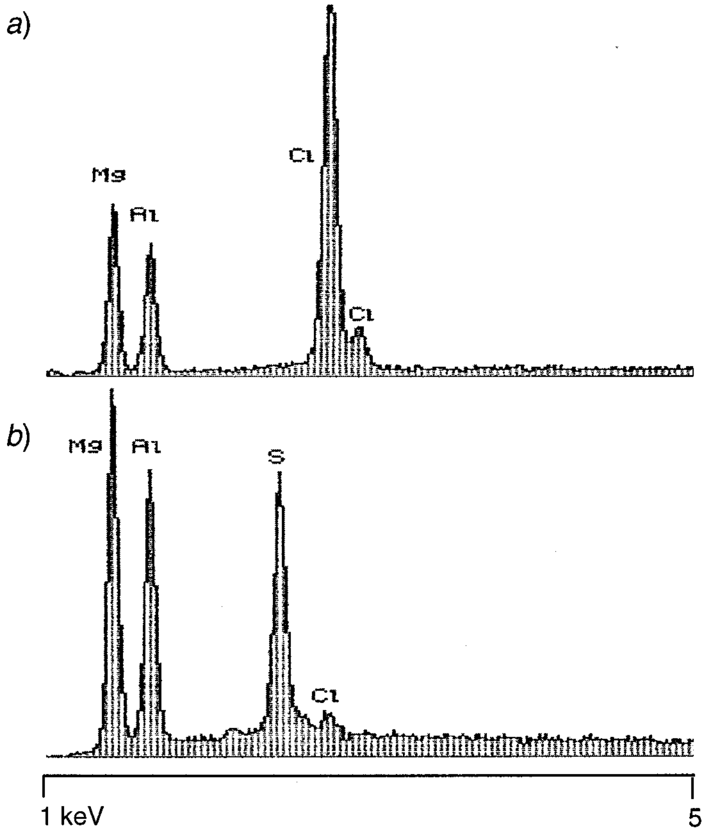

Fig. 2. *Electron-beam-excited X-ray fluorescence spectra of hydrotalcite minerals* (vertical axis: count rate). a) *The parent* Cl^-*-substituted mineral* $[Mg_2Al(OH)_6] \cdot [Cl \cdot 4\,H_2O]$. b) *The sulfite-substituted mineral* $[Mg_2Al(OH]_6] \cdot [\frac{1}{2}\,SO_3 \cdot 4\,H_2O]$ obtained from the corresponding Cl^--substituted mineral by substitution with Na_2SO_3. From the relative peak-intensities, a Mg/Al/S ratio of *ca.* 2 : 1 : 0.5 was determined (taking into account the individual response factors).

spectrometry, which allowed qualitative and quantitative determination of the composition of the hydrotalcite mineral before and after treatment with Na_2SO_3 (*Fig. 2*).

Alternatively, $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\,SO_3 \cdot 4\,H_2O]$ was formed by direct precipitation from aqueous solutions of $MgCl_2$, $AlCl_3$, and Na_2SO_3 with NaOH solution, washing of the amorphous sample with degassed H_2O, and annealing at 130° for 3 days in the presence of Na_2SO_3 (*Scheme 1*)^5). After careful washing with degassed H_2O, the product $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\,SO_3 \cdot 4\,H_2O]$ was analyzed by iodometry, X-ray powder-diffraction measurements, X-ray fluorescence spectroscopy, and IR spectroscopy. Iodometry indicated the presence of the expected amount of SO_3^{2-} ions. The X-ray-diffraction data of the products obtained by substitution and by direct precipitation

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[5]) Annealing at lower temperatures or for a shorter time resulted in less-ordered mineral samples.

were more or less identical (*Fig. 1*). X-Ray fluorescence spectroscopy revealed a molar ratio Mg/Al/S of 1.9 : 1.0 : 0.5, agreeing well with the proposed structure of the new, sulfite-containing DLH. IR spectroscopy of dried and powdered samples showed the sorbed sulfite to be present entirely as SO_3^{2-} rather than as metasulfite ($S_2O_5^{2-}$) or bisulfite (HSO_3^-)6).

