Journal of Hazardous Materials 178 (2010) 450–454

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Arsenic(III) methylation in betaine–nontronite clay–water suspensions under environmental conditions

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ARTICLE INFO

Article history:
Received 5 November 2009
Received in revised form 4 January 2010
Accepted 20 January 2010
Available online 28 January 2010

Keywords:
Methyl transfer
Abiotic
Remediation
Toxicity
Soils
Sediments

ABSTRACT

This paper reports arsenic methylation in betaine–nontronite clay–water suspensions under environmental conditions. Two nontronites (<0.05 mm), NAu-1 (green color, Al-enriched) and NAu-2 (brown color, Al-poor, contains tetrahedral Fe) from Uley Mine - South Australia were selected for this study. Betaine ($pK_a = 1.83$) was selected as methyl donor. The reaction between $5\,g\,L^{-1}$ clay, 20 ppm As(III), and 0.4 M betaine at $7 \leq pH_0 \leq 9$ under anoxic conditions was studied. The presence of nontronite clays were found to favor As(III) conversion to monomethylarsenic (MMA). Arsenic conversion was found to be as high as 50.2 ng MMA/ng $As(III)_0$. Conversion of As was found to be more quantitative in the presence of NAu-2 ($(Na_{0.72})\,[Si_{7.55}\,Al_{0.16}Fe_{0.29}][Al_{0.34}\,Fe_{3.54}\,Mg_{0.05}]\,O_{20}(OH)_4$) than NAu-1 ($(Na_{1.05})\,[Si_{6.98}\,Al_{0.95}Fe_{0.07}][Al_{0.36}\,Fe_{3.61}\,Mg_{0.04}]\,O_{20}(OH)_4$). The inherent negative charge at the nontronite tetrahedral layer stabilizes positively charged organic intermediate-reaction species, thereby leading to decreases in the overall methylation activation energy. The outcome of this work shows that nontronite clays catalyze As methylation to MMA *via* non-enzymatic pathway(s) under environmental conditions.

1. Introduction

The environmental toxicity of arsenic depends heavily on speciation. As(III)-bearing compounds are two to three times more toxic than As(V)-bearing compounds [1–3], while reduced, inorganic arsenic found in sulfide minerals is relatively low in toxicity. Inorganic forms of arsenic, either As(III) or As(V) compounds, are significantly more toxic than many As-organic complexes. For instance, arsenobetaine ($Me_3As^+CH_2CO_2$; (trimethylarsonio)acetate; $LD_{50} = 10\,g\,kg^{-1}$, mouse, oral; [4]), which has been found in high levels in fishery products, presents an acute toxicity approximately one three-hundredth that of arsenic trioxide [arsenite; As_2O_3: $LD_{50} = 0.03\,g\,kg^{-1}$, mouse, oral]. Arsenobetaine is chemically stable, has a low affinity for animal and human tissues, and is rapidly excreted from the human body [5–7]. On the other hand, other arsenochemicals such as As(III)-methyl species [e.g., methylarsenoic acid ($MMAs = H_2AsO_2CH_3$) or dimethylarsinous acid [$DMAs = HAsO_2(CH_3)_2$] present comparable toxicity or higher than inorganic species, iAs(III) or iAs(V) [8–13].

In nature, the methylation of arsenic has been attributed to the metabolic activity of fungi, bacteria, molds, mammals, or aquatic organisms [14–16]. The biological methylation of arsenic has been proposed to occur by alternating reduction of As(V) to As(III), and oxidative methylation [16–18], where methyltransferase and reductase act as electron-transfer mediators [19]. To the authors' knowledge, little work has been conducted to elucidate arsenic methylation pathway(s) at the pore water interface under abiotic environmental conditions. The affinity of soluble inorganic arsenic for environmental iron minerals [20,21], and humic acids or low-molecular weight organic matter [16,22] is well known. A recent report compares the adsorption behavior of inorganic

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doi:10.1016/j.jhazmat.2010.01.102

Table 1
Chemical composition, structural formulae, and particle-size distribution of NAu-1 and NAu-2.

