Kinetics of Decomposition of Thiocyanate in Natural Aquatic Systems

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ABSTRACT: Rates of thiocyanate degradation were measured in waters and sediments of marine and limnic systems under various redox conditions, oxic, anoxic (nonsulfdic, nonferruginous, nonmanganous), ferruginous, sulfidic, and manganous, for up to 200-day period at micromolar concentrations of thiocyanate. The decomposition rates in natural aquatic systems were found to be controlled by microbial processes under both oxic and anoxic conditions. The Michaelis–Menten model was applied for description of the decomposition kinetics. The decomposition rate in the sediments was found to be higher than in the water samples. Under oxic conditions, thiocyanate degradation was faster than under anaerobic conditions. In the presence of hydrogen sulfide, the decomposition rate increased compared to anoxic nonsulfdic conditions, whereas in the presence of iron(II) or manganese(II), the rate decreased. Depending on environmental conditions, half-lives of thiocyanate in sediments and water columns were in the ranges of hours to few dozens of days, and from days to years, respectively. Application of kinetic parameters presented in this research allows estimation of rates of thiocyanate cycling and its concentrations in the Archean ocean.

INTRODUCTION

Thiocyanate (NCS⁻) is formed in various natural and industrial processes. It was found in waste waters from coal and oil processing, steel manufacturing, and the petrochemical industry.125 Thiocyanate concentrations of up to 17 mmol·L⁻¹ were detected in coal plant wastewaters134 and in gold extraction wastewaters.16 In electroplating, dyeing, photo-finishing, thiourea, and pesticide production the concentration of NCS⁻ in wastewater effluents is in the range of 0.09–2 mmol·L⁻¹.19 Thiocyanate is toxic to aquatic species with LC₅₀ values of 0.01 to 0.5 mmol·L⁻¹ reported for Daphnia magna.10

Natural sources of thiocyanate include plants, biological and abiotic decomposition of organic matter, and in vivo detoxification of cyanide.11–14 Several species of bacteria, algae, fungi, plants, and animals are physiologically capable of detoxifying cyanide, and in most cases one of the end products of detoxification is thiocyanate.10,15 Another important mechanism of thiocyanate formation in natural aquatic systems is the reaction between hydrogen cyanide and sulfide oxidation intermediates, which contain sulfur–sulfur bonds, such as colloidal sulfur,16 polysulfides,17 thiosulfate, and tetrahionate.18,19 Reaction with thiosulfate is ~1000 times slower than reaction with polysulfides,17,20,21 and is catalyzed by Cu(II) and sulfur transferases from the rhodanese family.15,25 Concentrations of hydrogen cyanide in polluted aquatic systems may reach levels toxic to aquatic life.15 In nonpolluted aqueous systems, hydrogen cyanide concentrations are usually very low due to fast degradation by plants, fungi and bacteria in aquatic systems, as well as to chemical transformations, volatilization and adsorption.24–26

The presence of thiocyanate was recorded in various natural nonpolluted aquatic systems, for example in stratified lakes Rogoznica in Croatia (up to 288 nmol·L⁻¹) and Green Lake (NY, USA) (up to 274 nmol·L⁻¹).17 In these lakes thiocyanate is produced in the anoxic, sulfide-rich sediments and diffuses to the chemocline, where it is consumed by oxidative processes, which are likely biologically enhanced. In the oxic North Sea water thiocyanate was detected at concentrations up to 13 nmol·L⁻¹.16 In saltmarsh sediment of the Delaware Great Marsh, thiocyanate concentrations are up to 2.28 μmol·L⁻¹ in pore-water and up to 15.6 μmol·kg⁻¹ in wet sediment.26 In these sediments, concentrations of thiocyanate precursors, cyanide-reactive zerovalent sulfur and free hydrogen cyanide are as high as 78 μmol·L⁻¹ and 1.9 μmol·L⁻¹, respectively. Coexistence of hydrogen cyanide, polysulfides and thiocyanate allows attribution of thiocyanate formation to the abiotic reactions between hydrogen cyanide and reduced sulfur species. Thiocyanate was also found in concentrations 23–40 μmol·L⁻¹ in the Red Sea Atlantis II Deep brine.27 Reactions between abiotically formed hydrogen cyanide and reduced sulfur species were proposed as the source of thiocyanate in the brine.
same processes were proposed to result in thiocyanate formation in the hydrothermal springs and pools in the Yellowstone National Park, where it was detected at concentrations 133–791 μmol·L⁻¹.⁴¹,³⁸