All the sulfite-containing DLHs were sensitive to atmospheric O_2, particularly in a dry state, and were rapidly converted to the corresponding SO_4^{2-} derivatives, as indicated by change of the basal reflection to 8.7 Å that correlated with loss of SO_3^{2-} (determined by iodometry). Drying of the DLH sulfites resulted in reversible contractions of the hydrated sulfite interlayers as indicated by X-ray powder-diffraction measurements. In a wet state (removal of excess H_2O by short exposure to a stream of N_2), the sulfite-containing DLHs showed typical interlayer spacings of *ca.* 11 Å, whereas, in a dry state (drying *in vacuo* at elevated temperature), the corresponding distances were *ca.* 8 Å. Upon exposure of such dry samples to moisture, the original structure could be completely reconstituted (*Fig. 3*)7).

2. *Aldehyde-Adduct Formation.* The experiments on interaction of formaldehyde, glycolaldehyde, and glyceraldehyde with the sulfite-substituted DLH $[Mg_2Al(OH)_6] \cdot [½\, O_3 \cdot 4\, H_2O]$ showed uptake of the three aldehydes, presumably by formation of the aldehyde-sulfite adduct in the mineral interlayer (*Scheme 2*). In contrast, no such uptake could be detected with the corresponding Cl^-- and SO_4^{2-}-substituted minerals $[Mg_2Al(OH)_6] \cdot [Cl \cdot 4\, H_2O]$ and $[Mg_2Al(OH)_6] \cdot [½\, SO_4 \cdot 4\, H_2O]$, respectively. The experiments were carried out at ambient temperature, by adding various amounts of the solid minerals to degassed D_2O solutions of formaldehyde, glycolaldehyde, and glyceraldehyde, respectively, in various concentrations (additionally, all solutions contained pentaerythritol as internal NMR standard). The suspensions were shaken under N_2 at ambient temperature. In periodic intervals, aliquots of the mixtures were withdrawn, filtered (or centrifuged), and the filtrates (or supernatants) were analyzed by ^{1}H-NMR spectroscopy. From the ratio of the integrated aldehyde signals and the internal standard signals, the amount of remaining aldehyde in the supernatant was determined. At the end of the experiments, the minerals were dissolved with ion-exchange resin (H^+ form), and the resulting solutions, which contain the previously sorbed materials, were analyzed by ^{1}H-NMR spectroscopy. By such investigations, it could be established that the internal reference (pentaerythritol) was not sorbed into the minerals, and that the eventually sorbed aldehydes remained unchanged. The results from such experiments are presented in the *Table*, and *Figs. 4* and *5*.

With a 0.20M concentration of formaldehyde, 20% had been sorbed after 24 h as a result of sulfite-adduct formation in the hydrotalcite interlayer. In the same time interval, 65% and 70% of glycolaldehyde and glyceraldehyde, respectively, had been sorbed and thus removed from solution (*Fig. 4*, and *Table*). Within this time period, equilibrium had been reached (*Fig. 5*). The sorption of aldehydes, driven by sulfite-

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6) The IR spectrum of this mineral showed a typical signal at $\tilde{\nu} = 956$ cm^{-1} that correlates well with the characteristic signal for Na_2SO_3 at $\tilde{\nu} = 960$ cm^{-1} [23]. In contrast, the characteristic signals for $NaHSO_3$ and $Na_2S_2O_5$ are at $\tilde{\nu} = 980$ and 973 cm^{-1}, respectively [23].

7) After aldehyde adduct formation with the interlayer sulfite ion, no corresponding contraction is observed upon drying, indicating that the aldehydes replace, upon adduct formation, part of the H_2O molecules associated with the sulfite ions.

