Properties of synthetic ferrihydrite as an amino acid adsorbent and a promoter of peptide bond formation

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Summary. Ferrihydrite, an iron oxide hydroxide, is found in all kinds of environments, from hydrothermal hot springs to extraterrestrial materials. It has been shown that this material is nanoporous, and because of its high surface area, it has outstanding adsorption properties and in some cases catalysis properties. In this work we studied the adsorption properties of ferrihydrite with respect to amino acids. Samples of pure ferrihydrite were synthesised and exposed to solutions of amino acids including both proteinaceous and non-proteinaceous species. These experiments revealed important characteristics of this mineral as both an adsorbent of amino acids and a promoter of peptide bond formation.

Keywords: Ferrihydrite – Amino acid adsorption – Peptide bond formation

Introduction

Ferrihydrite is a naturally-occurring iron oxide hydroxide of bulk composition $5Fe_2O_3 \cdot 9H_2O$ (Cornell and Schwertmann, 1996). Several formulae have been proposed: $Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$ (Russell, 1979), $Fe_{1.55}O_{1.66}(OH)_{1.33}$ (Stanjek and Weidler, 1992). The composition of synthetic ferrihydrite is believed to be between $Fe_2O_3 \cdot 3H_2O$ and $Fe_2O_3 \cdot 2H_2O$ with $Fe_5O_{12}H_9$ as the most generally accepted ratio (Eggleton and Fitzpatrick, 1988).

Ferrihydrite has a nanoporous texture yielding ultra-high surface areas of $\sim200\,m^2/g$ (Cornell and Schwertmann, 1996). This property classifies ferrihydrite among materials, such as clays and active carbon, that are strong adsorbents of organic or inorganic compounds. In fact, ferrihydrite has been shown to adsorb metal ions (Cornell and Schwertmann, 1996), phosphates (Gruenhagen et al., 1997), sugars (Cornell, 1985), herbicides (Schwandt et al., 1992; Leone et al., 2001), and other organic molecules such as mugineic acid (Inoue et al., 1993). In addition to being a good adsorbent, ferrihydrite is also an efficient catalyst of some reactions, *e.g.* the conversion of cyanamide into urea (Amberger and Vilsmeier, 1978). In the past, three other types of naturally-occurring materials have been shown to present such properties of adsorption and/or catalysis: active carbon (Brownlee et al., 2001), phyllosilicates (Greenland et al., 1965; Paecht-Horowitz et al., 1970; Basiuk et al., 1990–1991; Bujdák et al., 1995; Ferris et al., 1996) and Fe/Ni sulfides (Huber and Wächtershäuser, 1998). Iron oxides such as ferrihydrite should be considered as a fourth type of surface allowing the adsorption and the chemical reactions of organic molecules.

Ferrihydrite is currently found in all kinds of environments, from hydrothermal hot springs to extraterrestrial materials (see Discussion). Therefore, the demonstration of its properties has important implications in environmental sciences as well as in prebiotic chemistry. In this regard, we wanted to evaluate the capabilities of this iron hydroxide to both adsorb and polymerize amino acids. Using a pure variety of synthetic ferrihydrite, we investigated the adsorption of the main proteinaceous amino acids as well as of some amino acids rarely found in natural peptides. We also attempted to promote the polymerisation of amino acids by ferrihydrite avoiding the use of any type of chemical activation that could artificially enhance the yields. These experiments resulted in the adsorption of all the amino acids studied as well as in the formation of peptide bonds.

Materials and methods

Synthesis of ferrihydrite

Ferrihydrite was prepared following the 2-line ferrihydrite synthesis described in Schwertmann and Cornell (2000): 40 g of Fe(NO$_3$)$_3$ were dissolved in 500 ml of distilled water and the solution was neutralised with NaOH. The precipitate was collected by centrifugation, extensively washed with distilled water and lyophilised.

Amino acids

The amino acid standard H (a commercial mixture of 17 proteinaceous amino acids plus ammonia) was purchased from Pierce (Rockford, Illinois). The radioactive amino acids were obtained as follows: [U-^{14}C]Gly (3.9 GBq/mmol) from CEA (Saclay, France), and [1-^{14}C]α-aminoisobutyric acid (Aib; 2.1 GBq/mmol), L-[U-^{14}C]Ala (5.5 GBq/mmol) and L-[U-^{14}C]Glu (9.7 GBq/mmol) from Amersham Pharmacia Biotech Europe (Orsay, France).