Although concentrations of thiocyanate in modern aquatic systems are low,²⁶,¹⁹,²⁰,²⁸ this may not be the case for the iron-rich water column of the Archean ocean. Existence of large atmospheric fluxes of both hydrogen cyanide and zerovalent sulfur to Archean ocean has been suggested.⁵⁰–⁵⁴ These works provide constraints on cyanide and zerovalent sulfur fluxes but lack of data regarding rates of thiocyanate degradation under environmental conditions in the presence of dissolved iron(II) prevents estimation of thiocyanate concentrations and its fate in the Archean ocean.

Multiple investigations focused on the isolation and identification of microorganisms that are responsible for thiocyanate biodegradation under controlled conditions.²⁶–⁵⁵ Thiocyanate-degrading bacteria have been isolated from activated sludge,⁴¹ steel plant wastewater,²⁵ gold mine tailing sites,⁴³,⁵⁰,⁵¹ and extreme alkaline⁵⁰ and hypersaline⁵⁰,⁵⁶ environments. The end products of NCS⁻ degradation are ammonium, carbon dioxide, and sulfate, subsequent to the formation of cyanate⁵⁰–⁶² or carbonyl sulfide⁶³–⁶⁷ as intermediates. A variety of autotrophic bacteria are capable of using NCS⁻ as their sole energy source via sulfur oxidation. Chemolithotrophic bacteria utilize hydrogen sulfide formed on the initial step of NCS⁻ degradation and products of its incomplete oxidation (polysulfide, elemental sulfur, or thiosulfate) as an energy source for growth, oxidizing sulfide to sulfate.⁵¹,⁶³,⁶⁸,⁶⁹ Utilization of nitrogen released from thiocyanate as ammonia has also been reported.⁵⁰ A number of heterotrophic bacteria utilize NCS⁻ as a source of nitrogen and sulfur⁴⁶,⁵⁰,⁵²,⁷⁰,⁷¹ as well as energy source.³⁸,⁴¹ Heterotrophic bacteria were shown to utilize thiocyanate at concentrations as high as 100 mmol·L⁻¹.⁷⁰

In biotechnological systems for thiocyanate removal, which are operating under high concentrations of thiocyanate (up to 120 mmol·L⁻¹ and oxic conditions¹⁰,³⁶,⁴³,⁷²–⁷⁹), rates of thiocyanate decomposition are high. Under oxic conditions the rates may be as high as 83 mmol·L⁻¹·d⁻¹ at 1 mmol·L⁻¹ concentration of thiocyanate (Table 1). Thiobacillus species isolated from steel plant wastewater, are able to degrade 5.2 mmol·L⁻¹ of NCS⁻ over 8 days under anaerobic denitrifying conditions.⁷³ Rates of thiocyanate degradation depend not only on oxygen concentrations,⁴³,⁵³,⁶⁸,⁷⁰ but also on concentrations of nutrients. It was shown that concentrations of NH₄⁺ > 70 μmol·L⁻¹ may inhibit⁷⁶ and phosphate concentrations >500 μmol·L⁻¹ may stimulate thiocyanate biodegradation.⁷⁶

Currently, metabolic pathways for thiocyanate degradation are known and the rates of its degradation in bioreactors are published, but no data on kinetics of decomposition of thiocyanate in natural aquatic systems is available. The main aim of the present research is to fill this gap and to provide constraints on rates of decomposition of thiocyanate in limnic and marine water columns and sediments at various redox conditions, which are relevant for modern and ancient natural aquatic systems. To achieve this goal, we have determined kinetic parameters of thiocyanate degradation in natural aquatic and sedimentary systems at various salinities and concentrations of thiocyanate, oxygen, hydrogen sulfide, and iron(II).