	Structural formulae[a]
NAu-1	$(Na_{1.05})\,[Si_{6.98}Al_{0.95}Fe_{0.07}][Al_{0.36}Fe_{3.61}Mg_{0.04}]O_{20}(OH)_4$
NAu-2	$(Na_{0.72})\,[Si_{7.55}Al_{0.16}Fe_{0.29}][Al_{0.34}Fe_{3.54}Mg_{0.05}]O_{20}(OH)_4$

	Chemical composition (%)[a,b]						
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	Na_2O
NAu-1	51.4	35.9	8.1	3.6	0.2	0.2	0.03
NAu-2	56.2	37.8	3.1	2.3	0.25	0.02	0.14

	Particle-size distribution[c]			
	>2 μm	0.5–2 μm	0.2–0.5 μm	<0.2 μm
NAu-1	8	4	6	82
NAu-2	5	5	9	82

	Mineralogical composition[d]									
	NAu-1						NAu-2[e]			
	A	B	C	D	E		A	B	C	D	E
Nontronite	90	49	86	93	>99	Nontronite	95	10	83	99	>99
Kaolin	4	4	7	4	(···)[f]	Plagioclase	5	68	10	(···)	(···)
Quartz	2	13	1	<1	(···)	Quartz	<1	10	2	<1	(···)
Biotite	<1	2	1	(···)	(···)	Biotite	(···)	4	(···)	(···)	(···)
Goethite	3	31	5	3	(···)	Talc	(···)	3	5	(···)	(···)

[a] Keeling et al. [26].
[b] MnO (%) ≤ 0.02, K_2O (%) ≤ 0.01, P_2O_5 (%) ≤ 0.01, SO_3 (%) ≤ 0.004, ZrO_2 (%) ≤ 0.01, Sr (%) ≤ 0.003.
[c] $n = 6$, C.V. = 3%.
[d] Columns A, B, C, D, and E refer to size fractions bulk, 2 μm, 0.5–2 μm, 0.2–0.5 μm, <0.2 μm, respectively.
[e] Ilmenite (5%) was found to be present in fraction B only.
[f] (···) = below detection limits.

[iAs, i.e., As (III) or As(V)], monomethyl [MMAs], and [DMAs] on goethite and 2-line ferrihydrite surfaces at $3 \leq pH \leq 11$ [23]. Unlike for the case of inorganic or organic As(V) species, MMAs(III) and DMAs(III) showed negligible adsorption on goethite or ferrihydrite at $4 \leq pH \leq 7$ (0.44 g Fe L^{-1}, 13.3 mmol $As(III)_0$ L^{-1}). By contrast, the adsorption behavior of As approached quantitative adsorption across at $3.5 \leq pH \leq 11$, and surface excess values (n) at pH = 4 and 7 corresponded to 0.14 and 0.2 mol As mol Fe^{-1}, respectively (0.2 mol L^{-1} $[As]_{eq}$). Arguably, methylation conveys alterations on As(III) binding mechanism(s). The poor adsorption of As(III) organic species by either mineral surface was postulated as evidence for non-specific adsorption.

Clays ($d < 2$ μm) are ubiquitous naturally occurring small-sized particles and are commonly found in wide range of environmental compartments, from sediments in the bottom of the ocean to atmospheric aerosols in the upper stratosphere. Clays constitute the most important earth's reservoir of iron, a key element for triggering fundamental metabolic pathways to sustain life. Little quantitative information exists, however, on whether iron-rich smectite clay minerals can induce arsenic methylation. Early work has reported that organic arsenicals such as arsanilic acid (*p*-aminophenylarsenic acid) can be retained in up to 80% in the soil fraction by 1:1 or 2:1 phyllosilicates, kaolinite, montmorillonite or vermicullite [14,24]. The extent of adsorption of disodium methanearsonate has been found to correlate with the soil clay content (kaolinite > vermiculite > montmorillonite; [25]). Reportedly, shales and clays can accumulate up to 500 ppm arsenic [24]. Phyllosilicates have been shown to enhance arsenite oxidation to arsenate [20]. Thus, studying the biogeochemistry and environmental fate of arsenic and, in particular, its speciation and transformation pathways at the clay–water interface deserve further scrutiny.