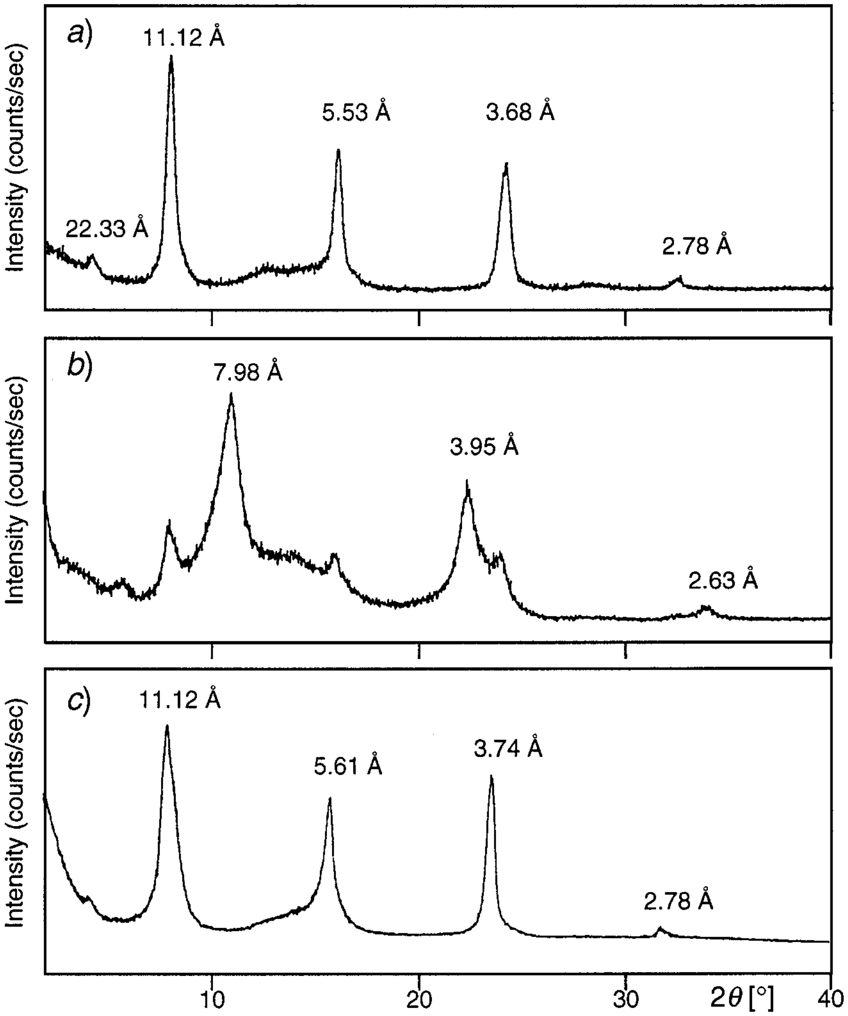


Fig. 3. a) *XRD Spectrum of a hydrotalcite-sulfite mineral dried shortly by a stream of* N_2. b) *Vacuum drying of this mineral at 50° for 20 h results in buckling of the main hydroxide sheet* (broadened reflections) *and shrinkage of the interlayer spacing* (basal reflections displaced toward higher *Bragg* angles 2Θ) *due to removal of* H_2O *molecules from the hydrated, sulfite-substituted interlayer.* When the same experiment is carried out after sulfite-aldehyde adduct formation, no contraction took place, indicating that the aldehyde partially or entirely replaces the H_2O of hydration around the sulfite ions. c) *Upon restitution of the* H_2O *of hydration by exposure to a* H_2O*-saturated atmosphere, the original interlayer spacing and structural order were restored and the metal-hydroxide sheets straightened out.*

Scheme 2. *Reversible Uptake of Aldehydes by Adduct Formation with Sulfite Ions, Localized in the Hydrotalcite Interlayers*

$$\boxed{Mg_2Al(OH)_6^+}\left[\tfrac{1}{2}(SO_3^{=})\cdot 4H_2O\right] \overset{\mathbf{RCHO}\,/\,H_2O}{\rightleftarrows} \boxed{Mg_2Al(OH)_6^+}\left[\tfrac{1}{2}(\mathbf{RCHO}\cdot SO_3^{=})\cdot 4H_2O\right]$$

Table. *Experiments on Interaction of Aldehydes with DLH* $[Mg_2Al(OH)_6]\cdot[\frac{1}{2}SO_3\cdot 4\,H_2O]$[a])

