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Probing the surface structure of divalent transition metals using surface specific solid-state NMR spectroscopy

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1 Probing the surface structure of divalent transition
2 metals using surface specific solid-state NMR
3 spectroscopy

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8 **RECEIVED DATE**

9 TITLE RUNNING HEAD: NMR spectroscopic investigation of divalent metal sorption

10 **ABSTRACT**

11 Environmental and geochemical systems containing paramagnetic species could benefit
12 by using nuclear magnetic resonance (NMR) spectroscopy due to the sensitivity of the spectral
13 response to small amounts paramagnetic interactions. In this study, we apply commonly used
14 solid-state NMR spectroscopic methods combined with chemometrics analysis to probe sorption
15 behavior of the paramagnetic cations Cu²⁺ and Ni²⁺ at the amorphous silica surface. We exploit
16 the unique properties of paramagnets to derive meaningful structural information in these
17 systems at low, environmentally relevant cation surface loadings by comparing the NMR
18 response of sorption samples to paramagnetic free samples. These data suggest that simple
19 sorption models where the cation sorbs as inner sphere complexes at negatively charged,

deprotonated silanol sites is appropriate. These results help constrain sorption models that are used to describe metal fate and transport.

KEYWORDS: Solid-state NMR spectroscopy, paramagnets, sorption

INTRODUCTION

Models which can accurately predict the fate and transport of subsurface contaminants are an area of intense geochemical research. Extensive work has gone into developing models which can accurately predict the behavior of sorbed cations based solely on measured solution chemistry.[1-6] These models are based on electrostatic interactions between solution species and mineral surfaces, and have demonstrated some success in modeling the sorption behavior over a range of solution chemistries. However, these models are often over defined, and therefore need accurate spectroscopic studies to constrain input parameters.

Detailed structural information about the sorbed cation complexes has been gleaned from various spectroscopic investigations of reactions between divalent metals and minerals surfaces. Specifically, we focus on the previous work aimed at the interactions of paramagnetic cations Cu^{2+} and Ni^{2+} with silicate mineral surfaces. A wealth of information about the sorption of Cu on the amorphous silica surface has been derived from X-ray adsorption (XAS) and electron paramagnetic resonance (EPR) spectroscopic studies.[7-12] These studies find that the Cu binds strongly to the silica surface as inner sphere complexes, and that Cu dimers can form at low surface coverages.[9, 10] Contrasting EPR results have also suggested that surface sorption is limited and that $\text{Cu}(\text{OH})_2$ precipitation dominates.[7, 8] Similarly, XAS methods have also been applied to the study of Ni interactions with mineral surfaces.[13-16] These studies have suggested that at short reaction times the Ni forms inner sphere complexes, but that at longer times the reactions are dominated by the formation of Ni surface precipitates [13].

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3 43 The study of Cu and Ni containing systems by NMR spectroscopy presents some unique
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5 44 challenges and opportunities to derive structural information from simple NMR experiments. In
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8 45 the fields of environmental chemistry and geochemistry the study of systems containing
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10 46 paramagnetic species with NMR spectroscopy has largely been avoided due to the perception
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12 47 that their presence precludes the observation of useful structural information. Therefore, most
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14 48 NMR based sorption studies have focused on loading surfaces with moderately high
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16 49 concentrations of diamagnetic species such as Na^+ , Cs^+ , Al^{3+} and PO_4^{3-} which are easily
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18 50 observed with standard solid state NMR methods.[17-21] However, strong interactions between
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20 51 NMR observable nuclei and the unpaired electrons present in paramagnetic species have been
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22 52 successfully exploited to derive precise structural information on organo-metallic complexes [22,
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24 53 23].
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29 54 In this study, we exploit what are traditionally considered the detrimental effects of
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31 55 paramagnetic species on the NMR spectral response to derive information about the surface
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33 56 structure of sorbed metal species at low, environmentally pertinent surface loadings. We present
34
35 57 the results of NMR spectroscopic investigation of Cu^{2+} and Ni^{2+} sorption on the amorphous silica
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37 58 surface. The methods employed here allow us to identify the surface ligand with which these
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39 59 cations interact. It is largely assumed based on electrostatic arguments that these cations should
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41 60 prefer to bind at negatively charged surface sites (i.e. >SiO^-), no study has directly investigated
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43 61 this assertion.
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48 62 MATERIALS AND METHODS

