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Species sensitivity of zeolite minerals for uptake of mercury solutes

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ABSTRACT

The uptake of inorganic Hg^{2+} and organometallic CH_3Hg^+ from aqueous solutions by 11 different natural zeolites has been investigated using a batch distribution coefficient (K_d) method and supported by a preliminary voltammetric study. The effect of mercury concentration on the K_d response is shown over an environmentally appropriate concentration range of 0.1–5 ppm inorganic and organometallic Hg using a batch factor of 100 ml g^{-1} and 20 h equilibration. Analcime and a Na-chabazite displayed the greatest methylmercury uptakes (K_d values at 1.5 ppm of 4023 and 3456, respectively), with mordenite as the smallest at 578. All uptake responses were greater for methylmercury than for the inorganic mercuric nitrate solutions, suggesting a distinctive sensitivity of zeolites to reaction with different types of solute species. It is likely that this sensitivity is attributable to the precise nature of the resultant Hg-zeolite bonds. Additionally, both the Si-Al ratio and the Na content of the initial natural zeolite samples are shown to influence the K_d responses, with positive correlations between K_d and Na content for all zeolites excluding mordenite.

KEYWORDS: natural zeolites, methylmercury, ion exchange, environmental geochemistry, aqueous solutes, heavy metals.

Introduction

MERCURY emissions to the atmosphere and aquatic environments are globally significant and well documented. A large number of environmental studies have monitored the concentrations, forms and fate of environmental Hg (e.g. Dopp *et al.*, 2004; Lawson *et al.*, 2001; Fergusson, 1990), and many have attempted to determine the geochemical controls on species distribution and behaviour (e.g. Hammerschmidt and Fitzgerald, 2004; Jay *et al.*, 2000; Baeyens *et al.*, 1998; Paquette and Helz, 1997; and Walcarius *et al.*, 1999 on mineral sorption). Studies focussing on organic substances have highlighted the competitiveness of sulphur in the binding of Hg (Yin *et al.*, 1997; Reddy and Aiken, 2001; Bell *et al.*, 2004; and a review by Ravichandran, 2004). Biochemical research on organomercury compounds is also active (Leiva-Presa *et al.*, 2004; Wilhelm *et al.*, 2004), with an overview of toxicity of organometallic compounds produced by Dopp *et al.*, (2004). The biological fate of methylmercury continues to be investigated, mainly in studies on fish (Boudou and Ribeyre, 1997; Ribeiro *et al.*, 1999).

Early reports on interactions of Hg with zeolites have been stimulated by the need to control gas and vapour-phase emissions of Hg and S associated with industrial-scale incineration (Jurng *et al.*, 2002; Morency, 2002; Sarbak, 1996). However, research on Hg removal using zeolites in aqueous systems is in its infancy. Much of the work has been on the performance of Greek zeolitic tuffs, with notable contributions by Misaelides *et al.* (1994, 1996) on clinoptilolite, Soupioni *et al.* (1999) on mordenite, Rajec *et al.*

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(1999) on clinoptilolitic tuffs and Haidouti (1997) on soil inactivation of Hg by the zeolites of Thrace, Greece. Sersen *et al*. (2005) reported on the protection of maize from Hg chloride solutions using Slovakian zeolitic tuffs in hydroponic growth experiments. Godelitsas and Armbruster (2003) examined effects of transition metal-modified HEU-type zeolites, and found that Hg tended to be surface-sorbed in these conditions. Where zeolites have been modified by, or exposed to organic compounds, Hg uptake is seen to be improved (Gebremedhin-Haile *et al*., 2003; Moreno-Gutierrez and Olguin, 2003, on Mexican erionite).

Studies that explore the structural relationship of exchanged Hg species with the zeolite framework are sparse. Garcia *et al*. (1999) concluded that the exchange rate of Hg onto clinoptilolite, erionite and mordenite was controlled by the Si:Al ratio of the minerals. Zhen and Seff (1999), using zeolite X, reported Hg at seven different sites, mainly co-ordinated to framework oxygens. For two key sites, the Hg^{2+} ions were co-ordinated to strongly electronegative framework oxygens in the bridging areas between sodalite units. Clusters of Hg-Cl were also observed within cavities.

In this paper, data on the aqueous ion exchange of Hg^{2+} and CH_3Hg^+ are presented for five natural clinoptilolites, mordenite, phillipsite, analcime, stilbite, chabazite and laumontite.