Incubation time: 24 h				c(Aldehyde) = 0.1M			
c(Aldehyde) [M]	Uptake [%]			Incubation time [h]	Uptake [%]		
	Form-aldehyde	Glycol-aldehyde	Glycer-aldehyde		Form-aldehyde	Glycol-aldehyde	Glycer-aldehyde
0.02	< 2	13	15	1	5	8	12
0.02	< 2	15	16	1	6	9	14
0.05	2	30	40	2	8	14	20
0.05	5	28	38	2	9	13	19
0.10	13	50	52	4	10	20	26
0.10	15	47	59	4	11	19	27
0.20	20	65	70	8	12	33	40
0.20	22	62	67	8	13	33	42
				16	14	43	51
				16	12	42	52

[a]) All reactions were carried out in duplicate at ambient temperature in D_2O, employing a 1:1 ratio of (immobilized) sulfite/aldehyde. The uptake was monitored by ^1H-NMR spectroscopy with pentaerythritol as internal standard.

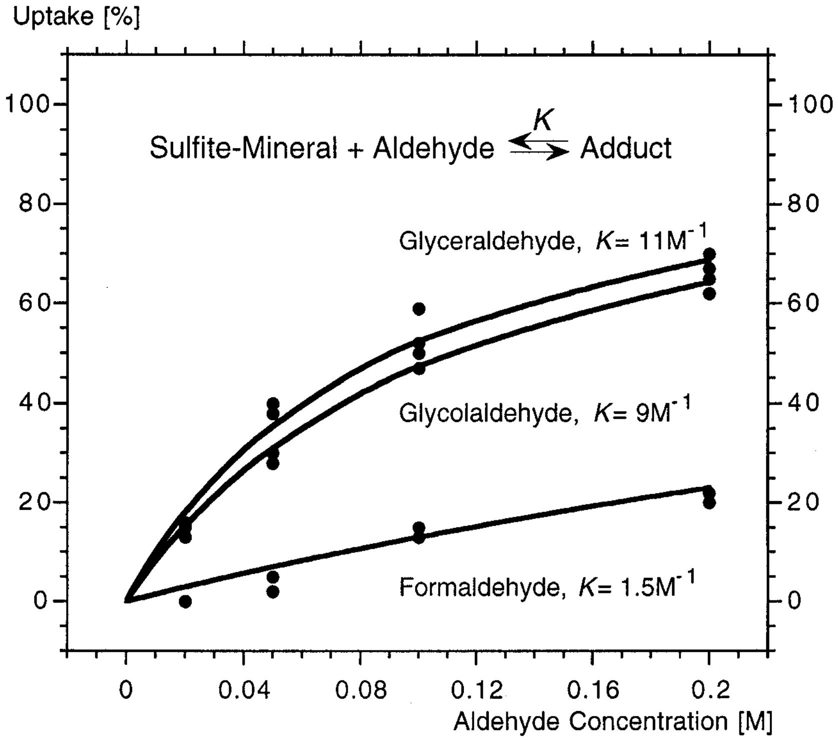


Fig. 4. *Uptake of aldehydes by hydrotalcite-sulfite as a function of aldehyde concentration in solution.* Conditions: 1 equiv. sulfite/aldehyde; ambient temperature, 24 h. The fraction of aldehyde remaining in solution was determined by ^1H-NMR spectroscopy of the supernatant (pentaerythritol as internal standard). All experiments were carried out in duplicate. The lines represent the calculated curves for the indicated K values.

