Hydration is the Key for Gold Transport in CO_2-HCl-H_2O Vapor

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Abstract

Carbon dioxide (CO_2) is a major component of volcanic gases and ore-forming hydrothermal fluids. However, there is a poor understanding of the effect of CO_2 on the speciation of metal complexes and on ore mineral solubility. To address this deficiency, we conducted *ab initio* molecular dynamic (MD) simulations of the behavior of $AuCl_{(aq)}$ in the CO_2-H_2O system at 340 ºC, 118-152 bar and 800 ºC, 265-291 bar for CO_2 mole fractions (X_{CO_2}) of 0.1-0.9. The MD simulations indicate that the linear $[H_2O\text{-}Au\text{-}Cl]^0$ structure of gold chloride is not affected by CO_2 at X_{CO_2} up to 0.8 at 340 ºC and up to 0.5 at 800 ºC, whereas the "dry" $[AuCl]^0$ species predominates at X_{CO_2} >0.8 at 340 ºC and >0.5 at 800 ºC. The number of water molecules hydrating the $AuCl_{(aq)}$ complex decreases systematically with increasing CO_2 mole fraction and increasing temperature. Results of Au solubility experiments at 340 ºC in CO_2-H_2O solutions show that the addition of CO_2 does not enhance Au solubility. We conclude that hydrated chloride species with linear geometry are the main means for transporting gold in CO_2-H_2O-HCl fluids, and that Au solubility decreases in CO_2-bearing hydrothermal fluids as a result of the decrease in hydration of the Au complexes. This contrasts with the behavior of other divalent transition metals (*e.g.*, Fe, Co, Ni, and Zn). We attribute this contrasting behavior to differences in the electronic configuration of Au(I)/Cu(I)/Ag(I) and the divalent transition metal ions.

Keywords

Molecular dynamic simulation, gold solubility, vapor transport, CO_2-rich geo-fluids, hydration.

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1 Introduction

Carbon dioxide (CO_2) is one of the major components of geological fluids[1] and is the second most common magmatic volatile after H_2O[2]. It is also a common component of the fluid inclusions trapped in minerals in a variety of hydrothermal ore deposits[3]. In the case of orogenic gold deposits, the abundance of CO_2-rich fluid inclusions has given credence to the suggestion that CO_2 may have played a role in ore formation either by promoting metal transport[4] or deposition[5].

Despite the prevalence of CO_2 in geological fluids, few studies have investigated the role of CO_2 in mineral solubility and metal speciation in hydrothermal systems. Adding CO_2 to water decreases the dielectric constant of the latter[6-7], thereby enhancing ion-pairing[6], decreasing the solubility of some minerals[7-9], and decreasing hydration numbers around ions[10-11]. Based on studies of Cu solubility in HCl-H_2O vapor (fluid density <0.2 g cm^{-3})[12], which attributed steep increases in Cu solubility with increasing water activity to the increase in the hydration of the Cu(I) chloride complexes, van Hinsberg *et al.*[13] proposed that CO_2 fluxes can reduce ore mineral solubility and lead to the formation of potentially economic deposits. In contrast, Kokh *et al.*[14] concluded that CO_2 has no significant impact on the solubility of Au, Mo, Pt, and Cu but enhances the solubility of Fe, Zn and Sn at 450 ºC and 600-700 bar (fluid density ~0.5 g cm^{-3}). Kokh *et al.*[15] found that CO_2 had no effect on the partitioning of Fe/Cu/Au between brine and vapor at 350 ºC and up to 100 bar in sulfide-rich systems, but enhanced Au partitioning into the vapor relative to Cu/Fe in the S-free system, probably via the formation of carbonyl vapor species. Overall, these studies show that the effect of CO_2 on Au behavior in high temperature CO_2-rich vapor and supercritical fluids can be complex. They highlighted a need for a molecular-level understanding of the hydration of Au complexes in CO_2-bearing fluids in order to help understand and predict the behavior of

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Au in CO_2-bearing fluids. Previous experimental and computational studies[16-18] have established that $AuCl_{(aq)}$ is the dominant Au complex in CO_2-free low-density (<0.35 g/cm^3) HCl-H_2O solutions. Experimental studies[16-17] have shown that hydrated $AuCl_{(aq)}$ species are capable of carrying significant amounts of Au in acidic HCl-H_2O vapors at 230-450 ºC, and a MD study[18] revealed the correlation of the change of $AuCl_{(aq)}$ hydration with the fluid density.