Aim

The aim of this study was to determine and compare likely ion exchange reactions between aqueous organometallic and inorganic Hg species and different natural zeolites. Kinetic data and the effect of the solid:solution ratio (batch factor) were also determined.

Approach

In the first set of experiments, an electrochemical method of analysis was employed (differential pulse anodic stripping voltammetry, DPASV) for direct determination of Hg in the experimental solutions. In this pilot study, only a small number of samples was possible because of the quality procedures required for this method (daily fresh reagents and standards, electrode cleaning routines, duplication, etc.). The second, main set of experiments was carried out using a radiotracer, in a two-stage process whereby the zeolites were first labelled with ^{22}Na, and then introduced to the Hg solutions. Determination of Hg uptake into zeolites was by liquid scintillation counting of ^{22}Na released from exchange sites into solution in the second stage. The radiotracer (isotope dilution analysis) approach enabled rapid, high-throughput data collection, as it is a well established, high-precision technique requiring only simple preparation for multiple samples. The combined data provide a mutually consistent, robust set of results.

Materials and methods

Zeolite samples

Zeolites were selected mainly on the basis of their channel sizes and also on their commercial availability. Five different clinoptilolites were compared including three newly investigated ones from Mongolia (Table 1). These zeolitic tuff samples have been shown to contain only minor impurities of ~5% calcite and <2% alkali feldspar (Dyer *et al.*, 2006). Other zeolite mineral samples used were mordenite, phillipsite, analcime, stilbite, laumontite and a chabazite previously converted to a near-homoionic Na form (Table 1).

Reagents

All chemicals used in this study were analytical-grade reagents. ^{22}Na (as nitrate) was supplied by Amersham International, UK. Methylmercury chloride (CH_3HgCl) was supplied as a solid by Alpha Aesar. Aqueous solutions of this were prepared by serial dilution, after initial dissolution in analar acetone. Note: this substance requires particular care and precautions in handling (high flux fume cupboard, special gloves, waste containment, etc.) due to its extreme toxicity. Mercuric nitrate ($Hg(NO_3)_2$) solutions were prepared by dilution of a commercial AAS standard. Sodium thiocyanate was dissolved in deionized water from the pure solid.

Voltammetric study

Preliminary tests to determine optimal analytical conditions for DPASV were undertaken. The electrode configuration was (1) 2 mm gold disc (working), (2) Ag/AgCl (reference) and (3) platinum (counter), attached to a BAS CV50 Potentiostat (C2 Cell Stand). Deposition potential was selected on the basis of prior experiments at −1000 mV, similar to Meyer *et al.* (1996) and

TABLE 1. Details of the natural zeolite samples.

Label	Zeolite	Composition	Si:Al	Na:Al	Locality	Reference
HEU1	Clinoptilolite	$K_{2.34}Na_{0.08}Ca_{0.63}Mg_{1.11}[Al_{5.9}Si_{25.0}O_{72}]\cdot nH_2O$	4.24	0.01	Ergene, Mongolia	Dyer *et al.* (2006)
HEU2	Clinoptilolite	$K_{2.48}Na_{1.45}Ca_{0.80}Mg_{0.55}[Al_{6.6}Si_{31.2}O_{72}]\cdot nH_2O$	4.73	0.22	Tsagaantsav, Mongolia	Dyer *et al.* (2006)
HEU3	Clinoptilolite	$K_{2.86}Na_{0.94}Ca_{0.70}Mg_{0.58}[Al_{6.4}Si_{30.2}O_{72}]\cdot nH_2O$	4.72	0.15	Tushleg, Mongolia	Dyer *et al.* (2006)
HEU4	Clinoptilolite	$Na_{3.73}K_{0.43}Ca_{0.47}Mg_{0.39}[Al_{6.16}Si_{30}O_{72}]\cdot 22.7H_2O$	4.87	0.61	Mud Hills, Death Valley Junction, California, USA	Dyer and Jozefowicz (1992)
HEU5	Clinoptilolite	$Na_{1.93}K_{2.40}Ca_{0.49}Mg_{0.40}[Al_{6.1}Si_{30.4}O_{72}]\cdot nH_2O$	4.98	0.32	Vulture Creek, Zululand, South Africa	Supplied by Pratley Co.
MOR	Mordenite	$Na_8[Al_8Si_{40}O_{96}]\cdot 24H_2O$	5	1.00	Lovelock, Nevada, USA	Rice *et al.* (1992)
PHI	Phillipsite	$K_2CaNa_4[Al_8Si_{10}O_{32}]\cdot 12H_2O$	1.25	0.50	Pine Valley, Nevada, USA	Dyer and Jozefowicz (1992)
ANA	Analcime	$Na_{16}[Al_{16}Si_{32}O_{96}]\cdot 16H_2O$	2	1.00	Wikieup, Arizona, USA	Wilkin and Barnes (1998)
STI	Stilbite	$Na_{0.9}K_{0.1}Ca_{4.0}[Al_{9.2}Si_{26.7}O_{72}]\cdot 31.1H_2O$	2.90	0.10	Edinbane, Isle of Skye, Scotland	Dyer and Faghihian (1998)
CHA	Na-chabazite	$Na_{6.7}Ca_{0.2}[Al_7Si_{29}O_{72}]\cdot 30.4H_2O$	4.14	0.96	Bowie, Arizona, USA	Dyer and Zubair (1998)
LAU	Laumontite	$Ca_{4.8}Na_{0.4}[Al_{9.4}Si_{15.8}O_{48}]\cdot 15.3H_2O$	1.68	0.04	Bernisdale, Isle of Skye, Scotland	Dyer *et al.* (1991)