### MATERIALS AND METHODS

**Materials.** Solutions for measurements of the kinetics parameters of thiocyanate degradation were prepared in Milli-Q water, Mediterranean Sea water, Red Sea water, Lake Kinneret (Lake Tiberias) water. slurries were prepared from Red Sea and Lake Kinneret sediments. All reagents were purchased from Sigma-Aldrich and were at least 98% pure. Potassium thiocyanate (KSCN) (99%), sodium sulfide nonahydrate (Na₂S·9H₂O) (98%), and iron(II) sulfate heptahydrate (FeSO₄·7H₂O) (99%) were used without further purification. Nitrogen gas (99.9999%) was purchased from Maxima ltd, Israel. Test tubes, screw caps with hole and septum, and aluminum caps were purchased from Romical, Ltd., Israel, and Labco, Ltd., UK; butyl rubber stoppers were purchased from Geo-Microbial Technologies, Inc., USA.

**Samples Preparation and Treatment.** Water and sediment samples were collected from various locations in

<table>
<thead>
<tr>
<th>Table 1. Rates of Thiocyanate Degradation in Natural and Controlled Systems</th>
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<tbody>
<tr>
<td>system</td>
</tr>
<tr>
<td>Lake Kinneret and Mediterranean Sea water</td>
</tr>
<tr>
<td>Lake Kinneret and Mediterranean Sea water</td>
</tr>
<tr>
<td>Lake Kinneret and Red Sea sediment</td>
</tr>
<tr>
<td>Lake Kinneret and Red Sea sediment</td>
</tr>
<tr>
<td>gold mine tailing storage facility microbial consortium in synthetic medium</td>
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<tr>
<td>wastewater with cultivated microorganisms</td>
</tr>
<tr>
<td>Lake Kinneret and Mediterranean Sea water</td>
</tr>
<tr>
<td>Lake Kinneret and Red Sea sediment</td>
</tr>
<tr>
<td>gold mine tailing storage facility microbial consortium in synthetic medium</td>
</tr>
<tr>
<td>wastewater with cultivated microorganisms</td>
</tr>
<tr>
<td>water enrichment with Klebsiella species</td>
</tr>
<tr>
<td>enrichment cultures from steel plant wastewater</td>
</tr>
<tr>
<td>enrichment cultures from steel plant wastewater</td>
</tr>
<tr>
<td>activated sludge</td>
</tr>
<tr>
<td>enrichment cultures from steel plant wastewater</td>
</tr>
<tr>
<td>activation sludge</td>
</tr>
<tr>
<td>brine liquor with mixed methanogenic cultures</td>
</tr>
<tr>
<td>a simulated wastewater containing phenol, thiocyanate, and ammonia-nitrogen</td>
</tr>
<tr>
<td>• Lake Kinneret and Mediterranean Sea water</td>
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</tbody>
</table>
Israel (Tables 2 and 3). Sediment cores and water samples were collected from the Red Sea (29°30’N, 34°55’E), the Mediterranean Sea (32°49’N, 34°59’E), and Lake Kinneret (32°50’N, 35°35’E) in May 2015–December 2016. Sediment samplings were performed with a multicorer, Lake Kinneret, and Red Sea waters were sampled with Niskin bottles, Mediterranean Sea water was sampled manually near the shore. The water and cores were stored at 25 ± 1 °C in the dark and processed in <1 day after sampling.

The rates of decomposition of thiocyanate in water were measured in the following sets of samples: (1) oxic water sample without pretreatment; (2) anoxic, nonsulfidic water samples, which were stripped of oxygen or hydrogen sulfide by purging for 90 min with nitrogen in a glovebag; (3) ferruginous, prepared by adding of iron sulfate to the target concentration 100 μmol·L−1 of Fe(II); (4) sulfidic, prepared by adding sodium sulfide to the target concentration 10 μmol·L−1 of S(II) and 50 μmol·L−1 H2SO4 for pH adjustment (Table 2). Nonautoclaved water samples were distributed to 12 mL test tubes. The tubes were filled without a headspace and hermetically closed using a screw cap with hole and septum. The rates of decomposition of thiocyanate in the sediments were measured in the samples from the locations presented in Table 3. Both Red Sea (Gulf of Aqaba) water and sediment cores were sampled at 561 m water depth. The cores were sectioned into slices: 1–10 cm (oxic), 12–17 cm (anaerobic zone, [H2S], [Fe2+], [Mn2+] < 1.5 μmol·L−1). Sulfidic Lake Kinneret water and sediment cores were sampled below the chemocline at 37 m depth. The cores were sectioned into slices: 5–10 cm (sulfidic), 12–17 cm (anaerobic zone, [H2S], [Fe2+], [Mn2+] < 2.5 μmol·L−1), and 20–25 cm (ferruginous zone). Additional core was sampled above the chemocline at 32 m water depth for oxic (upper 0–5 mm) sediment layer.