Adsorption

Suspensions of ferrihydrite were prepared by mixing the mineral (150 mg) with solutions (1.5 ml) of individual amino acids. The following amino acids were employed at 100 μM: L-alanine, D-alanine, glycine, L-norvaline, L-α-aminobutyric acid, β-alanine and Aib; DL-isovaline was used at 200 μM owing to a poor response factor upon analysis. The Pierce standard mixture (100 μM of each amino acid) was also tested. The experiments were carried out at the pH of the amino acid solutions, *i.e.* between 5 and 6. Blanks without ferrihydrite were performed. The suspensions were turned (35 rpm) in closed vials at room temperature in a test tube rotator. After rotating for 24 h or one week, the suspensions were centrifuged and the supernatants filtered on 0.2-μm filters. Amino acids in the filtrates and in the blanks were analysed with a Biotronik LC2000 analyser using *o*-phthalaldehyde/2-mercaptoethanol as the post-column derivatisation reagent (Roth and Hampaï, 1973; Benson and Hare, 1975). No degradation occurred in the blanks even after a 1-week rotation time.

Binding isotherms

Mixtures containing ferrihydrite (20 mg) and solutions (200 μl) of radiolabelled amino acids (*ca.* 8 kBq) at different concentrations were shaken at room temperature for 24 h. Blanks without ferrihydrite were performed. In order to avoid interferences with added compounds, no titration was done, except for L-Glu (pH 6.2) owing to its very acidic character and to its insufficient solubility. The suspensions were centrifuged and the supernatants were filtered on 0.2-μm filters. Radioactivity in the filtrates and in the blanks was measured by liquid scintillation using the Aqualyte scintillation fluid (J. T. Baker, Deventer, the Netherlands). The data were fit to the Langmuir isotherm equation

$$A = A_{max} K_{ads} C / (1 + K_{ads} C)$$

where A is the ratio of moles of adsorbate/mass of adsorbent, K_{ads} the adsorption constant, A_{max} the maximal adsorption capacity and C the concentration of unadsorbed amino acids (Cornell and Schwertmann, 1996); the MDFitt software developed by M. Desmadril (UMR 8619 CNRS, Orsay, France) was used for this purpose.

Oligopeptide synthesis

We performed two types of experiments referred to as "wet" and "dry". For the wet experiment, we mixed 100 mM glycine or L-alanine (2 ml) with ferrihydrite (200 mg) in a pressure-closed vial. The vial was kept at 95°C for 24 h or one week with constant agitation (35 rpm). For the dry experiment, we used identical amino acid solutions (0.5 ml) and ferrihydrite (50 mg), but the suspension was poured into a Petri dish and dried at room temperature to form a homogeneous layer covering all the mineral surface. Then the Petri dish was heated at 95°C for 24 h or one week. In both cases ferrihydrite was centrifuged (after resuspension in water in the case of the dry experiment) and washed twice with water. The supernatant and washings were filtered on 0.2-μm filters and lyophilised. Finally, the lyophilisates were taken up in 200 μl of water. In each case, a blank without ferrihydrite was performed.

Amino acids and peptides were analysed: i) with the Biotronik LC2000 analyser; ii) by HPLC on a Hyperchrome SC18 column (Bischoff, Leonberg, Germany) with the following mobile phases at 0.5 ml/min: A, 0.1% trifluoroacetic acid; B, 50 mM KH$_2$PO$_4$, 7.2 mM sodium hexanesulphonate, adjusted to pH 2.5 with phosphoric acid; C, 50 mM NaH$_2$PO$_4$, 5 mM sodium dodecyl sulphate, adjusted to pH 2.5 with phosphoric acid; D, eluent C/acetonitrile 9/1 (v/v). Detection was performed at 195 nm. Ten-μl aliquots were injected. Identification and quantitation were carried out with respect to commercial standards. HPLC detection limits were 40 pmol for (Gly)$_2$ and 100 pmol for (Gly)$_3$, (Ala)$_2$ and (Ala)$_3$.