We selected two iron-rich nontronite clays to study the plausible methylation of inorganic arsenic in aqueous solution at ambient temperature. The chemical composition of these clays differs primarily because the total aluminum and tetrahedral Fe content. As evidenced by infrared spectroscopy, NAu-2 contains significant quantities of tetrahedral Fe [26]. Betaine (*N,N,N*-trimethylglycine; $pK_a = 1.83$) was selected as a methyl donor.

2. Materials and methods

2.1. Source of clays

Nontronites (NAu-1, green color, Al-enriched and NAu-2, brown color, Al-poor, contains tetrahedral Fe) from Uley Mine - South Australia were purchased from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, Indiana). NAu-1 contains minor kaolin and quartz. NAu-2 contains fewer total impurities in the form of carbonate and iron oxyhydroxides ([26], Table 1). The clays were used as received.

2.2. Reaction of inorganic arsenic, nontronite clay, and methyl donors

Suspensions containing 20 ppm As(III) ($AsNaO_2$, Fluka Chemika, Switzerland), 5 g L^{-1} nontronite (NAu-1 or NAu-2), and 20 ppm betaine (Sigma–Aldrich, Milwaukee, WI) were prepared. Suspensions were placed in 50-mL Nalgene bottles and stirred at 150 rpm for 48 h, then centrifuged at 4000 rpm for 50 min or until separation of the clay fraction was achieved. The supernatant solution was decanted, filtered using 0.022 μm-Millipore syringe filters, and analyzed for arsenic speciation (below).

All solutions and suspensions were prepared using N_2-purged nanopure water. Adjustments of pH values were achieved by adding aliquots of 0.01 M HCl or NaOH standard solutions. Experiments were conducted by duplicates and samples were discarded after sacrificed.

Table 2
Nomenclature of arsenic species determined in As suspensions using HG-CT-AAS: inorganic arsenic, iAs ($iAs^{III} + iAs^{V}$); monomethyl arsenic, MMAs ($MAs^{III} + MAs^{V}$); and dimethyl arsenic, DMAs ($DMAs^{III} + DMAs^{V}$).

Name	Abbreviation	Chemical formulae
Arsenite, arsenious acid	iAs^{III}	$As(OH)_3$
Arsenate, arsenic acid	iAs^{V}	$AsO(OH)_3$
Monomethylarsonic acid	$MMAs^{V}$	$CH_3AsO(OH)_2$
Monomethylarsonous acid	$MMAs^{III}$	$CH_3As(OH)_2$
Dimethylarsinic acid	$DMAs^{V}$	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	$DMAs^{III}$	$(CH_3)_2AsOH$

2.3. *Arsenic speciation*

Arsenic species in supernatant solutions were analyzed by HG-CT-AAS using a PerkinElmer Model 3100 AA spectrometer (PerkinElmer, Norwalk, CT, USA) equipped with a conventional quartz tube atomizer as described elsewhere [27]. Briefly, hydrides (i.e., arsine and the methyl-substituted arsines) were generated in a reaction with sodium borohydride ($NaBH_4$; EM Science, Gibbstown, NJ, USA) in the presence of concentrated HCl (Sigma–Aldrich, St. Louis, MO, USA). Under these conditions, hydrides are generated from both trivalent and pentavalent arsenic species [27,28]. Arsenic species were analyzed by a recently developed automated HG-CT-AAS technique using a PerkinElmer Model 5100 PC AA spectrometer equipped with the multiatomizer and a FIAS200 flow injection accessory [29,30]. Unlike the conventional HG-AAS, the new method provides low detection limits (DLs) needed for analysis of arsenic species in small samples. Before analysis, each supernatant solution was treated with 2% L-cysteine hydrochloride (EMD Chemicals Inc., Darmstadt, Germany) for 70 min at room temperature. Treatment with cysteine reduces all pentavalent arsenic species to trivalency. Hydrides were generated from 0.5-mL aliquots of cysteine-treated samples by reaction with $NaBH_4$ in a Tris–HCl (Sigma–Aldrich) buffer (pH 6) as previously described [29,30]. HG-CT-AAS was developed for the oxidation-state-specific speciation analysis of arsenic, but under current operating conditions both procedures described above determined total iAs [$\sum_{iAs} = iAs(III) + iAs(V)$], MMA [$\sum_{MMA} = MMA(III) + MMA(V)$], and DMA [$\sum_{DMA} = DMA(III) + DMA(V)$] (Table 2). Details on the calibration and method validation are reported elsewhere [29]. Concentrations of iAs, MMA, and DMA were expressed as nanograms of arsenic per millilitre of supernatant solution.