49 63 *Sorption Experiments*

50
51 64 The Cu^{2+} and Ni^{2+} sorption experiments were conducted as a function of surface loading
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53 65 at pH 8 and 9, respectively. pH conditions were maintained through the periodic addition of 0.01
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66 N NaOH by a Metrohm Titrando 902 autotitration unit. To ensure surface equilibration, 0.5 g of
67 high surface area amorphous silica (Mallinkrodt silica: 306 m²/g surface by BET, 75 – 100 μm
68 particle size) was reacted in 100 ml of 0.1 M NaCl solution at the desired pH for 22 hrs before
69 proceeding with the sorption reaction. After the equilibration step, an aliquot of the cation stock
70 solution (10 mM CuCl₂ or 1 mM NiCl₂) was added in order to achieve the desired initial
71 concentration (Table 1) and the system was allowed to react for 2 hrs. For NMR analyses, the
72 samples were collected by suction filtration, and dried overnight at 60 °C. ¹H NMR data (vide
73 infra) showed that a hydration layer remained on the silica surface following the drying
74 procedure indicating that it did not significantly alter the surface structure. Final surface loadings
75 were determined from solution chemistry by collecting 10 mL aliquots of the reaction solution
76 immediately after the 22 hr equilibration period and after the 2 hr sorption reaction. These
77 solutions were filtered through a 0.2 μm syringe filter and submitted to ICPMS analysis. Control
78 samples for baseline comparison of the NMR response were produced at pH 8 and 9 by
79 immediately halting the reaction after the equilibration step. A sample of the pH 9 control sample
80 was also physically mixed with Ni(OH)₂ colloids in an agate mortar and pestle in order to test the
81 response to the presence of a separate precipitated phase.

82 *NMR Spectroscopy:*

83 Solid-state ²⁹Si single pulse (SP) and ²⁹Si{¹H} cross polarization magic angle spinning
84 (CP/MAS) experiments were conducted on a 300 MHz Tecmag Apollo spectrometer at operating
85 frequencies of 59.63 and 300.19 MHz for ²⁹Si and ¹H, respectively. The ²⁹Si{¹H} CP/MAS
86 spectra were collected over a range of CP contact times at spinning rate of 3 kHz using a
87 Chemagnetics probe configured for 7.5 mm (o.d.) rotors. A 6 μs ¹H excitation pulse was used
88 and ²⁹Si was matched on the +1 sideband of kaolinite. All ²⁹Si spectra were referenced with

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3 89 respect to tetramethylsilane (TMS) using an external kaolinite standard ($\delta_{\text{Si}} = -92$ ppm). ^1H single
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5 90 pulse (SP) MAS NMR spectra were collected on a 400 MHz Bruker Avance spectrometer at an
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8 91 operating frequency of 400.06 MHz. The samples were contained in 4 mm (o.d) rotor and spun
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10 92 at a 12 KHz spinning rate with a 4 mm Bruker triple resonance probe. Standard inversion
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12 93 recovery techniques were employed to measure ^1H spin-lattice relaxation constants (T_1). All ^1H
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14 94 spectra were collected with a 6 μs excitation pulse and are referenced with respect to an external
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16 95 sample of TMS ($\delta_{\text{H}} = 0$ ppm). In order to quantify the NMR spectral intensities for all NMR
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18 96 experiments, the samples were loaded in pre-weighed ZrO_2 ceramic rotors, and their weights
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20 97 recorded.
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24 98 ***Chemometrics analysis of NMR data***