Results

Characterisation of the synthetic ferrihydrite

We prepared appreciable amounts of synthetic mineral as indicated in Material and methods. It was characterised as a pure material by Mössbauer spectroscopy (performed at room temperature and at 77 K), X-ray diffraction (XRD) and analytical TEM, by comparing the spectra and diffraction lines to the ones already published (Tomeoka and Buseck, 1988; Brearley, 1989; Cornell and Schwertmann, 1996; Schwertmann and Cornell, 2000). The product thus synthesised, defined from its XRD pattern as the 2-line variety (Cornell and Schwertmann, 1996), was then used for adsorption and oligopeptide formation experiments. Further details concerning the characterisation (spectra, diffraction lines, diffraction rings) can be found elsewhere (Matrajt, 2001; Matrajt et al., 2003).

Adsorption

Under our experimental conditions most amino acids, tested either individually or in a mixture (standard from Pierce), were adsorbed by more than 60% after a 24-h incubation (Fig. 1). Expressed as the ratio mass of adsorbate/mass of adsorbent, this roughly corresponds to $\geq$60 ppm. Identical results were observed after one week of incubation (not shown). The acidic amino acids (Glu and Asp) were totally adsorbed, presumably owing to their negative charge, which strongly interacts with the positive charge of the iron ions in the ferrihydrite. No significant adsorption differences were observed between the non-proteinaceous amino acids norvaline, α-aminobutyric acid and β-alanine, on one hand, and the proteinaceous amino acids, on the other hand. The experimental error
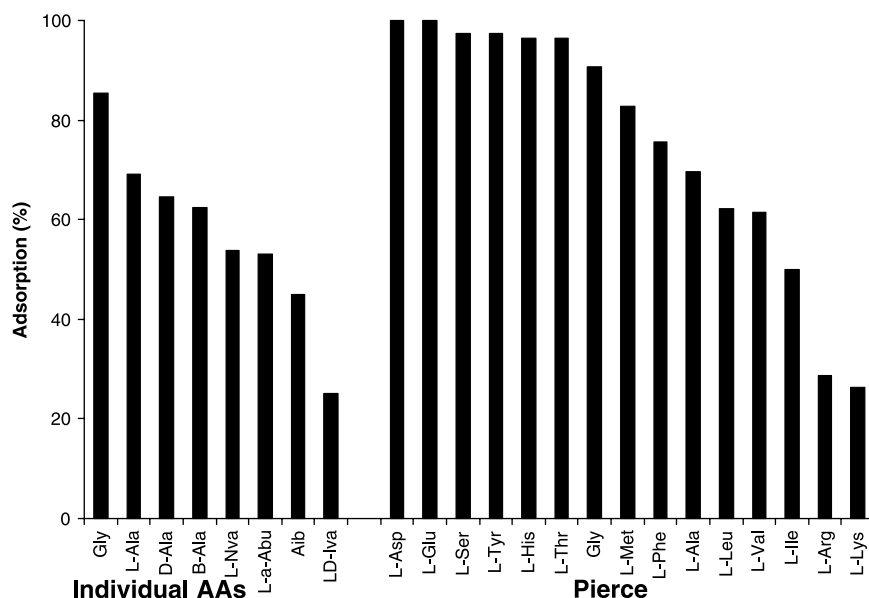
Fig. 1. Adsorption of different amino acids on ferrihydrite after 24 h (identical results were obtained after one week). Amino acids were tested either individually (left) or as part of the Pierce standard mixture (right). The adsorption values represent the mean of at least two experiments; the standard error is $\leq 8\%$, except for Lys (16%), Arg (13%), Aib (11%) and isovaline (17%). Proline and cystine, which are included in the Pierce standard mixture, cannot be detected by the analytical method used. *L-a-Abu*, L-α-aminobutyric acid; *Iva*, isovaline; *L-Nva*, L-norvaline, *B-Ala*, β-alanine

being taken into account, the adsorption values found for both enantiomers of alanine were similar, so there was no enantiomeric selection, at least for this amino acid; experiments with other couples of enantiomers will be necessary to generalize this statement. The least adsorbed amino acids were the basic ones (Lys and Arg) and the α-methyl ones (Aib and isovaline). The latter amino acids, which are non-proteinaceous, are abundantly found in hydrous carbonaceous chondrites such as Murchison (Cronin and Pizarello, 1983) and in peptaibol antiobiotics produced by *Trichoderma* and *Emericellopsis* fungi (Chugh and Wallace, 2001).