Stata 8.0 (Stata Corp., College Station, TX, USA) and Instat (GraphPad Software Inc., San Diego, CA, USA) statistical software packages were used for data analyses. Differences in the percentages of arsenic species and the species ratios were evaluated by unpaired *t*-test. The nonparametric Spearman correlation was used to analyze associations between the concentrations of arsenic species, the percentage of arsenic species, or ratios of arsenic species in supernatant solutions. Differences or correlation with $p < 0.05$ were considered to be statistically significant.

2.4. *Total soluble Fe analysis*

Determinations of total soluble Fe that were conducted by atomic absorption spectrometry using a Varian, SpectrAA 110 equipped with an acetylene-air oxidant flame (AAS-F) at 248.3 nm.

2.5. *Surface analyses*

Surface and chemical analyses of clay samples were conducted by energy dispersive spectroscopy (EDS). A Cambridge-Leica Stereoscan 440 Scanning Electron Microscope equipped with an Oxford, model Pentafet was used. Backscattering-electron micrographs were obtained for all samples.

3. Results and discussion

3.1. *Arsenic methylation in nontronite suspensions*

Nontronite samples were reacted with As(III) and betaine at pH 7 or 9 and extracted for analyses. As evidenced by HG-CT-AAS results (Table 3 top, 5th and 6th columns), nontronites facilitated transformation of As(III) to MMA. The formation of MMA in clay-free experiments was found below detection limits. Recoveries of total As [inorganic (iAs) + organic] varied from 5.05 to 55.1%. The extent of As methylation ranged from 4.7 to 50.2 ng MMA per ng $As(III)_0$. The conversion of As to MMA was found to be more quantitative in the presence of NAu-2 over NAu-1.

The effect of the extent of clay dissolution on As speciation was evaluated. Elemental analysis of NAu-1 and NAu-2 supernatant solutions adjusted at $pH_0 = 7$ showed the accumulation of Fe after 24 h to approximate 2 and 12 ppm, respectively. The present results are in agreement with the idea that the dissolution of NAu-2 conveys a faster depletion rate of the total surface sites. At the same time, data showing a higher extent of As conversion in NAu-2 suspensions (Table 3 top, 5th and 6th columns) can be attributed to a higher number of adsorption active sites available for organic arsenic, and that the formation of MMA is surface-controlled. A similar scenario is proposed to explain the relative recovery of total arsenic over $As(III)_0$. Results listed in Table 3 (top, 3rd to 6th columns) show that recoveries for iAs are lower than organic arsenic, within error [29,30], regardless of the initial reaction conditions.

The precipitation of arsenic at the clay surface was also evaluated. EDS analyses of nontronite samples showed: O–K 25.4 ± 2.7% (w/w) (44.1 ± 3.1% atomic, $n = 7$); Mg–K 0.94 ± 0.2% (w/w) (1.01 ± 0.3% atomic, $n = 7$); Al–K 3.3 ± 1.8% (w/w) (3.3 ± 1.8% atomic, $n = 7$); Si–K 34 ± 1.8% (w/w) (33.2 ± 2.1% atomic, $n = 7$); Ca–K 1.7 ± 0.4 (1.01 ± 0.4, $n = 6$); 32.3 ± 2 (15.8 ± 1.7, $n = 6$); As–L 0.18 ± 0.09 (0.08 ± 0.04, $n = 5$); Cu–K 0.4, $n = 1$; K–K 7 (5, $n = 1$); W–M 3 (0.5, $n = 1$); and C.V. 8.67%. Arsenic contents in clay samples either before or after reaction ($[As(III)]_0 = 20$ ppm, 0.5 M betaine at pH_0 7 or 9) were found to be comparable. We do not discard the possibility of small-sized arsenic precipitates below detection limits (<0.01%), however. How the presence of positively charged iron oxides such as goethite (p.z.c. = 7.8 [31]; Table 3) may affect the reaction mechanism(s) of arsenic methylation in nontronite–methyl donor suspensions deserves further scrutiny.