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27 99 Chemometric methodologies are a powerful group of techniques that extract relevant
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29 100 spectral information from subtle variations in large multidimensional data sets.[24-26] Here two
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31 101 subsets of chemometrics are utilized: evolving factor analysis (EFA) and multivariate curve
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33 102 resolution (MCR). First EFA[27] is applied to the compiled CP NMR dataset whose rows are
34
35 103 comprised of a single CP spectrum for a characteristic contact time and the columns represent
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37 104 the intensity change for a discrete frequency as a function of contact time. The advantage of
38
39 105 EFA is that it merely seeks to compile those components who share similar variant behavior into
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41 106 separate factors and is independent of a chemical model. Those factors that show more variance
42
43 107 than the variance of the original spectra contain the dynamics of interest. All other factors were
44
45 108 discarded. Then these kept factors are fed into a multivariate curve resolution method utilizing an
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47 109 alternating least squares algorithm (MCR-ALS) to iteratively deconvolute the spectroscopic data
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49 110 matrix (D) into a pure component (C) and pure spectra (S^T) profile according to:
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$$D = CS^T + E \tag{1}$$

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E is the residual matrix and contains the variance unexplained by $\mathbf{CS}^T$, here it is assumed to be independent and have constant variance. The subtleties of this technique are explained thoroughly in the literature [28, 29]. This so called soft-model (or model-free) approach is advantageous when a hard-model is unavailable or inadequately describes the spectral response.

RESULTS AND DISCUSSION

Identification of ligand adsorption sites

At face value, the individual $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS spectra of the sorption samples do not appear much different from the control samples (Figure 1). They all have the same three major peaks present at -93.4, -103.1, and -113.2 ppm which are typically assigned to the Q^2 , Q^3 , and Q^4 silica sites. The Q^n notation refers to the number of bridging oxygens shared with surrounding silica tetrahedra with the Q^2 and Q^3 site sites representing silanol sites whose remaining oxygens are terminated with silanol protons, and the Q^4 site representing fully coordinated internal siloxane groups.[17, 30] Although presence of paramagnetic cations does not change observed peak chemical shifts or widths in the sorption samples, there are large decreases in the integrated spectral intensities of these peaks (Figure 1). Given that individual CP/MAS spectra cannot be treated quantitatively[31], we must consider how the intensity of these peaks vary as a function of the CP contact time to quantify the effects the paramagnetic species have in these systems.

We have applied chemometrics analysis to the variable contact time $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS spectra, and have identified two unique spectral components whose presence we attribute to the existence of protonated (Figure 2A, blue) and deprotonated (Figure 2A, red) silica surface sites. We see that the two spectral components contain contributions from all three silica sites, but have very different intensity profiles (Figure 2B). The lesser of the two components has an intensity profile which grows in rapidly with an average T_{SiH} of 1.0 ms, and decays away with an

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3 135 average $T_{1\rho,H}$ of 3 ms. This behavior is characteristic of silica sites which are directly bound to
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5 136 protons [30, 31], and we assign this component to protonated surface silanols ($>\text{SiOH}$). The
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8 137 other site, however, exhibits the opposite behavior with its intensity growing in more slowly and
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10 138 with no observed $T_{1\rho,H}$ decay. If the intensity of this second site is instead plotted as a function
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12 139 of the square root of the contact time then there is a clear linear region in the middle of the
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14 140 profile (Figure 2). This observed behavior is characteristic of a diffusion limited process [32].
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16 141 Therefore, we assign this component to deprotonated silica species, because they are spatially
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18 142 distinct from protons and are observed in the CP/MAS spectra only by long range couplings
19
20 143 through spin diffusion. This is further corroborated by the large presence of the Q^4 siloxane
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22 144 groups in this component which are by definition deprotonated and are present due to long range
23
24 145 couplings (Figure 2A, red). The Q^2 and Q^3 sites contained in this fraction we assign to
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26 146 deprotonated surface silanol groups ($>\text{SiO}^-$). We attribute the contribution of the Q^4 sites to
27
28 147 direct coordination or close proximity ($<5 \text{ \AA}$) to the protonated surface silanol groups. Since
29
30 148 these Q^4 are contained within the bulk silica and unlikely to be important in the sorption process,
31
32 149 they will not be discussed further. All other discussion will center on the Q^2 and Q^3 silanol
33
34 150 surface sites.