This study explores the role of CO_2 in the speciation, hydration and solubility of Au using *ab initio* MD simulations coupled with a limited number of solubility experiments. The Au(I)-HCl-CO_2-H_2O system at 340-800 ºC was chosen because CO_2-bearing vapors are common in a variety of hydrothermal ore systems, and recent experimental and MD studies have provided us with a detailed understanding of Au(I) complexing and hydration in the CO_2-free system[17-18]. The Au-Cl system is also well suited for this study on a theoretical level, because the stability of the $AuCl_{(aq)}$ species over a wide range of P,T, and hydration structure facilitates study of the effect of CO_2 on a single complex. Here, we used *ab initio* molecular dynamic simulations to investigate the changes brought upon by increasing CO_2 contents (X_{CO_2} = 0.1-0.9) on the hydration of $AuCl_{(aq)}$. In order to determine if the major trends predicted by the *ab initio* MD simulations are reproduced in real fluids, we performed a few exploratory solubility experiments at 340 ºC in HCl-CO_2-H_2O fluid, complementing the data obtained by Hurtig and Williams-Jones[17] for the CO_2-free system.

2 Methods

2.1 *Ab initio* molecular dynamics simulation

Ab initio MD simulations of $AuCl_{(aq)}$ in CO_2-H_2O mixture fluids were conducted using the Car-Parrinello molecular dynamics[19] (CPMD, code version 3.17.1) method. Our previous *ab initio* MD studies demonstrated the capacity of the CPMD to describe the geometry and nature of metal complexes (Cu(I)-HS-Cl[20], Au(I)-Cl[18], Au(I)-S_3[21], Zn(II)-Cl-HS[22-23], Pd(II)-

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Cl-HS[24]) in aqueous solutions over a wide range of solution density and composition. The CPMD implements density functional theory (DFT) using a plane-wave basis set and pseudo-potentials to simulate the presence of the core electrons. The PBE exchange correlation-functional[25] was used with a cut-off gradient correction of 5×10^{-5}. Vanderbilt ultrasoft pseudo-potentials in the CPMD package were employed together with plane-wave cutoffs of 25 Ry (340.14 eV), a time-step of 3 a.u. (0.073 fs) and a fictitious electron mass of 400 a.u. (3.644×10^{-28} kg). All MD simulations were performed in the NVT ensemble, and temperature was controlled by the Nosé thermostat for both the ions and electrons.

All the simulations were conducted within a $30\times30\times30$ Å^3 cubic simulation box. Each simulation box contained 50 molecules of H_2O+CO_2 with a CO_2 mole fraction in the range from 0.1 to 0.9 (Table 1), one Au atom and one Cl atom. The chosen system allows us to investigate the role of CO_2 in the fluid using first principle methods by a simple and tractable model, and also provides a direct comparison with available experimental data, which show that $AuCl_{(aq)}$ is the dominant species in low density, dilute Cl fluids[8, 17]. Molecular Dynamic simulations were conducted for 340 ºC and 800 ºC. The pressure of the simulation box was calculated using equations-of-state (EOS) for CO_2-H_2O mixtures at high T-P[26-28]. This provided a direct comparison between simulation and experiment as we conducted both in constant volume boxes and autoclaves, respectively. Periodic boundary conditions were applied during the simulations to eliminate surface effects. Gold(I) ions behave effectively as infinitely diluted as the distance between the Au atoms in periodic boxes is 30 Å, making Au-Au interaction are negligible. We also showed in our previous study[18] that the size of the simulation box (50 solvent molecules) is suitable: simulations of Cu(I)-Cl complexes in systems containing 55 or 110 water molecules provided hydration structures that were indistinguishable. Despite the relatively small total number of CO_2/H_2O molecules in this study, MD simulations with the box size of $30\times30\times30$ Å^3 are relatively resource-intensive.

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All the simulations were run for 29-32 picoseconds (400,000 ~ 450,000 MD steps), which is long enough to provide reasonable statistics for the structural properties, the hydration number and the solvent environment as demonstrated in our previous study[18]. More than two million CPU hours were used to conduct these simulations. The simulation systems chosen in this study provide a reasonable prediction of the structural properties and hydration within manageable CPU hours.

To compare the effect of adding CO_2 to H_2O, five simulations were conducted for 340 ºC with the same number of H_2O molecules (15-45 H_2O) and no CO_2 molecules (Table 1) in the simulation box. In each simulation, the initial coordination of the atoms was calculated using classical MD, applying the TIP4P potential for water and the MSM3 model for CO_2[29], together with the approximated pair potentials derived from finite cluster calculations for Au–Cl and Au–O interactions[18].