3.2. *Mechanism of arsenic methylation in betaine–nontronite clays aqueous suspensions*

The formation of MMA can be explained because arsenic methylation–oxidation reaction according to [32]:

$$As(OH)_3 + CH_3^+ \rightarrow (CH_3)AsO(OH)_2 + H^+ \tag{1}$$

At $7 \leq pH \leq 9$, methane arsenic acid ($pK_{a1} = 3.61$; $pK_{a2} = 8.24$ at 18 °C; [25]) is predominantly in the mono- and di-protonated forms. Betaine ($pK_a = 1.83$) methyl group transfer is favored in the presence of nontronite (point of zero charge, $p.z.c._{mont} = 2.5$; [31]). The negative charge at the clay surface stabilizes positively charged organic intermediate-reaction species, thereby leading to decreases in the activation energy for methyl transfer. Dehydrochlorination of 1,1,1-trichlorethane to 1,1-dichlorethene by chemically and microbially reduced smectite minerals has been explained because the stabilization of carbocation intermediates at the clay–water interface [33]. Gaussian-2 COSMO calculations [31] show that the second methylation of $As(III)_0$ [as $As(OH)_3$] is the most endothermic. Those findings help explaining in part the lack of evidence for the formation of DMA ($pK_a = 6.2$) (Table 3, top).

Table 3
Arsenic methylation in betaine–nontronite clay suspensions.[a].

Nontronite	Arsenic compartmentalization[b]				
	pH_0	iAs (μg)		MMA (ng)	
		ng iAs g clay^{-1}	ng iAs ng $As(III)_0{}^{-1}$	ng MMA g clay^{-1}	ng iAs ng $As(III)_0{}^{-1}$
NAu-1	7	20.2	5	(···)[c]	(···)
NAu-2		9.5	3	19	5
NAu-1	9	0.1	0.03	95	24
NAu-2		19.5	5	201	50

Soluble-reaction products identification[d]

Solution composition	m/z values						
	491.3	374.2	257.1	4693	352.2	235.1	118.1
Betaine	18.42	10.53	85.82	11.84	43.42	100	5.92
Betaine + As(III)	3.05	2.44	20.73	6.71	38.41	100	4.88
Betaine + As(III) + NAu-2	5.92	3.95	24.34	11.18	35.52	100	5.92

[a] *Reaction conditions*: Arsenic initial concentration, $[As(III)]_0$, 20 ppm; clay concentration = 5 g L^{-1}; betaine initial concentration = 0.4 M.

[b] In all samples the concentrations of DMAs was found to be below detection limits < 0.2 ng L^{-1}.

[c] (···) = below detection limits < 0.1 ng L^{-1} supernatant solution after extraction.

[d] *Reaction conditions*: Arsenic initial concentration, $[As(III)]_0$, 20 ppm; clay concentration = 5 g L^{-1}; betaine initial concentration = 0.4 M. In all cases the initial pH, pH_0, was adjusted to 9.