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41 151 With the assignment of these components to $>\text{SiOH}$ and $>\text{SiO}^-$ surface groups we can
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43 152 begin to draw conclusions about the sorption of Cu^{2+} and Ni^{2+} to the silica surface. We find that
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45 153 changes in the integrated CP signal intensity can be attributed to the sorption of Ni and Cu
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47 154 metals occurs as inner sphere complexes at $>\text{SiO}^-$ surface sites (Figures 3 and 4). When we
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49 155 compare the weight normalized spectral components of the sorption samples to those of the
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51 156 control samples, we observe only slight changes in signal intensity for the protonated fraction,
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53 157 but major changes in the deprotonated fraction. Assuming a conservative surface silanol density
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of 2 $\mu\text{mol}/\text{m}^2$ for amorphous silica at pH 8/9,[17] and the amount of Cu and Ni uptake, then surface coverage ranges from about 0.1 to 3% (Table 1). For both the Cu and Ni samples, we observe large systematic decreases in the signal intensity of the $>\text{SiO}^-$ component as a function of surface loading. For the Cu samples, the intensity of the Q^3 peaks relative to those of the control reduces by 37.6% for the lowest concentration sample (0.33 % surface coverage) and 56.6 % for the highest concentration (3.23 % surface coverage). For the Ni samples, these same peaks reduce by 62.5 % for the low concentration sample (0.08 % surface coverage), and 70.9 % for the high concentration sample (2.7 % coverage). If the intensity losses were the result of site blockage alone we should expect these to be proportional to the surface coverage. However, we note the largest decreases in the Ni system where the coverage is lowest. We attribute the larger decreases to the more paramagnetic character of the Ni^{2+} cation which has two unpaired electrons compared to the single unpaired electron in the Cu^{2+} cation. The observed effects appear to result only through the interactions with the silica surface with paramagnetic species.

We clearly observe a systematic effect in the CP/MAS data as we increase the concentration of paramagnetic species, but we need to test if these effects result only from through bond interactions with the surface, or if they would also occur if a distinct precipitated phase is present. When we analyze the data collected for the pH 9 control sample and the physical mixture of $\text{Ni}(\text{OH})_2$ colloids (not shown) we observe no differences between the observed intensities and that of the pristine pH 9 control sample. The absence of an effect in this sample supports our interpretation that intensity changes result from bonding interactions between the sorbed metal species and the $>\text{SiO}^-$ groups on the amorphous silica surface. Therefore, we propose that in the absence of sorbed paramagnets, ^1H magnetization diffusion is efficient between the $>\text{SiOH}$ and $>\text{SiO}^-$ groups (Figure 5A). In the presence of the sorbed

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3 181 paramagnetic species this diffusion is inhibited due to the unpaired electron density interacting
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5 182 strongly with the $>\text{SiO}^-$ (Figure 5B) causing the characteristic decrease in signal intensity we
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8 183 observe with increasing sorbent concentration. These data also suggest that the transition
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10 184 between sorption and precipitation could be identified with NMR spectroscopy with increased
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13 185 surface loadings.

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15 186 All the above structural observations are only possible because of spectral interferences
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17 187 from paramagnetic species. Similar to the above $\text{Ni}(\text{OH})_2$ colloid experiment, the absence or
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20 188 decrease in the EPR spectral response in Cu uptake experiments has been used as evidence for
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22 189 either the precipitation of $\text{Cu}(\text{OH})_2$ or the formation of diameric Cu-hydroxide species [7, 8, 12]
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24 190 The understanding is that these phase loses the paramagnetic character of the Cu^{2+} and will not
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26
27 191 cause a response in the EPR experiment. Therefore, the presence of such a phase in our samples
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29 192 would be equally ineffective at producing the NMR responses we observe. The large spectral
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32 193 response observed for our highest Cu loadings suggests that none of the previously suggested
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34 194 Cu-hydroxide phases have formed in our experiments.