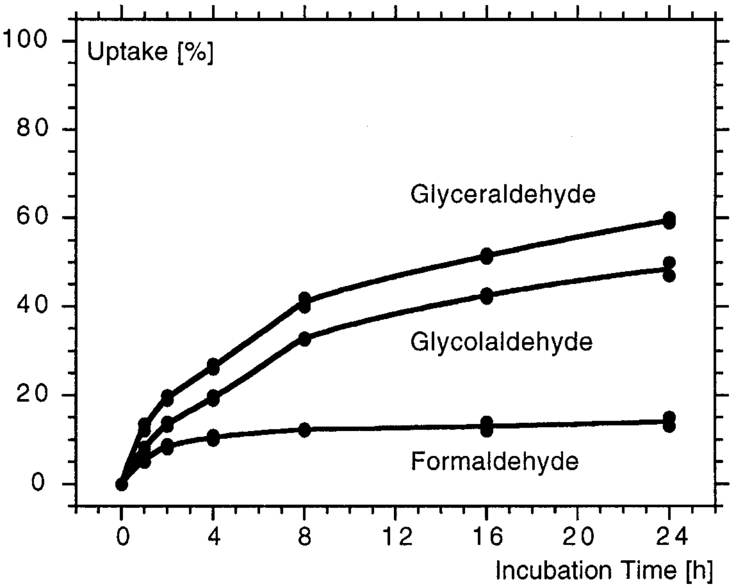


Fig. 5. *Time-dependent uptake of the aldehydes by hydrotalcite-sulfite.* Conditions: 0.1M aldehyde, 1 equiv. sulfite/aldehyde; ambient temperature. The individual values were determined by ^{1}H-NMR spectroscopy according to *Fig. 4*.

adduct formation in the hydrotalcite interlayer, proved to be more efficient for glycolaldehyde and glyceraldehyde than for formaldehyde. The amount of sorption was concentration-dependent, indicating an equilibrium process.

Assuming a bimolecular process between the immobilized sulfite ions and the three aldehydes, the individual equilibrium constants were calculated from the concentration-dependent uptake after 24 h (*Fig. 4*). The reaction with the three aldehydes was characterized by $K = 1.5$, 9, and 11 M^{-1} for formaldehyde, glycolaldehyde, and glyceraldehyde, respectively. This translates into a negligible uptake of formaldehyde at concentrations < 50 mM.

The time-dependance of the aldehyde-uptake by the sulfite-containing minerals is presented in *Fig. 5*. At 0.1M aldehyde concentrations (1:1 ratio to immobilized sulfite) and at ambient temperature, equilibrium was reached in *ca.* 24 h. The initial uptake was relatively fast (*ca.* 50% of the final value was reached within *ca.* 4 h), followed by uptake at a much slower rate. This observation is in agreement with a slow, two-dimensional diffusion of the aldehydes within the interlayers of the sulfite-substituted minerals.

After this study, we carried out similar experiments with the corresponding Mn mineral $[Mn_2Al(OH)_6]\cdot[\frac{1}{2}SO_3\cdot n\ H_2O]$, which was obtained from the parent Cl^--containing mineral by the substitution method. Due to its extreme sensitivity towards oxidation by air, it was not possible to characterize the mineral adequately. However, we carried out some preliminary studies concerning its interaction with formaldehyde, glycolaldehyde, and glyceraldehyde, respectively. Such experiments were only poorly reproducible, but compared to the Mg mineral, we found, in general, faster and more-efficient uptake of all three aldehydes investigated.

In a separate set of experiments, chloride- and hydroxy-substituted hydrotalcites were exposed to solutions of formaldehyde sulfite and glycolaldehyde sulfite. Their concentrations were varied from 3 to 100 mM and the pH values from 7 to 11. As determined by NMR spectroscopy of the supernatants and the mineral phase (after dissolution with ion-exchange resin (H^+ form)), dissociation of inorganic sulfite was observed to occur in all of these experiments; the inorganic sulfite subsequently entered the mineral interlayer alone, leaving the aldehyde in solution.