Fischer *et al.* (1999) who used −1500 mV, but with a glassy carbon electrode. A more extreme deposition potential of −2000 mV was used by Diederich *et al.* (1994), whereas Tercier *et al.* (1995) deposited Hg at −400 mV for up to 15 min. Deposition time was then selected as 300 s on the basis of early optimization experiments, and a magnetic stirrer was employed. Since thiocyanate solutions complex well with Hg and have been demonstrated as highly effective in the electrochemical analysis of Hg and other metals (Meyer *et al.*, 1996; Diederich *et al.*, 1994), the optimum concentration of NaSCN solution was investigated (ammonium thiocyanate was used initially, but found to give a higher baseline than NaSCN). It was found that a solution concentration of 0.05 M NaSCN provides a good, low baseline, at the crucial potential of +300 mV for Hg analysis. However, for effective electrode cleaning between samples, by repeated cycling of the Au electrode through positive and negative potentials, a stronger solution of 0.25 M NaSCN was used in addition to regular polishing with an alumina suspension. No difference in current response was found between solutions purged with oxygen-free nitrogen and unpurged solutions. Therefore, no purging stage was undertaken. A scan rate of 20 mV s^{-1} was found to be sensitive, yet generally free of noise. For the experimental runs, quality control factors such as duplication and repeated blank testings were undertaken.

The Mud Hills clinoptilolite (HEU4, see Table 1), was selected for this study. 14 ml aliquots of the mercury solutions (1 ppm and 500 ppb) were added to 0.7 g samples of the zeolite (0.5−2 mm fraction). Procedural blank samples included one with the Hg solutions only, and one with the clinoptilolite and deionized water (DW) only. All samples were then agitated for 20 h on mineralogical rollers before centrifugation at 3000 rpm for 10 min. 5 ml aliquots of the experimental solutions were taken and made up to 10 ml with NaSCN and DW. Analytical standards for DPASV were prepared from Hg nitrate and CH_3HgCl stocks, NaSCN and DW. Prior experiments had established that the equilibration time used was sufficient to achieve equilibrium.

Radiotracer study

Zeolite samples, crushed and sieved for the 155−350 μm fraction, were weighed into polyethylene reaction vessels (15 ml screw-top centrifuge tubes) to a precision of 0.1 mg. Tared 0.1 g samples were then labelled with ^{22}Na by the addition of 10 ml ^{22}Na stock solution. A blank sample of the stock was prepared for determination of the initial activity (A_0). After 3 days' agitation on mineralogical rollers, the suspensions were centrifuged for 10 min (3000 rpm using a Centaur MSE-2 (Orme) centrifuge). Then 1 ml aliquots of the solutions were removed and mixed with 9 ml of scintillation cocktail (Aquasafe 300 plus), to determine radioactivity in a Canberra-Packard 1900 CA Tri-Carb liquid scintillation counter. The counting time of 30 min was predetermined to give a count rate precision of 1−2% relative standard deviation. The activity (in counts per minute per ml 'cpm') in the labelled zeolite (A_z) is calculated thus:

$$A_0 - A_t = A_z \qquad (1)$$

where: A_0 = initial solution activity (cpm/ml), A_t = final solution activity (cpm/ml) and A_z = specific activity in zeolite (cpm/ml) which can be converted to solid specific activities (cpm/*m*). The A_0 was retained as a blank for K_d determinations.