For experiments under anoxic conditions, the cores were cut under a constant flow of nitrogen and immediately transferred to a glovebag with N2 atmosphere. For killed control experiments, marine and limnic waters were sterilized by autoclaving at 120 ± 3 °C for 20 min to prevent the effect of microbial community from the water column on the degradation rate in sediment samples. Sediments were diluted (1:1) with autoclaved bottom water (except for oxic Kinneret sediment, which was diluted with autoclaved oxic water from 1 m depth) and transferred to the 50 mL test tubes, which were hermetically closed using a hand crimper with a rubber stopper and aluminum cap. For experiments under simulated anoxic conditions, autoclaved oxic seawater and sulfidic limnic water were purged with nitrogen under a nitrogen atmosphere in a glovebag. Sulfidic conditions were simulated by addition of the sodium sulfide as described above. After distribution to the test tubes, slurry samples were spiked by KCNS solution to the target concentrations of NCS− in slurry pore-waters: 3, 10, 30, 100, and 1000 μmol·L−1. The rates of NCS− decomposition at concentrations >1 mmol·L−1 were not measured as (1) these concentrations are not relevant for natural aquatic systems and (2) some works36,73 report that at these concentrations the microbial decomposition of thiocyanate is substrate-inhibited; although there is also evidence for high thiocyanate decomposition rates at higher concentrations.

For each water and sediment sample, an identical sample autoclaved at 120 ± 3 °C for 20 min was prepared in order to provide a sterilized control. All types of autoclaved samples were prepared in 35 mL (water samples) and in 50 mL (sediment samples) tubes and were hermetically closed with a rubber stopper and aluminum cap.

All sterilized and nonsterilized samples were prepared and analyzed in triplicates. Hermetically closed samples were incubated at 25 ± 1 °C. Subsamples were taken from the samples by syringes immediately prior to analysis. Subsampling of anoxic samples was carried out in the glovebag (typically <0.2% O2 v/v) to maintain anoxic conditions in the sample. The rate of thiocyanate decomposition was studied by measurement of thiocyanate concentrations in multiple subsamples during 35–200 day period.

Analytical Methods. Thiocyanate was quantified by an Agilent Technologies 1200 HPLC system with multiple wavelength UV–visible detector operated at 220 nm. A Nomura Chemical, Japan, Develosil RPAPQUEOUS C30 reverse phase column (150 mm × 4.6 mm × 5 mm) was used for HPLC separation of thiocyanate. The column was modified according to Rong et al.32 by pumping 5% aqueous solution of PEG-20 000 at 0.3 mL·min−1 rate for at least 3 h. Hydrogen sulfide was measured spectrophotometrically by the methylene blue method according to Cline83 by LaMotte SMART Spectro spectrophotometer. Fe2+ was quantified spectrophotometrically by ferrozine method according to Stookey.84 Manganese was analyzed spectrophotometrically using the 1-(2-Pyridylazo)-2-naphthol (PAN) method.85 Oxygen level was monitored using an optical oxygen meter with a Retractable Needle-Type Oxygen microsensor (tip diameter ~50 μm, MDL of 0.625 μmol·L−1, Firestone-Pyrosence) placed on a micromanipulator.60 Data was collected via microprofiling software (Profix) with 2-point calibration. The optode needle was inserted into the sample through the septum of the HPLC-vial which was filled and closed in the glovebag.