35
36 195 *Identification of external versus internal sorption sites*
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38
39 196 Powerful information about the bonding environment of these cations can also be gleaned
40
41 197 by directly observing ^1H in a ^1H SP/MAS NMR experiment (Figure 6). These results indicate
42
43 198 that the surface sorbed metal species strongly interact with surface water species, but interact less
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45
46 199 strongly with $>\text{SiOH}$. This is evidenced by again comparing the NMR signal obtained for control
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48 200 samples to that of the samples containing surface sorbed metals. What is immediately apparent is
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50 201 the suppression of the 4.7 ppm peak corresponding to water sorbed to the dried silica surface
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53 202 from the spectra of the sorption samples (Figure 6). Also observed is the conspicuous emergence
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55 203 of a strong, sharp (0.1 ppm FWHM) ^1H peak near 2 ppm from isolated, weakly H-bonded SiOH
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groups ($>\text{SiOH}_w$)[30]. Since the silica we used is mesoporous with a significant amount of internal porosity[33], we interpret these $>\text{SiOH}_w$ sites as silanols contained within internal pore spaces. This peak is present in spectra of the control samples, but significantly muted compared to the strong signal from surface water species. In the spectra collected for the Ni samples, the mobile water peak is entirely suppressed, unmasking the sharp peak from $>\text{SiOH}_w$ and a peak at 5.5 ppm from strongly H-bonded $>\text{SiOH}$ groups ($>\text{SiOH}_s$).[30] This peak is also present as a shoulder in all other ^1H spectra, but difficult to resolve from the main H_2O peak. These $>\text{SiOH}_s$ sites represent silanols on the external surface which are hydrogen bonded to the surface water species. The strong suppression of the water peaks indicates that these surface waters are strongly interacting with the paramagnetic cation species, and the $>\text{SiOH}$ surface groups are largely unperturbed. The proton NMR provide complementary evidence that Ni and Cu sorb to the $>\text{SiO}^-$ sites near surface water.

The measured ^1H relaxation properties (T_1) can be related to the relative proximity of the surface protonated species to the sorbed paramagnetic species, and can be used to further constrain the structural models for the sorption process (Table 2). The results, again, indicate that the paramagnets are most closely associated with sorbed surface water, but do exert some influence on the $>\text{SiOH}_s$ and $>\text{SiOH}_w$ species. The observed ^1H T_1 can be thought to contain contributions from two separate interactions through the relation:

$$1/T_1 = 1/T_{1P} + 1/T_{1\text{dia}} \quad (1)$$

where $1/T_{1P}$ is the contribution from the paramagnetic species, and $1/T_{1\text{dia}}$ is the contribution from all other diamagnetic interactions (e.g. ^1H - ^1H spin diffusion, and ^1H - ^{29}Si dipole coupling).[23] The paramagnetic contribution here is proportional to the distance (r) between ^1H and the paramagnet center and the number of the paramagnetic species (N_P).[34]

227
$$1/T_{1P} \propto N_P \cdot 1/r^6 \tag{2}$$

228 We use the above relationships only as guides for the discussion of the measured T_1 values and
229 how we can relate these to relative proximity of the paramagnet species. In general, we can state
230 that the T_1 of a ^1H species will decrease if either the distance to the paramagnet decrease, or the
231 density of paramagnets increases. We note the most dramatic decreases of the T_1 values relative
232 to the control for the residual water peaks, followed by the $>\text{SiOH}_s$ sites (Table 2). With the
233 exception of the highest surface loading Cu sample, the T_1 of the $>\text{SiOH}_w$ is largely unaffected.
234 These data indicate that in the Cu system, at the highest loadings, the paramagnet is in close
235 enough proximity to affect the relaxation properties of the $>\text{SiOH}_w$. In all other samples, the
236 paramagnet species are most closely associated with surface sorbed water, and the strongly H-
237 bonded silanol sites.

238 *Sorption complexation models*

239 We frame these results within the context of simple sorption models where the metals
240 sorb to a single type of surface site. In the Ni system we propose that the sorption behavior
241 observed can be explained by a single surface reaction.

243 The ^1H data indicate that the Ni does not interact with the internal silanol sites ($>\text{SiOH}_w$), and
244 that all the sorption reactions occur at the external surface sites. In the Cu system, the data
245 suggests that a two stage sorption model is necessary to describe the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS and ^1H
246 NMR data. At lower concentrations the Cu sorbs following the reaction:

248 As these external sites become less favorable at higher surface coverages the Cu then sorbs at
249 sites within the internal pore spaces via:

6 251 This second step is evidenced by the shortening of the $>\text{SiOH}_w$ T_1 as the Cu loading increases
7
8 252 which indicates a closer association of the Cu with these internal sites. It is unclear why these
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10 253 same processes are not active in the Ni system. One possible explanation could be that diffusion
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12 254 of large Ni complexes to these internal sites is limited. More work is necessary to determine if
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14 255 these processes are active. In general, these results agree well with previous solution chemistry
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16 256 studies which predict the inner sphere sorption of Cu and Ni at the silica surface. [3, 35] We
17
18 257 believe that the NMR techniques presented here can be easily extended to probe a range of
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20 258 interactions between paramagnetic sorbates and diamagnetic surfaces. The results of such studies
21
22 259 should help grow our understanding of the basic reactions needed to model the fate and transport
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24 260 of metals.
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268

269 FIGURE CAPTIONS

270 **Figure 1.** $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS spectra collected contact time of 2ms (left) and 7 ms (right) for the
271 pH 9 control sample, and two Ni sorption samples.

272

273 **Figure 2.** Results of chemometrics analysis for the pH 9 Control sample **A.** The two components
274 which fully describe the intensity variation. **B.** The intensity versus contact time profiles for the
275 $>\text{SiO}^-$ and $>\text{SiOH}$ components. **C.** The intensity profile of the $>\text{SiO}^-$ The dotted lines are present
276 only to guide the eye.

277

278 **Figure 3.** The results of chemometrics analysis for the **a – b)** Cu and **c – d)** Ni sorption samples
279 compared to that obtained for their respective control samples. All spectra were collected for the
280 same number of acquisitions (4096) and their intensities are scaled based on their measured
281 weights.

282

283 **Figure 4.** Schematic representations of ^1H magnetization transfer (blue arrows) through spin
284 diffusion between different surface silica sites. **A.** In the absence of paramagnetic cations
285 magnetization is shuttled from the $>\text{SiOH}^0$ (blue) to the $>\text{SiO}^-$ groups (red). **B.** The presence of a
286 $>\text{SiOM}^+$ (red and green) surface species blocks the magnetization transfer due to the presence of
287 unpaired electrons (represented by the green circle).

288

289 **Figure 5.** Sample ^1H NMR spectra collected for the **a)** pH 9 control sample, and the highest
290 loaded **b)** Cu and **c)** Ni samples.

TABLES

Sample	pH	M ²⁺ _{initial} (μmol)	M ²⁺ _{final} (μmol)	% _{removed}	Bulk coverage (nmol M ²⁺ /m ² SiO ₂)	% coverage
Cu 01	8	1.0	0.012	98.8	6.5	0.33
Cu 1	8	10.0	0.15	98.5	64.4	3.23
Ni 01	9	1.0	0.75	24.6	1.6	0.08
Ni 1	9	10.0	1.73	82.6	54.0	2.71

Table 1: Results of solution chemistry measured for the sorption experiments. The % coverage is calculated assuming a surface silanol density of 2 $\mu\text{mol}/\text{m}^2$ (see text).

Sample	Site	Chemical Shift (ppm)	T ₁ (ms)
Control pH 9	>SiOH _s	5.82	250±2
	H ₂ O	4.74	155±1
	>SiOH _w	2.38	581±15
Cu 01	>SiOH _s	5.46	140±1
	H ₂ O	4.92	89.2±0.1
	>SiOH _w	2.38	612±
Cu 1	>SiOH _s	5.54	110±1
	H ₂ O	4.56	38.1±0.1
	>SiOH _w	2.37	317±1
Ni 01	>SiOH _s	5.48	105±1
	H ₂ O	-	-
	>SiOH _w	2.38	685±1
Ni 1	>SiOH _s	5.48	106±1
	H ₂ O	-	-
	>SiOH _w	2.38	564±1

Table 2: ¹H MAS NMR results for the sorption samples.