Labelled zeolites were then washed three times in deionized water before mixing with the Hg solutions (10 ml per sample, giving a predetermined batch factor of 100:1). After agitation on mineralogical rollers for 20 h and centrifugation (as above), 1 ml aliquots of the sample solutions were mixed with 9 ml of scintillation cocktail for analysis. Results are expressed as mineral-solution distribution coefficients, K_d, defined as the activity sorbed per gram of the zeolite divided by its activity per ml at equilibrium. Values were determined using the following equation:

$$K_d = \frac{A_z - A_t}{A_t} \times \frac{V}{M} \qquad (2)$$

where: A_z = initial activity in zeolite (cpm/ml), A_t = equilibrium solution activity (cpm/ml), V = volume of solution (ml) and M = weight of zeolite (g).

Results

Pilot experiments (voltammetric analysis)

In Fig. 1, current responses for typical DPASV runs are given. It can be seen that no Hg is detected at the crucial potential of 270(±30) mV for all sample solutions that interacted with clinoptilolite (HEU4) for 20 h. The two Hg

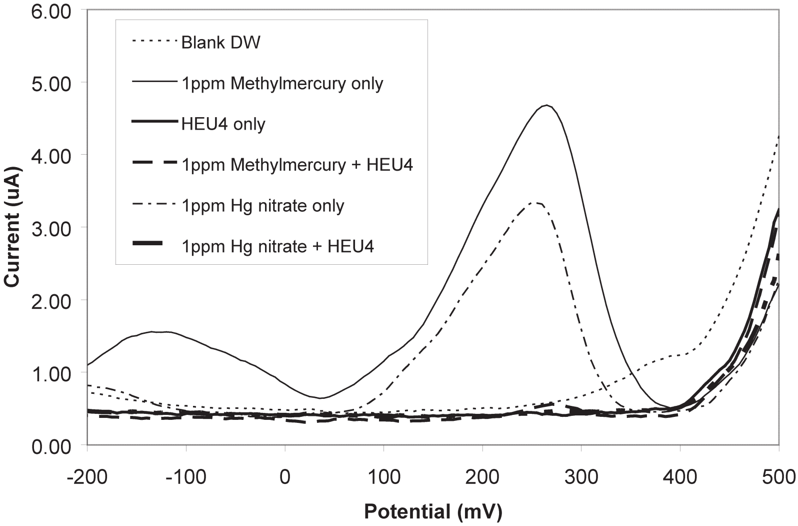

FIG. 1. Current responses (differential pulse anodic stripping voltammetry) for the pilot experiment showing removal of Hg solutes where HEU4 was present.

solutions used, 1 ppm CH_3HgCl and 1 ppm $Hg(NO_3)_2$, both give good peaks after 20 h of agitation alone in the sample vials, indicating that there was no significant loss of Hg through volatilization during the experiment.

Main experiments (radiochemical analysis)

Equilibration time

From initial kinetic tests, all zeolite-solution mixtures equilibrated within 12 h. For practical purposes, a contact time of 20 h was selected.

Batch factor

The effect of batch factor (*V/M*) was examined for all zeolites, using 1 ppm methylmercury solutions. In Fig. 2, it can be seen that there is a linear relationship for all zeolites, up to a batch factor of 200 ml g^{-1} and 100 ml g^{-1} was chosen as a convenient experimental batch factor. At 400–500 ml g^{-1}, much greater K_d values were observed for chabazite, analcime, stilbite and laumontite. This awaits further study and may be associated with the formation of hydrolysis products.