Approach for Estimation of NCS− Degradation Rate. Quantitative interpretation of biodegradation kinetics is based

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Table 2. Sampling and Processing Protocols for Preparation of Water Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>System</th>
<th>Depth (m)</th>
<th>Sampling Date</th>
<th>Initial Conditions</th>
<th>Treatment</th>
<th>Final Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-1</td>
<td>Lake Kinneret</td>
<td>1</td>
<td>17 Jun, 2015</td>
<td>Oxic</td>
<td>No</td>
<td>Oxic, pH 8.1</td>
</tr>
<tr>
<td>WC-2</td>
<td>Lake Kinneret</td>
<td>37</td>
<td>17 Jun, 2015</td>
<td>Sulfidic</td>
<td>N2 purge</td>
<td>[O2] &lt; 1 μmol·L−1, [H2S] &lt; 1 μmol·L−1, pH 7.8</td>
</tr>
<tr>
<td>WC-4</td>
<td>Lake Kinneret</td>
<td>37</td>
<td>17 Jun, 2015</td>
<td>Sulfidic</td>
<td>N2 purge, FeSO4 spiking</td>
<td>Ferruginous ([Fe(II)] = 81 μmol·L−1), pH 7.9</td>
</tr>
<tr>
<td>WC-5</td>
<td>Mediterranean Sea</td>
<td>1</td>
<td>1 May, 2015</td>
<td>Oxic</td>
<td>No</td>
<td>Oxic, pH 8.4</td>
</tr>
<tr>
<td>WC-6</td>
<td>Mediterranean Sea</td>
<td>1</td>
<td>1 May, 2015</td>
<td>Oxic</td>
<td>N2 purge</td>
<td>[O2] &lt; 1 μmol·L−1, pH 8.4</td>
</tr>
<tr>
<td>WC-7</td>
<td>Mediterranean Sea</td>
<td>1</td>
<td>1 May, 2015</td>
<td>Oxic</td>
<td>N2 purge, Na2S spiking</td>
<td>Sulfidic ([H2S] = 118 μmol·L−1), pH 8.3</td>
</tr>
<tr>
<td>WC-8</td>
<td>Mediterranean Sea</td>
<td>1</td>
<td>1 May, 2015</td>
<td>Oxic</td>
<td>N2 purge, FeSO4 spiking</td>
<td>Ferruginous ([Fe(II)] = 95 μmol·L−1), pH 8.7</td>
</tr>
</tbody>
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RESULTS AND DISCUSSION

In all sterilized samples (water and sediments), the variation of thiocyanate concentrations was <3% of initial concentration during the whole incubation period (data not shown). This indicates chemical stability of thiocyanate in aquatic systems in a wide range of environmentally relevant conditions, for example, in the presence as well as in the absence of sediments, oxygen, hydrogen sulfide, and dissolved iron in marine, as well as in limnic waters.

In all nonautoclaved samples with initial thiocyanate concentrations of 3 μmol-L⁻¹, decomposition was not observed during the first 26–100 days of incubation, except for oxic sediments and some oxic Mediterranean seawater samples in which the lag periods were <12 h and <12 days, respectively (Table 4). With an increase of NCS⁻ concentrations, the lag period increased by 25–63%. After the lag period, the thiocyanate concentrations decreased in all nonsterilized samples. The lag period likely reflects the time which is required for adaptation to a new substrate and an increase in substrates degradation via catalyzed reactions, which are carried out by the organisms bearing the specific enzymes. Therefore, rates of substrate degradation are generally dependent on the enzyme and substrate concentrations (e.g., Michaelis–Menten kinetics model).