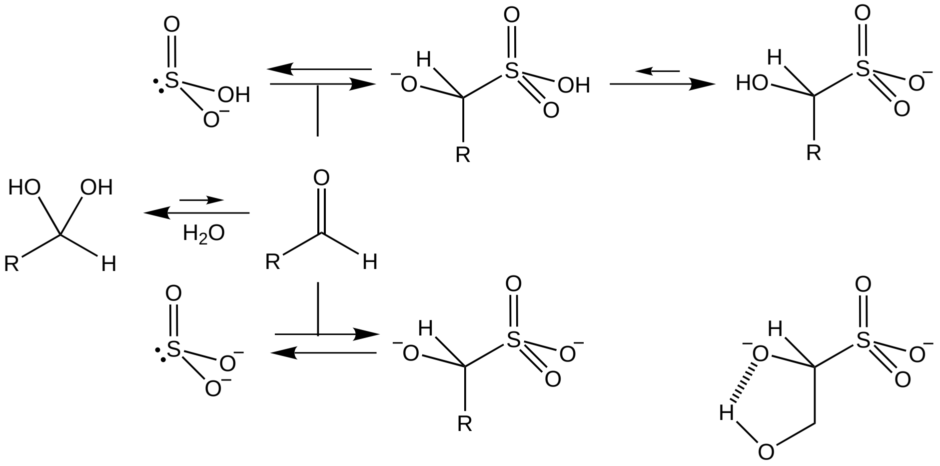
All three aldehydes employed in this study are almost completely hydrated in aqueous solution; nevertheless the small equilibrium concentration of the carbonyl form is sufficient to allow fast addition reactions of nucleophiles, such as the sulfite ion (*Scheme 3*). By X-ray diffraction, we were unable to observe any significant changes of the mineral structure upon adduct formation with aldehydes. However, drying of aldehyde-containing derivatives did not result in the characteristic contraction of the interlayers, as observed with the parent sulfite minerals. We estimate that the sulfite ions in the interlayer of the DLH minerals are surrounded by *ca.* 4–6 molecules of H_2O. Most likely, upon reaction with an aldehyde, some of these H_2O molecules are replaced, resulting in a local, but not a global rearrangement of the initial mineral structure upon adduct formation.

Addition of SO_3^{2-} to an aldehyde results in the reversible formation of a quite basic organic oxyanion species. By protonation of this rather unstable intermediate, the equilibrium of the reaction can be shifted towards adduct formation. Consequently, formation of aldehyde-sulfite adducts in solution is carried out with HSO_3^- rather than with SO_3^{2-}; after addition, a proton migration from the sulfite moiety to the oxyanion can occur, leading directly to a product with only one stabilized charge localized on the sulfite moiety.

In our minerals, the sulfite ions are responsible for compensating the excess positive charges of the mineral interlayers. They are an integral part of their structure and could not be protonated without destruction of the mineral. However, partial stabilization of the oxyanion center of a corresponding adduct could occur by H-bond formation (= partial protonation) by associated H_2O molecules or, in the case of glycolaldehyde and glyceraldehyde, by the vicinal OH group (*Scheme 3*). The quite efficient uptake of these two aldehydes ($K \approx 10\ \mathrm{M}^{-1}$), compared with the rather inefficient uptake of formaldehyde ($K \approx 1.5\ \mathrm{M}^{-1}$), could be the consequence of such stabilization by intramolecular H-bond formation.

Concluding Remarks. – The observation of the sorption of aldehydes in the sulfite-containing hydrotalcite interlayer may have some relevance for speculations about prebiotic chemistry. These should be viewed in the context of the efficient concentration and aldolization of simple aldehyde phosphates from dilute (micromolar) solution into the aqueous interlayer of mixed-valence DLH minerals with the hydrotalcite structure [19] [20]. These experiments, together with the demonstration of an efficient aldehyde phosphorylation by *Krishnamurthy et al.* [20], the replication experiments by *Inoue* and *Orgel* [24], and the demonstration of nucleotide oligomerization by *Ferris* and *Ertem* [25] have weakened the objections against RNA as a molecule too complex to have served as an initial component in the emergence of life.

Scheme 3. *Formation of Aldehyde Adducts with Hydrogen Sulfite and Sulfite, Respectively.* In the case of hydrogensulfite, the oxyanion intermediate is stabilized by protonation. The oxyanion present in adducts formed from sulfite and glycolaldehyde (or glyceraldehyde, resp.) can be stabilized by an intramolecular H-bond.



The present results add to this picture by demonstrating a mechanism for bringing uncharged aldehyde species into the catalytic reaction space of DLH-type minerals, where the possibility for phosphorylation and selective transformation into specific sugar phosphates exists. So far, however, such experiments were studied only sequentially, employing purified materials and different conditions for every individual step. Furthermore, we have no evidence that the immobilized aldehydes are capable of undergoing further reactions inside the mineral interlayers. Therefore, to make the presented scheme credible as a natural process, extensive additional investigations are required.