The adsorption values found for L-Ala and Gly individually or in the Pierce standard mixture were similar; furthermore, all amino acids in the mixture were adsorbed to a certain extent (total amount adsorbed: ≥ 1300 ppm), suggesting that ferrihydrite possesses a very strong adsorption capacity. In order to verify it, binding isotherms for three amino acids (Gly, L-Ala and Aib) were constructed and the constants determined (Table 1). The low adsorption constants found revealed a weak free energy of binding. Curiously, L-Ala and Gly (two α-H amino acids) had lower adsorption constants than Aib (an α-methyl amino acid). This was compensated by very high maximal adsorption capacity values (22810 and 36260 ppm for L-Ala and Gly, respectively, *vs* 4570 ppm for Aib). The same type of experiment was attempted with

Table 1. Adsorption constants (K_{ads}) and maximal adsorption capacity values (A_{max}) for three amino acids

Amino acid	K_{ads} (M^{-1})	A_{max} (mol/g)
Aib	92.6 ± 2.6	$(4.43 \pm 0.09)10^{-5}$
Gly	34.7 ± 9.0	$(4.83 \pm 0.51)10^{-4}$
L-Ala	43.5 ± 0.8	$(2.56 \pm 0.02)10^{-4}$

L-Glu; however, no isotherm could be constructed since this amino acid was, up to 10 mM, totally and very strongly adsorbed onto the mineral (an adsorption capacity value of 14700 ppm at 10 mM was determined).

Synthesis of peptide bonds

After having demonstrated that ferrihydrite is an adsorbent of amino acids, we tested its ability to promote the synthesis of peptide bonds (Table 2). As described in Material and methods, we performed two types of experiments referred to as "wet" and "dry" in order to simulate a liquid environment (*e.g.*, ocean, lake) or desert conditions, respectively. In both experiments, the formation of dipeptides (Gly)$_2$ and (Ala)$_2$ was observed after 24 h; the amounts produced were significantly higher than those obtained from blanks without ferrihydrite (Table 2A), suggesting that the mineral does behave as

Table 2. Oligopeptide formation in the presence of ferrihydrite at 95°C

Compound	Wet + ferrihydrite	Blank	Dry + ferrihydrite	Blank
A. 24 hours				
Gly	64 ± 4	100 ± 3	33 ± 2	88 ± 6
$(Gly)_2$	0.021 ± 0.009	0.0058 ± 0.0012	0.096 ± 0.017	< 0.0016
$(Gly)_3$	<0.001	<0.001	<0.004	<0.004
Ala	80 ± 1	102 ± 2	46 ± 1	101 ± 1
$(Ala)_2$	0.0044 ± 0.0019	<0.001	0.091 ± 0.013	<0.004
$(Ala)_3$	<0.001	<0.001	<0.004	<0.004
B. One week				
Gly	65 ± 6	87 ± 2	8 ± 1	92 ± 3
$(Gly)_2$	0.035 ± 0.018	0.012 ± 0.003	0.070 ± 0.035	<0.0016
$(Gly)_3$	<0.001	<0.001	<0.004	<0.004
Ala	52 ± 2	78 ± 2	17 ± 2	93 ± 1
$(Ala)_2$	0.0034 ± 0.0017	0.0037 ± 0.0022	0.059 ± 0.018	<0.004
$(Ala)_3$	<0.001	<0.001	<0.004	<0.004

Results are expressed in % relative to the molar amount of amino acid engaged. For Gly and Ala, the values represent the mean ± SD of three analyses with the amino acid analyser. For dipeptides, they represent the mean ± SD of analyses in at least two different chromatographic conditions