In natural aquatic systems degradation of thiocyanate may be performed by a single organism, as well as by microbial consortium. It has been shown that the Michaelis–Menten model 87 (eq 1) can be applied for description of microbial utilization of cyanide and thiocyanate in activated sludge reactors, as well as for determination of the effect of concentration of organic pollutants on their biodegradation rate by natural microbial communities. 88 Thus, in this study we will define “apparent” parameters of Michaelis–Menten model, which correspond to degradation of thiocyanate by nondefined microbial community. Katayama et al. 63 showed that thiocyanate-degradation catalyzed by enzyme isolated from Thiothrix thioparus cells, followed Michaelis–Menten-type kinetics. In this work, the Michaelis–Menten model was applied to nonautoclaved samples.

\[
V = \frac{[S]V_{\text{max}}}{[S] + K}
\]  

(1)

where \( V \) is the rate of thiocyanate decomposition at the given concentration (μmol·L⁻¹·day⁻¹), \( V_{\text{max}} \) is the apparent maximum rate of thiocyanate decomposition (μmol·L⁻¹·day⁻¹), \( K \) is the apparent half-saturation constant (corresponding to the substrate concentration at which the reaction rate is 50% of the \( V_{\text{max}} \) (μmol·L⁻¹)), and \( [S] \) is the concentration of substrate (μmol·L⁻¹).

Specific degradation rate at each initial substrate concentration was analytically estimated by fitting the data for decrease of concentration versus time. An overall dependence was established by plotting the calculated thiocyanate degradation rates versus initial thiocyanate concentrations. For estimation of the specific degradation rate, reaction rate was measured only on the initial stage of thiocyanate degradation, where thiocyanate degradation rate had linear dependence on time. Apparent \( V_{\text{max}} \) and \( K \) values were calculated by fitting curves to data using nonlinear regression and performing a nonlinear fit analysis in MATLAB.
cell concentrations as a response to thiocyanate amend-
ment.43,51

On the basis of the specific degradation rate at each initial
substrate concentration, the apparent kinetic parameters of the
Michaelis–Menten model for each analyzed system were
determined (Table 5). Experimental rates and the model data
versus initial NCS − concentration were plotted; the thiocyanate
decomposition rates and their Michaelis–Menten model fits are
presented in Figure 1. Apparent parameters of the Michaelis–
Menten model were used to calculate thiocyanate half-lives at
different concentrations (Figure 2). The lag time was not
included in determination of the half-life time.

**Degradation of NCS − in Water Columns. Influence of**
**redox conditions.** The thiocyanate degradation rates in Lake
Kinneret waters decreased in the following order: oxic > sul
dic > anoxic > ferruginous (Figures 1a and 2a). In seawater
samples, the trend was similar: oxic > sulfidic ≈ anoxic > ferruginous (Figures 1b and 2a). Relatively low rate of thiocyanate
degradation under anaerobic conditions is characteristic for thiocyanate-decomposing bacteria and may be
explained by lower yield of metabolic energy associated with
utilization of electron acceptors, which are weaker than oxygen.33,59,80 Since the only electron acceptor proven to
support thiocyanate oxidation by bacteria in the absence of oxygen is nitrate, degradation of thiocyanate in these systems is
likely to be nitrate-limited. In the anoxic waters of Lake
Kinneret, nitrate concentrations are <37 μmol·L −1, but can be
as well <4 μmol·L −1 in the benthic boundary layer.50 The
difference in thiocyanate decomposition rates in the absence
and in the presence of dissolved iron and hydrogen sulﬁde may be
attributed to differences in microbial community structure in the
presence of different electron donors. Calculated concentrations of thiocyanate-iron complex, Fe(SCN) +, are
<0.08 μmol·L −1. This concentration corresponds to the sample
with the highest concentrations of Fe +3 (95 μmol·L −1) and
thiocyanate (1 mmol·L −1) and the stability constant of 0.84
mol ·L −1·L for Fe(SCN) + complex.91 Therefore, iron complex-
ation should not signiﬁcantly affect the observed decrease of
iron or thiocyanate concentrations.