The relatively low affinity of the aldehydes, particularly of formaldehyde, for the immobilized sulfite ions is certainly a significant problem, given the improbable nature of the concept of a 'prebiotic soup' [26], contrasting with the high dilution imposed by the large volumes of even small compartments of the hydrosphere [18]. A sufficiently high (> 50 mM) concentration of simple aldehydes could possibly have been achieved in percolating solutions in soils formed from carbonaceous meteorites and cometary impact residues. Preconcentration would, however, probably have been needed for constructive processing of aldehydes and, in general, of all organic molecules invoked in prebiotic reactions. Such preconcentration may be offered by the eutectic freezing mechanism demonstrated by *Sanchez et al.* [15]. This process acting alone would suffer from the limitation of being non-discriminating, gathering a plethora of environmental organic and inorganic solutes. In combination with sorption by surface-active minerals as demonstrated here, an additional selective concentration event may have been achieved. This would require that aldehyde concentrations exceeding the order of 50 mM would have been reached in the eutectic liquid. Provided that surface-active DLH minerals are part of the muddy, sulfitic eutectic, further concentration to the order of 10M is conceivable by adduct formation in the aqueous interlayer of the minerals.

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Experimental Part

General. Chemicals were purchased from *Fisher* or *Aldrich* (highest-quality grade). Operations were performed at ambient temp. under N_2 (unless otherwise specified). O_2-Free H_2O was prepared by bubbling N_2 gas through H_2O. $[Mg_2Al(OH)_6] \cdot [Cl \cdot 4H_2O]$ (hydrotalcite-chloride) was prepared according to [27]. Aq. formaldehyde solns. were prepared from paraformaldehyde by boiling it with H_2O or D_2O until a clear soln. was obtained. The autoclaves used were lined with *Teflon*. The pH measurements were carried out with a *Beckman F 44* pH-meter. X-Ray powder-diffraction measurements were performed with a modified *General Electric XRD-5* diffractometer and monochromatized CuK_α radiation. X-Ray fluorescence measurements were carried out on a *Link Analytical QX2000 EDS* instrument, attached to a *Cambridge S360* scanning electron microscope. NMR Spectra were obtained on 200-MHz (*Bruker WM-200*) and 500-MHz (*Varian UN-500*) instruments with D_2O as solvent. IR Spectra were recorded on a *Perkin Elmer 1600 FTIR* spectrometer with dried and powdered mineral samples. Iodometric titrations were carried out according to the procedure of *Mitchell et al.* [28]: to a suspension of the mineral sample (100 – 200 mg) in aq. NaOH soln (0.1M, 2 – 3 ml), a known amount of an aq. KI_3 soln. (0.976M, 1 – 3 ml) was added. After shaking for 15 min, an aq. HCl soln. (10M, 1 – 2 ml) was added. The excess of I_2 was determined by back-titration of I_2 with aq. Na_2SO_3 solution (0.1M).

Preparation of $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\, SO_3 \cdot 4\, H_2O]$ (*Hydrotalcite Sulfite*). 1. *By Substitution*. $[Mg_2Al(OH)_6] \cdot [Cl \cdot 4\, H_2O]$ (5.0 g, 17 mmol, based on Cl^-) was added to a soln. of Na_2SO_3 (37.8 g, 300 mmol) in H_2O (200 ml) and shaken overnight. The suspension was centrifuged and washed with O_2-free H_2O until no SO_3^{2-} was detected in the washings. The mineral was stored as a suspension in H_2O. Iodometric titration of two dried samples (0.05 mbar, 100°, 14 h) revealed 2.27 and 2.26 mmol SO_3^{2-}/g mineral, resp. (calculated for $[Mg_2Al(OH)_6] \cdot [1/2\, SO_3]$: 2.30 mmol/g). X-Ray fluorescence spectroscopy (*Fig. 2*) gave a Mg/Al/S ratio of *ca.* 2 : 1 : 0.5. XRD (wet sample): *Fig. 1,b*.