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- 299
- 300 1. Davis, J. A.; James, R. O.; Leckie, J. O., Surface ionization and complexation at the
301 oxide/water interface: I. Computation of electrical double layer properties in simple electrolytes.
302 *Journal of Colloid and Interface Science* **1978**, 63, (3), 480-499.
 - 303 2. Dzombak, D. A.; Morel, F. o. M. M., Surface complexation modeling : hydrous ferric
304 oxide. Wiley: New York, 1990; p xvii, 393 p.
 - 305 3. Criscenti, L. J.; Sverjensky, D. A., The role of electrolyte anions (ClO(4)(-), NO(3)(-),
306 and Cl(-)) in divalent metal (M(2+)) adsorption on oxide and hydroxide surfaces in salt
307 solutions. *American Journal of Science* **1999**, 299, (10), 828-899.
 - 308 4. Sverjensky, D. A., Interpretation and prediction of triple-layer model capacitances and
309 the structure of the oxide-electrolyte-water interface. *Geochimica et Cosmochimica Acta* **2001**,
310 65, (21), 3643-3655.
 - 311 5. Criscenti, L. J.; Sverjensky, D. A., A single-site model for divalent transition and heavy
312 metal adsorption over a range of metal concentrations. *Journal of Colloid and Interface Science*
313 **2002**, 253, (2), 329-352.
 - 314 6. Karamalidis, A. K.; Dzombak, D. A., Surface complexation modeling : gibbsite. Wiley:
315 Hoboken, N.J., 2010; p xv, 294 p.
 - 316 7. Xia, K.; Mehadi, A.; Taylor, R. W.; Bleam, W. F., X-ray absorption and electron
317 paramagnetic resonance studies of Cu(II) sorbed to silica: Surface-induced precipitation at low
318 surface coverages. *Journal of Colloid and Interface Science* **1997**, 185, (1), 252-257.
 - 319 8. Xia, K.; Taylor, R. W.; Bleam, W. F.; Helmke, P. A., The distribution of Cu(II) on
320 boehmite and silica surfaces: Correlating EPR signal loss with the effective Bohr magneton
321 number of sorbed ions. *Journal of Colloid and Interface Science* **1998**, 199, (1), 77-82.
 - 322 9. Cheah, S. F.; Brown, G. E.; Parks, G. A., XAFS spectroscopy study of Cu(II) sorption on
323 amorphous SiO₂ and gamma-Al₂O₃: Effect of substrate and time on sorption complexes.
324 *Journal of Colloid and Interface Science* **1998**, 208, (1), 110-128.
 - 325 10. Cheah, S. F.; Brown, G. E.; Parks, G. A., XAFS study of Cu model compounds and Cu²⁺
326 sorption products on amorphous SiO₂, gamma-Al₂O₃, and anatase. *American Mineralogist*
327 **2000**, 85, (1), 118-132.
 - 328 11. Motschi, H., Correlation of EPR-parameters with thermodynamic stability constants for
329 copper(II) complexes Cu(II)-EPR as a probe for the surface complexation at the water/oxide
330 interface. *Colloids and Surfaces* **1984**, 9, (4), 333-347.
 - 331 12. Hyun, S. P.; Cho, Y. H.; Hahn, P. S., An electron paramagnetic resonance study of Cu(II)
332 sorbed on quartz. *Journal of Colloid and Interface Science* **2003**, 257, (2), 179-187.
 - 333 13. Roberts, D. R.; Scheidegger, A. M.; Sparks, D. L., Kinetics of Mixed Ni-Al Precipitate
334 Formation on a Soil Clay Fraction. *Environmental Science & Technology* **1999**, 33, (21), 3749-
335 3754.
 - 336 14. Scheinost, A. C.; Ford, R. G.; Sparks, D. L., The role of Al in the formation of secondary
337 Ni precipitates on pyrophyllite, gibbsite, talc, and amorphous silica: a DRS study. *Geochimica et*
338 *Cosmochimica Acta* **1999**, 63, (19-20), 3193-3203.
 - 339 15. Scheinost, A. C.; Sparks, D. L., Formation of Layered Single- and Double-Metal
340 Hydroxide Precipitates at the Mineral/Water Interface: A Multiple-Scattering XAFS Analysis.
341 *Journal of Colloid and Interface Science* **2000**, 223, (2), 167-178.