**Comparison between Marine and Limnic Systems.** In oxic
Mediterranean Sea water, the thiocyanate half-life was shorter
than in oxic Lake Kinneret water. We attribute this difference to
faster adaptation of local microbial communities in seawater to
the observed decrease of oxygen.

| Table 4. Lag Times for Thiocyanate Decomposition at 3 μmol·L −1 Concentration |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| system                        | time            | final conditions | oxic            | anoxic          | sulfidic        | ferruginous      | manganous       |
| Lake Kinneret water           | incubation period (d) | 156             | 164             | 112             | 142             |
|                               | lag time (d)    | 37              | 74              | 58              | 72              |
| Mediterranean Sea water       | incubation period (d) | 164             | 164             | 130             | 141             |
|                               | lag time (d)    | <12             | 79              | 71              | 75              |
| Lake Kinneret sediment        | incubation period (d) | 35              | 150             | 150             | 150             |
|                               | lag time (d)    | <1              | 46              | 35              | 45              |
| Red Sea sediment              | incubation period (d) | 35              | 157             | 157             | 157             |
|                               | lag time (d)    | <1              | 35              | 26              | 45              | 45              |

| Table 5. Coefﬁcients of the Michaelis–Menten Equation a |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| sample no.                         | system          | initial conditions | final conditions | K (μmol·L −1) | V max (μmol·L −1·day −1) |
| WC-1                               | LK              | oxic            | oxic            | 48 ± 11        | 0.450 ± 0.032   |
| WC-2                               | LK              | anoxic          | anoxic          | 59 ± 17        | 0.145 ± 0.014   |
| WC-3                               | LK              | sulfidic        | sulfidic        | 48 ± 13        | 0.355 ± 0.030   |
| WC-4                               | LK              | sulfidic        | ferruginous      | 29 ± 10        | 0.052 ± 0.006   |
| WC-5                               | MS              | oxic            | oxic            | 9 ± 3          | 0.905 ± 0.07    |
| WC-6                               | MS              | anoxic          | anoxic          | 31 ± 8         | 0.167 ± 0.010   |
| WC-7                               | MS              | sulfidic        | sulfidic        | 75 ± 20        | 0.251 ± 0.023   |
| WC-8                               | MS              | ferruginous      | ferruginous      | 18 ± 3         | 0.035 ± 0.006   |
| S-1                                | LK              | oxic            | oxic            | 61 ± 10        | 52 ± 3          |
| S-2                                | LK              | anoxic          | anoxic          | 57 ± 20        | 0.351 ± 0.029   |
| S-3                                | LK              | sulfidic        | sulfidic        | 89 ± 29        | 0.663 ± 0.039   |
| S-4                                | LK              | ferruginous      | ferruginous      | 28 ± 8         | 0.081 ± 0.006   |
| S-5                                | RS              | oxic            | oxic            | 65 ± 24        | 48 ± 2          |
| S-6                                | RS              | anoxic          | anoxic          | 58 ± 12        | 0.356 ± 0.019   |
| S-7                                | RS              | sulfidic        | sulfidic        | 69 ± 21        | 0.575 ± 0.044   |
| S-8                                | RS              | ferruginous      | ferruginous      | 55 ± 18        | 0.155 ± 0.014   |
| S-9                                | RS              | manganous       | manganous       | 51 ± 14        | 0.166 ± 0.021   |

WC, water column; S, sediment; LK, Lake Kinneret; MS, Mediterranean Sea; RS, Red Sea.

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Figure 1. Thiocyanate degradation rates as a function of the initial thiocyanate concentration in Lake Kinneret water (a) and Mediterranean Sea water (b), in oxic Lake Kinneret and Red Sea sediments (c), anoxic Lake Kinneret sediment (d), and anoxic Red Sea sediment (e). Open symbols represent experiment data; solid symbols represent apparent K of the Michaelis–Menten equation; broken lines represent the model based on the apparent Michaelis–Menten kinetic parameters. Black color represents samples under oxic conditions, red color represents samples under anoxic conditions, green color represents samples under sulfidic condition, blue color represents samples under ferruginous conditions, and purple color represents samples under manganous conditions.
Degradation of NCS⁻ in Sediments. Influence of Redox Conditions. In both marine (Red Sea) and limnic (Lake Kinneret) sediments, NCS⁻ degradation was found to be faster than in aquatic samples, especially under aerobic conditions, due to the higher density of microbial biomass compared to water.⁹²,⁹³ Inoxic sediment samples a decrease of NCS⁻ concentration was observed already in <12 h. In the samples with an initial NCS⁻ concentration ≤300 μmol·L⁻¹, it was completely degraded in 14 days. The rates of NCS⁻ decomposition under various redox conditions change in the same order as in water samples: oxic > sulfidic > anoxic > ferruginous ≈ manganous (Figure 1c–e). Concentrations of nitrate in the anoxic Red Sea sediments are ≤6.5 μmol·L⁻¹ in the upper 5 cm and <1 μmol·L⁻¹ in the deeper sediments.⁹⁴,⁹⁵ In the anoxic sediments of Lake Kinneret concentrations of nitrate are ≤0.01 μmol·L⁻¹.⁹⁶