2. *By Precipitation*. A soln. of $MgCl_2 \cdot 6\, H_2O$ (8.06 g, 39.7 mmol) and of $AlCl_3 \cdot 6\, H_2O$ (4.82 g, 20 mmol) in O_2-free H_2O (100 ml) was added dropwise under a constant stream of N_2 to a soln. of Na_2SO_3 (63 g, 500 mmol) in H_2O (250 ml). Simultaneously, an aq. NaOH soln. (1M) was added at a rate to maintain a pH value of 8.5. After complete addition, the flask was sealed, and the resulting colorless suspension was stirred for 16 h under N_2. The suspension was centrifuged and most of the supernatant discarded. The solid along with 80 ml of the mother liquor was annealed in an autoclave at 130° for 3 days. The annealed crystalline solid was washed by centrifugation with O_2-free H_2O until complete absence of sulfite ion in the supernatant was indicated by iodometric titration. The washed solid was stored as a suspension in H_2O. Iodometric titration of two dried samples (0.05 mbar, 100°, 14 h) revealed 2.25 and 2.26 mmol SO_3^{2-}/g mineral, resp. (2.30 mmol/g calculated for $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\, SO_3]$). X-Ray fluorescence spectroscopy gave a Mg/Al/S ratio of *ca.* 1.9 : 1.0 : 0.5. XRD (wet sample): *Fig. 1,a*, and *Fig. 3,a* and *c*. XRD (dry sample): *Fig. 3,b*. IR: 3450v*s* (br.), 1196*m*, 1112*s*, 1023*w*, 956*s*.

Aldehyde-Adduct Formation. Experiment 1 (*Dependance on Concentration*). All experiments were carried out in duplicate, with two different batches of hydrotalcite-sulfite minerals. To solns. of formaldehyde, glycolaldehyde, and glyceraldehyde, respectively (0.25 mmol, $c = 0.02$, 0.05, 0.10, and 0.2M, resp.) in D_2O (containing pentaerythritol as NMR standard), $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\, SO_3]$ (120 mg, 0.25 mmol SO_3^{2-}) was added and the suspension shaken at frequent intervals. After 24 h, an aliquot was removed from each reaction mixture, centrifuged, and the supernatants were analyzed by ^{1}H-NMR spectroscopy. Only the starting aldehydes could be detected. The amount of aldehydes remaining in the supernatant soln. was obtained by comparing the integral ratio of the aldehyde signals to the signals of the standard with the corresponding ratios in the initial preparation. The results are presented in the *Table*. The mineral phases were dissolved by treatment with ion-exchange resin (*IR-120*, H^+ form); after filtration, the solns. were concentrated and the residues analyzed by ^{1}H-NMR spectroscopy. Quant. conversion of the aldehydes to the corresponding sulfite adducts was found. The individual equilibrium constants were determined by fitting the experimental values to the expression $K = c(\text{aldehyde adduct})/[c(\text{mineral}) \cdot c(\text{aldehyde in supernatant})]$, whereby $c(\text{aldehyde adduct}) = c(\text{total aldehyde}) - c(\text{aldehyde in supernatant})$ and $c(\text{mineral}) = c(\text{aldehyde in supernatant})$.

Experiment 2 (*Dependance on Time*). All experiments were carried out in duplicate, employing two different batches of hydrotalcite-sulfite minerals. To solns. of formaldehyde, glycolaldehyde, and glyceraldehyde, resp. (0.25 mmol) in D_2O (2.5 ml, containing pentaerythritol as NMR standard), $[Mg_2Al(OH)_6] \cdot [\frac{1}{2}\, SO_3]$

(120 mg, 0.25 mmol SO_3^{2-}) was added, and the suspensions were shaken at frequent intervals. After 1, 2, 4, 8, and 16 h, aliquots were removed, centrifuged, and the supernatants were analyzed by ^{1}H-NMR spectroscopy. Only starting materials could be detected. The amount of aldehydes remaining in the supernatants was obtained by comparing the integral ratio of aldehyde signals to standard signals with the corresponding ratios in the initial preparation. The results are presented in the *Table.*

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