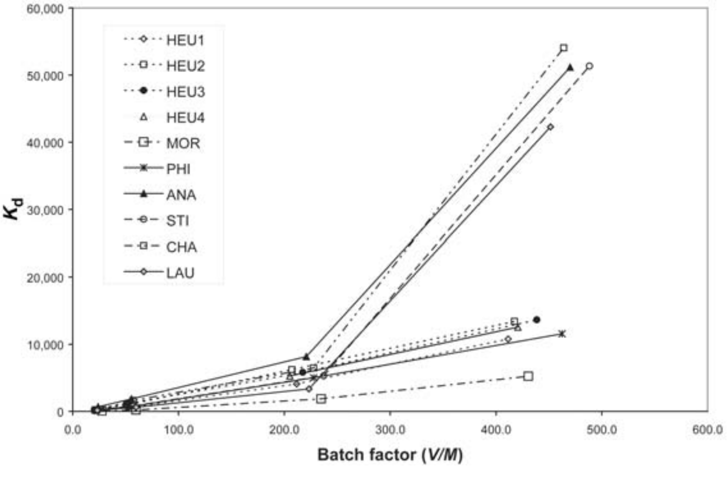

FIG. 2. Effect of batch factor (*V/M*) on distribution coefficients for 1 ppm methylmercury solutions.

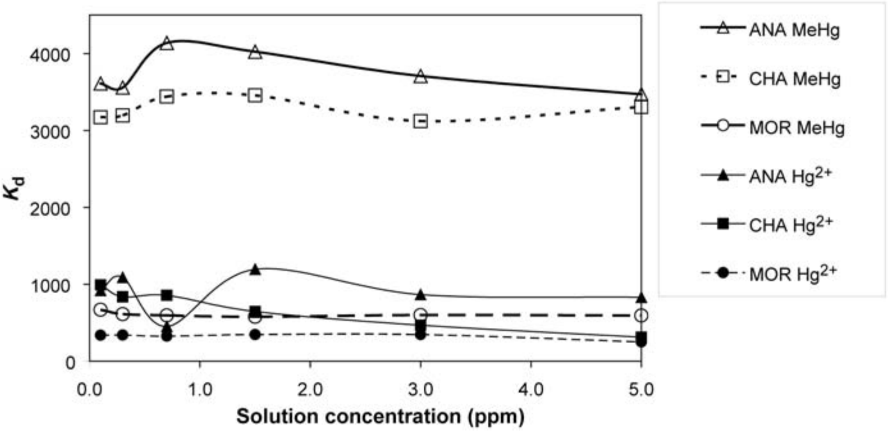

FIG. 3. Distribution coefficients for methylmercury (MeHg) and mercuric nitrate (Hg^{2+}) exchange with analcime, chabazite and mordenite.

Mercury concentration

Figures 3–5 show the K_d values observed for all zeolites to varying concentrations (0.1–5 ppm) of mercuric nitrate and methylmercury chloride. The results have been sub-grouped for clarity; Fig. 3 shows analcime, chabazite and mordenite, Fig. 4 shows stilbite, laumontite and phillipsite (note the different vertical axis scales) and Fig. 5 shows the clinoptilolites.

Discussion

Comparison of methods

Both the voltammetric and the radiotracer experiments provided consistent data on the reaction of aqueous Hg species with natural zeolites. The radiotracer study was more effective as a high-precision, sensitive and rapid technique for multiple samples. This enabled good analytical quality control features (replication, etc.) to be incorporated into the experimental design. Uptake of Hg solutes into clinoptilolite was supported by direct Hg analysis by differential pulse stripping voltammetry, but this study was comparatively slow. Using current parameters (small batch factor of 20:1 and high analytical solute concentration), it had a low sensitivity to species differences in uptake. However, the voltammetric results were useful for experimental verification, providing overall, a robust set of

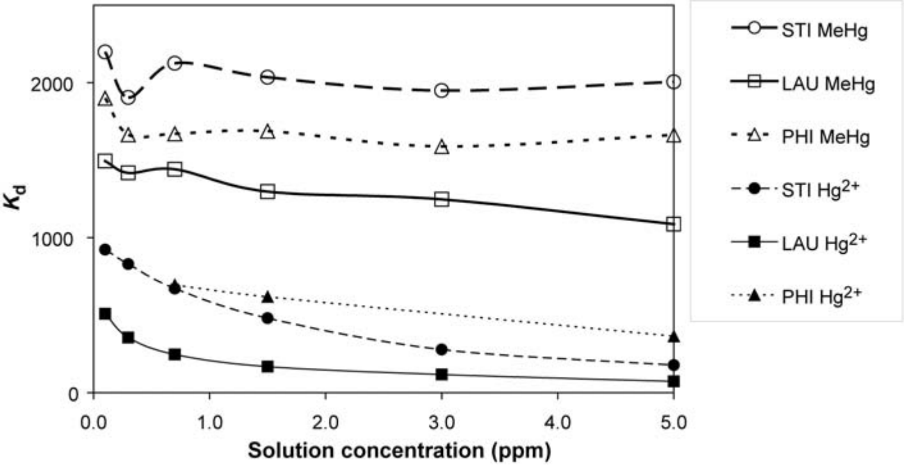

FIG. 4. Distribution coefficients for methylmercury (MeHg) and mercuric nitrate (Hg^{2+}) exchange with stilbite, laumontite and phillipsite.