a promoter of peptide bond formation. Diketopiperazines cyclo-$(Gly)_2$ and cyclo-$(Ala)_2$ were also detected, but they could not be quantitated owing to their early elution in overcrowded regions of the chromatograms Tripeptides $(Gly)_3$ and $(Ala)_3$ were searched for, but their content, if any, was below their detection limit. Dipeptides and diketopiperazines were identified by their retention times in at least two chromatographic conditions; however, owing to the numerous unknown peaks observed (*vide infra*) and in the absence of another independent analytical method, their identification should be considered as tentative. The dry experiment gave higher dipeptide yields than the wet one; this can be explained thermodynamically, since the reaction involves a loss of water. It is difficult to compare the values obtained ($\leq 0.1\%$) with those reported in the literature with other minerals since in most cases the conditions (temperature, time, concentration, use of chemical activation or of wet/dry cycles, etc.) are different; nevertheless, in two experiments performed under similar conditions, comparable yields (0.01–0.35%) were observed (Bujdák et al., 1994; Basiuk et al., 2000). Curiously, the yields did not increase with a 1-week reaction time (Table 2B). This might be due to the decomposition of the peptides formed. As a matter of fact, numerous unidentified peaks already observed after 24 h and likely corresponding to degradation products of the reactants (see the Gly and Ala yields in the dry experiment), became considerable after one week. Degradation has previously been recognised as an important factor in experiments of oligopeptide formation (Lahav et al., 1978;

Bujdák et al., 1994, 1995; Imai et al., 1999); furthermore, in the particular case of Fe(III)-containing catalysts, redox reactions have been observed (Wang, 1991).

Discussion

Ferrihydrite is a much widespread material. It is an important constituent of clays and soils (Chukhrov et al., 1972); it is part of the soluble fraction of weathered rocks, iron-rich ground waters (Eggleton and Fitzpatrick, 1988) and cold spring waters (Carlson and Schwertmann, 1981). It is considered as the iron oxide with the largest distribution in living organisms, where it is found in the form of ferritin, an iron storage protein (Cornell and Schwertmann, 1996). Moreover, ferrihydrite is present in some microbial communities living in hot springs (Wade et al., 1999; Boomer et al., 2000), where it is produced by bacteria as a result of their metabolism. In addition to its wide occurrence in terrestrial environments, ferrihydrite has been found in several different extraterrestrial materials: in Antarctic micrometeorites (Maurette, 1998; Matrajt, 2001), in interplanetary dust particles (Rietmeijer, 1996; Matrajt et al., 2002), and in several kinds of meteorites (Tomeoka and Buseck, 1988; Brearley, 1989; Keller and Buseck, 1990; Treiman et al., 1993; Lee et al., 1996). The study of its properties of adsorption and catalysis is therefore of great interest for Earth sciences, environmental sciences, astrophysics, life sciences, prebiotic chemistry, as well as health sciences since ferrihydrite has been

proposed as a phosphate binder for patients with chronic renal failure (Gruenhagen et al., 1997).

In the present work, we have examined the characteristics of amino acid binding to synthetic ferrihydrite. We have shown that synthetic ferrihydrite is a strong adsorbent of amino acids and a promoter of peptide bond formation. Other works examining adsorption of amino acids onto different kinds of surfaces were carried out in the past, but most of them dealt with clays rather than iron oxides. Holm et al. (1983) reported the adsorption of amino acids by synthetic akaganéite β-FeOOH $\cdot$ Cl$_n$ and measured adsorption values of 0.10–1.02 mmol/kg at 10 μM amino acid. In the present study, similar values (0.26–1.00 mmol/kg, Fig. 1) were obtained, but the amino acid concentration was 100 μM; however, we have found that ferrihydrite possesses huge maximal adsorption capacity values (44–483 mmol/kg, Table 1). Unfortunately, no binding isotherms were drawn by Holm et al. (1983), so the maximal adsorption capacity values for akaganéite are unknown. Nevertheless, we can conclude that both iron oxides are good adsorbents of amino acids. These results have important implications in the field of prebiotic chemistry where the search for replication matrices is essential. As mentioned earlier, phyllosilicates have often been assigned to this role; however, Holm et al. (1983) suggested that ''iron oxide hydroxide minerals are even more interesting candidates (. . .) since polymer molecules after formation can be released by reductive solution of the host structure''. In this regard, the observation in the present study of the ability of synthetic ferrihydrite to bring about amino acid condensation is important.

The extrapolation of the present results to naturally-occurring ferrihydrite must be envisaged since it has been demonstrated that this mineral adsorbs anions, cations and organic compounds (Cornell and Schwertmann, 1996). Therefore, other adsorbates might out compete amino acids for adsorption sites. However, this adsorption depends on pH, temperature and concentration. Further experiments, including some natural ligands along with some amino acids, should be performed in various conditions to evaluate the properties of ferrihydrite in the natural milieu.

Acknowledgements

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