Comparison between Marine and Limnic Systems. In contrast to water column, the differences in thiocyanate decomposition rates between limnic and marine sediments were minor (Figure 2b). The Lake Kinneret sediments are characterized by high concentration of methane (up to 3 mmol·L⁻¹).⁹⁶,⁹⁷ Our results did not demonstrate any effect of the presence of methanogenic microorganisms on the rates of thiocyanate degradation. This observation agrees well with the results reported by Hung and Pavlostathe⁶⁶ and Sahariah and Chakraborty,⁸¹ who found that thiocyanate is stable under the methanogenic conditions.

Comparison of Thiocyanate Degradation Rates in Natural Systems and under Controlled Conditions. Comparison of thiocyanate decomposition rates reported in present work and those calculated for the same range of thiocyanate concentrations from kinetic parameters measured under controlled conditions are presented in Table 1. The rates of decomposition in nonpolluted natural aquatic systems are expected to be much lower than in the industrial systems due to (1) much lower microbial density and (2) lower concentrations of nutrients. Indeed, rates of thiocyanate decomposition in oxic sediments were found to be lower by 2–4.5 orders of magnitude as compared to activated sludge and wastewater microbial cultures.⁶⁶,⁶⁹,⁷² Under anoxic conditions, NCS⁻ decomposition generally was not detected in industrial systems,⁶⁸,⁶⁹,⁸¹ except for steel plant wastewater with high concentrations of NCS⁻ (4.7–5.6 mmol·L⁻¹).⁵³ Rates of thiocyanate decomposition calculated from the data presented by Grigor’eva et al.⁵³ are only slightly higher than those detected in the anoxic sediments in this work at 1 mmol·L⁻¹ concentration (Table 1).

Although mechanisms and pathways of thiocyanate degradation under controlled conditions are well studied, detailed understanding of processes controlling stability of thiocyanate in natural aquatic systems is lacking. Future work should include detection of microbial species responsible for thiocyanate degradation in natural aquatic systems, evaluation of microbial community shifts as a response to thiocyanate pollution and identification of specific metabolic pathways of thiocyanate degradation under various environmental conditions.

Implications for the Archean Oceans. The Michaelis–Menten model for the ferruginous Mediterranean seawater was applied to estimate the steady-state concentration of thiocyanate in the Archean Ocean. Ferruginous conditions may have been a dominant characteristic of the anoxic oceanic water column throughout much of Earth’s history.⁹⁸ Based on estimated concentration of iron in the deep Archean ocean,⁹⁹–¹⁰¹ the flux of elemental sulfur produced by photolysis of SO₂,³²,³⁴ and sulfate concentrations in the Archean seawater,¹⁰⁵–¹⁰⁷ we have estimated concentration of polysulfides,¹⁰⁸ the most reactive zerovalent sulfur species in the Archean ocean to be in the 4–40 nmol·L⁻¹ range. Atmospheric reactions between methane and nitrogen compounds are thought to have led to the formation of free hydrogen cyanide,²⁹,³³ which is a precursor for the formation of thiocyanate. Calculated thiocyanate concentration in the Archean ocean based on rates of formation of thiocyanate from polysulfide and hydrogen cyanide¹⁰⁷ and on rates of its decomposition from this work is ~6.5 nmol·L⁻¹. An important point to note is that despite the very low concentration of NCS⁻, the entire deposition flux of HCN, which was suggested to be an important precursor of RNA, proteins, and lipids,¹⁰⁹ is lost via this pathway, with likely implications for estimates of cyanide concentrations.¹¹⁰ Work on a comprehensive model of the coupled sulfur and cyanide cycles is ongoing, and will be the topic of a future publication.
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