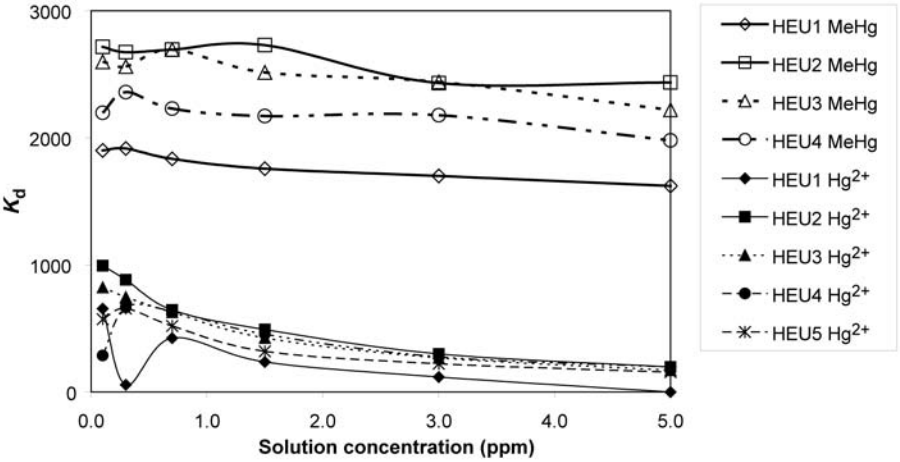

FIG. 5. Distribution coefficients for methylmercury (MeHg) and mercuric nitrate (Hg^{2+}) exchange with five clinoptilolites.

data. In addition, there remains the possibility of direct speciation determinations in the future (Ireland-Ripert *et al.*, 1982; Cano-Pavon *et al.*, 1999).

It should be noted that the basis of the Na-labelling approach lies in the prior knowledge of the comparative selectivity that clinoptilolite shows for various cations. In these, Na is commonly the least preferred cation, i.e. the most readily exchanged for other cations. An example of such a selectivity series is Pb > Ag > Cu ≈ Zn > Cd > Na (Tsitsishvili *et al.*, 1992); no similar series involving Hg is available. It will be appreciated that this does not preclude the exchange of other cations present in the initial labelling step. Justification for the use of the simple isotope dilution technique can be seen from the conformity in the results from this technique to the more experimentally demanding, and time consuming, electrochemical method of mercury analysis.

Distribution coefficients: analcime, chabazite, laumontite, mordenite, phillipsite, stilbite

Figures 3 and 4 show that the appreciable removal of methylmercury from aqueous solution is sustained over the whole of the concentration range studied. This is not so for mercury uptake which, in the same range, decreases markedly. This may be due to the propensity of the Hg^{2+} cation to form more complex species on hydrolysis and in the presence of carbonate species (Cotton and Wilkinson, 1999). Zeolites are known to take up carbon dioxide from the air, and also to yield an alkaline solution (~pH 10) in contact with water (Harjula *et al.*, 1993).

It should also be noted that in all instances the concentration of mercury species in solution is orders of magnitude less than the cation content of the zeolites, and this extends to sole consideration of the labelled Na content. The much greater K_d values seen for methyl mercury uptake, in comparison to those for mercury, strongly suggest that it is retaining the methyl group and acting as a monovalent cation. The maximum K_d values observed for these zeolites show the following order of preferences for both the methylmercury and mercury cations: ANA > CHA > STI > PHI > LAU >> MOR.

It is interesting to note that the uptake orders do not reflect the order of channel sizes present (MOR > CHA > STI > LAU > ANA > PHI: see Meier *et al.*, 1996) as might be expected for the bulky cations involved. This is in line with the preference of analcime for large, polarizable cations, e.g. its selectivity for lead (Tankawanit *et al.*, 2005). Because analcime is a Na-rich zeolite, and knowing that the Na cation is little preferred by zeolites, correlation with the amount of Na present can be considered. When the Na/Al contents, obtained from the formulae in Table 1, are ranked, the following order is seen: MOR ≈ ANA > CHA > PHI > STI > LAU.