16. Sheng, G.; Yang, S.; Sheng, J.; Hu, J.; Tan, X.; Wang, X., *Macroscopic and Microscopic Investigation of Ni(II) Sequestration on Diatomite by Batch, XPS, and EXAFS Techniques. Environmental Science & Technology* **2011**, 45, (18), 7718-7726.
17. Carroll, S. A.; Maxwell, R. S.; Bourcier, W.; Martin, S.; Hulse, S., *Evaluation of silica-water surface chemistry using NMR spectroscopy. Geochimica Et Cosmochimica Acta* **2002**, 66, (6), 913-926.
18. Houston, J. R.; Herberg, J. L.; Maxwell, R. S.; Carroll, S. A., *Association of dissolved aluminum with silica: Connecting molecular structure to surface reactivity using NMR. Geochimica Et Cosmochimica Acta* **2008**, 72, (14), 3326-3337.
19. Kim, Y.; Kirkpatrick, R. J., *Na-23 and Cs-133 NMR study of cation adsorption on mineral surfaces: Local environments, dynamics, and effects of mixed cations. Geochimica Et Cosmochimica Acta* **1997**, 61, (24), 5199-5208.
20. Li, W.; Feng, J.; Kwon, K. D.; Kubicki, J. D.; Phillips, B. L., *Surface Speciation of Phosphate on Boehmite (gamma-AlOOH) Determined from NMR Spectroscopy. Langmuir* **2010**, 26, (7), 4753-4761.
21. Mason, H. E.; Maxwell, R. S.; Carroll, S. A., *The formation of metastable aluminosilicates in the Al-Si-H₂O system: Results from solution chemistry and solid-state NMR spectroscopy. Geochimica et Cosmochimica Acta* **2011**, 75, (20), 6080-6093.
22. Wickramasinghe, N. P.; Ishii, Y., *Sensitivity enhancement, assignment, and distance measurement in ¹³C solid-state NMR spectroscopy for paramagnetic systems under fast magic angle spinning. Journal of Magnetic Resonance* **2006**, 181, (2), 233-243.
23. Wickramasinghe, N. P.; Shaibat, M. A.; Ishii, Y., *Elucidating connectivity and metal-binding structures of unlabeled paramagnetic complexes by C-13 and H-1 solid-state NMR under fast magic angle spinning. Journal of Physical Chemistry B* **2007**, 111, (33), 9693-9696.
24. Cordella, C., *Principal component analysis: the basic building block of chemometrics. Actual Chimique* **2010**, (345), 13-18.
25. Ayoko, G. A.; Mostert, M. M. R.; Kokot, S., *Application of chemometrics to analysis of soil pollutants. Trac-Trend Anal Chem* **2010**, 29, (5), 430-445.
26. Hasegawa, T., *Chemometrics for spectroscopic analysis. Anal Bioanal Chem* **2003**, 375, (1), 18-19.
27. Maeder, M., *Evolving factor analysis for the resolution of overlapping chromatographic peaks. Analytical Chemistry* **1987**, 59, (3), 527-530.
28. de Juan, A.; Tauler, R., *Chemometrics applied to unravel multicomponent processes and mixtures - Revisiting latest trends in multivariate resolution. Anal Chim Acta* **2003**, 500, (1-2), 195-210.
29. Tauler, R., *Multivariate curve resolution applied to second order data. Chemometr Intell Lab* **1995**, 30, (1), 133-146.
30. Liu, C. H. C.; Maciel, G. E., *The fumed silica surface: A study by NMR. Journal of the American Chemical Society* **1996**, 118, (21), 5103-5119.
31. Kolodziejewski, W.; Klinowski, J., *Kinetics of cross-polarization in solid-state NMR: A guide for chemists. Chemical Reviews* **2002**, 102, (3), 613-628.
32. Crank, J., *The mathematics of diffusion. Clarendon Press: Oxford*, 1956; p 347 p.
33. Loucaides, S.; Behrends, T.; Van Cappellen, P., *Reactivity of biogenic silica: Surface versus bulk charge density. Geochimica Et Cosmochimica Acta* **2010**, 74, (2), 517-530.

34. Voronov, V. K.; Keiko, V. V.; Moskovskaya, T. E., *Paramagnetic reagents for the study of the structure of heteroatomic compounds from the NMR spectra. Journal of Structural Chemistry* **1977**, 18, (5).
35. Vlasova, N. N., *Adsorption of Cu²⁺ ions onto silica surface from aqueous solutions containing organic substances. Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**, 163, (2-3), 125-133.

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