Results listed in Table 3 (top, 5th and 6th columns) show a higher extent of As(III) conversion in the presence of NAu-2 over NAu-1. These results agree well with reports on the higher reactivity of NAu-2 over NAu-1 as evidenced by their relative ability to induce lipid peroxidation, a major indicator of oxidative stress [34], for example. Existing structural differences between NAu-1 and NAu-2 are associated with the distribution of structural iron over the total structural iron content alone (35.21 and 37.85% Fe_2O_3, respectively; [3]). Reported X-ray pre-edge spectra for NAu-1 and NAu-2 samples reveal differences in intensity, position, and shape. Enhancements of the Fe K pre-edge intensity in NAu-2 and the change in pre-edge profile [35] has been attributed to increased structural disorder due to lowering in symmetry around 6-coordinated structural Fe(III) [36], or to appreciable amounts of Mg and/or Al within octahedral sites [37]. Lastly, experimental Fe(III)-O waveforms for NAu-2 was found to be lower in amplitude and shifted in comparison to NAu-1 [35]. Waveforms for NAu-2 are right-shifted at low Å^{-1}. Such phase shifts are consistent with shorter average Fe(III)–O bond distances and lower average coordination for NAu-2.Finally, a direct comparison of mass spectrometry analyses for suspensions bearing betaine, As and betaine, and As, clay, and betaine (Table 3, bottom) provides a clear indication of multiple fragmentation pathways. These results are consistent with evidence provided above showing that ubiquitous clay surfaces (e.g., smectites) can act as catalysts for the transformation of inorganic arsenic in the presence of a naturally occurring methyl donor (e.g., betaine). The present work adds to current knowledge on the conversion of inorganic arsenic to trimethylarsine oxide (97–99%) and tetramethylarsonium (CH_4As^+, 1%) in coenzyme B_{12}-bearing suspensions [7]; transformation of trimethylarsine oxide into arsenobetaine after arsenic carboxymethylation in a 2.0×10^{-7} M trimethylarsine oxide/5.0×10^{-3} M glutathione/5.0×10^{-3} M iodoacetic acid solution at pH 5 and 37 °C for 2 h [7]; demethylation of arsenobetaine (0.5 and 5 mg As L^{-1}; m/z 75) to dimethylarsine (m/z 139) and dimethylarsinoylacetate (m/z 181) with clinoptilolite zeolite ($(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$) at 25 °C after 14 d [38]; degradation of arsenobetaine to dimethylarsine, dimethylarsinoylacetate, and a demethylation product (m/z 165, 133, 121, 105, 89, 79) by a mixture of clinoptilolite and modernite zeolites after 56 d. In this regard, clinoptilolite zeolites are known to present a strong exchange affinity for $NH_4{}^+$. Mordenite zeolites ($(Ca,Na_2,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O$), on the other hand, are commercially used to catalyze acid-catalyzed isomerisation of alkanes and aromatics.

4. Conclusions

Nontronite clay minerals facilitated arsenic methylation in water suspensions at ambient temperature. The outcome of this work provides evidence to show non-enzymatic methylation of arsenic. The conversion of As(III) to methyl arsenic (MMA) was explained because methyl transfer at the clay–water interface. The negative charge of the clay surface helps to stabilize positively charged organic intermediate species. Additional work is need to assess how the role of dissolving vs. structural Fe on the complexation of arsenic by betaine at the clay surface and/or supernatant solution. Because small-sized particles present higher-dissolution rates than bulk material [39], differences in reactivity as function of particle size are predicted.

The present work provides evidence to show that non-enzymatic methylation of arsenic can proceed in up to 50% within 24 h. Iron-redox cycling in smectite clay minerals occurs as a result of burial, submersion, wetting, drying, and other events in natural soils and sediments. Electron transfer at the water interface of iron-rich clay minerals conveys electron delocalization throughout siloxane groups and the concomitant formation of channels and holes. A consequence is the polarization of adsorbed water. As the surface of smectite clay minerals hydrates, water molecules reorganize to participate in hydrogen bonding interactions with other water molecules, just as in bulk water, and to form hydrogen-bridging interactions with organic solutes [40,38]. Because clays can act as electron acceptors or donors [41] and catalyze a variety of chemical reactions, it follows that clay-surface chemistry will affect the fate of solutes such as arsenic (inorganic or organic) susceptible to redox transformations present in colloidal environs [42].

Acknowledgements

The authors express gratitude to Dr. Rebecca Sutton (Environmental Working Group) and Daria Kibanova (School of Chemistry, UNAM) for helpful comments, and M en C Luz C Sanchez Penia (Depto Toxicologia, CINVESTAV) for technical assistance. JHP and HCG thank the support of a DGAPA-UNAM undergraduate scholarship. This project was supported in part by UNAM (PUNTA-PAPIIT, Grant No: IN116007-2), CONACYT (SEP-CONACYT Ciencia Básica 2006, Grant No: 61670), CONACYT-CNRS grant program, and by ECACORE 2020 (SEMARNAT-CONACYT).

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