This is in line with the uptakes observed if the small uptakes shown by mordenite and, to a much lesser extent, stilbite, can be explained. The small value for mordenite is unexpected but can be accounted for by the known interruptions to cation exchange caused by its large number of 'stacking faults' which have the effect of blocking the channels in the structure through which cations have to move to achieve exchange (Townsend and Loizidou, 1984). The relatively poor performance of phillipsite can probably be accounted for by its K content which is the largest of this group of zeolites examined.

The K_d values do not show any clear correlation with zeolite framework charge (Si/Al), unlike Garcia *et al*. (1999), who concluded that Hg(II) uptake was mainly dependent on framework charge for their three zeolites studied; clinoptilolite, mordenite and erionite. However, we have been able to examine the possible effect of Si/Al ratio in sharper focus within the group of five clinoptilolites, such that major structural differences (channel size and geometry) are excluded. This is discussed below.

Clinoptilolites

A variety of clinoptilolites was chosen because of the wide distribution of tuffs rich in this zeolite in worked deposits in many different countries. Each deposit has differences in composition arising from its mode of genesis. Primarily these are variations in the Si/Al ratio of the aluminosilicate framework coupled with those of the alkali metal (Na, K), and alkaline earth

(Mg,Ca,Ba) cations available for exchange. This can be seen in Table 1.

The pore size of clinoptilolite has the largest maximum dimensions (0.76 nm) of the zeolites studied (Meier *et al*., 1996). This is not reflected in the magnitude of the distribution coefficients observed, in line with previous comments. Figure 5 illustrates the methyl mercury and mercury distribution coefficients for several clinoptilolites. The useful removal of methyl mercury shows a small reduction in efficiency over the concentration range examined, whilst mercury removal reduces to small values in the same range. This can be assigned to the reasons already discussed.

The generally greater K_d values of methyl mercury uptake are in conformity with the concept that zeolites with high Si content in their framework prefer large monovalent to divalent cations. This is why clinoptilolite is used industrially to remove radioisotopes of Cs from aqueous nuclear wastes, and ammonium from other waste solutions (Dyer, 2005). It may also be worth commenting that the high Si content will render the zeolite framework more hydrophobic (Weitkamp *et al*., 1993) and so more compatible with the organometallic species. The work of Gebremedhin-Haile *et al*. (2003) on the contribution of organic substances to Hg-zeolite interactions is consistent with this.

It can be seen that a complete interpretation of the results observed on this simplistic basis is not possible as the order of increasing Si/Al (see Table 1) is HEU1 < HEU3 < HEU2 < HEU4 < HEU5 whereas K_d values for methylmercury uptake (Fig. 5) follow the order: HEU2 > HEU3 > HEU4 > HEU1 (note, no values are available for HEU5).

The Na content of HEU1 is very small (Table 1) and this may be the reason for its poor performance. That said, a similar comparison to the Na content (as Na/Al) shows HEU4 to have an unexpectedly small methyl mercury uptake. This remains unexplained. The mercury distribution coefficients show similar trends, with HEU4 again being an anomaly.

Significance for environmental remediation

The experiments conducted here have been concerned with simple aqueous systems in order to isolate data on the solute-mineral interactions. For environmental applications, natural waters and soils are likely to be involved and their physical, chemical and biological characteristics will impact on the precise reactions that will occur (Fergusson, 1990). Further study on ion competition, desorption and selectivity sequences is required, plus field trials for potential applications on contaminated sites. Initial work on acid-modified and homoionic forms of the zeolites is being undertaken (Campbell *et al*., 2004).

Summary and conclusions

It has been demonstrated that minerals of the zeolite group are variously effective at taking up aqueous solutes of Hg. Uptake is partly dependent on Na content, and has some relation to Si:Al ratio. A strong factor however, is the zeolite sensitivity to solute species, with organometallic methylmercury displaying preferential uptake over inorganic (nitrate) solutes. An examination of the interactions of other organometallic compounds with zeolites to compare with existing data on inorganic heavy metal uptakes is clearly indicated and environmentally relevant.

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