The radial distribution functions (RDF) of Au-O pairs and their integrals were calculated to obtain the average coordination number (hydration number) using VMD[30]. Based on the radial distribution function plots (Fig. 1a,b) of Au-O pairs and previous MD studies of Au-Cl and Cu-Cl in low-density fluids[18], distance cut-offs of 3.0 Å and 5.0 Å were chosen to represent the first and second coordination shell, respectively.

2.2 Solubility experiment

In order to confirm the main trends predicted by the *ab initio* MD simulations, a limited set of experiments were conducted to determine Au solubility in HCl-CO_2-H_2O vapor at 340 ºC. The experiments were performed in titanium autoclaves, and the experimental and analytical techniques were similar to those employed in previous experimental studies of metal solubility in water vapor[16-17]. The experimental procedures will only be described

briefly and readers are referred to these papers for further details. For each experiment, the titanium autoclaves were loaded with ~ 0.5 g of 0.01 mol/kg HCl solution, a gold wire and MoO_2(s)/Mo_2O_3(s) (oxygen buffer) placed in separate quartz tubes, and a piece of dry ice (CO_2 solid). The precise amount of CO_2 in the cell was determined by weighing the cell before and after loading the dry ice, and is reported as a mole fraction in Table 2, together with other compositional data for the fluids. Experimental conditions were selected to ensure that the system was in the vapor state at 340 ºC. The total pressure was estimated using the equation of state for H_2O-CO_2 mixtures[26] from the known autoclave volume and the mass of H_2O+CO_2. The H_2O fugacity was calculated using the fugacity coefficients from the HCh database[31].

The experiments were run for 14 days to ensure that they reached equilibrium. Based on kinetic experiments at 300 ºC[16], equilibrium occurred in less than 10 days. The autoclaves were then quenched in a water bath before opening, and the condensates were collected and the autoclaves washed with a known amount (~ 5 ml) of aqua regia. Gold concentrations were measured by Neutron Activation Analysis (NAA) to an analytical precision of 10%; the detection limit was 0.8 ppb.

3 Results

3.1 MD Results reveal the hydration structure of Au in CO_2-rich fluids

The *ab initio* MD simulations revealed a systematic change in the hydration of $AuCl_{(aq)}$ as a function of CO_2 mole fraction. In all simulations, the CO_2 exits as individual molecules. There was no evidence of CO_2 complexing with Au to form stable Au-CO_2 species nor was carbonate (i.e., H_2CO_3/HCO_3^-/CO_3^{2-}) observed in the simulations (Fig, A1). For 340 ºC, most

of the MD simulations (X_{CO_2} = 0.1-0.8) predicted a distorted linear first-shell cluster, $[AuCl(H_2O)]^0$, with an Au-Cl bond-length of 2.22 Å, consistent with results of previous X-ray absorption spectroscopic and theoretical studies[18, 32-33]. The Au-O RDF (Radial Distribution Function) plots (Fig. 1a) show that the length of the Au-O bond in the $[AuCl(H_2O)]^0$ clusters increases with increasing CO_2 mole fraction from 2.12 Å at X_{CO_2} = 0.1 to 2.17 Å at X_{CO_2} = 0.8. When X_{CO_2} reached 0.86, the water molecule in the $[AuCl(H_2O)]^0$ cluster dissociated and formed an anhydrous complex, $[AuCl]^0$.

For 800 ºC, and X_{CO_2} = 0.1-0.5, the simulations yielded a linear first-shell cluster, $[AuCl(H_2O)]^0$, with an Au-O bond-length of 2.17-2.18 Å, *i.e.*, slightly longer than at 340 ºC (Fig. 1a,b). When X_{CO_2} reached 0.6, the bonding between Au and H_2O became less stable; a weak bond with a length of 2.0-2.8 Å was present, and corresponded to a first shell hydration number of 0.51 for a cutoff distance of 3.0 Å. With increasing X_{CO_2}, the proportion of the anhydrous complex, $[AuCl]^0$ (*e.g.*, Fig. 1d) increased; this species was dominant at X_{CO_2} = 0.7, and reached a proportion of 99% at X_{CO_2} = 0.9.

The MD simulations also revealed changes in the number of water molecules in the second coordination shell as a function of X_{CO_2}. For example, at 340 ºC, the small peak at a distance of 3-5 Å (Fig. 1a) corresponds to the second hydration shell of the Au-Cl clusters, and indicates the interaction between the first shell $[AuCl(H_2O)]^0$ cluster and water molecules in the solvent. The second H_2O shell (peak B in Fig. 1) is weakly bonded to the $[AuCl(H_2O)]^0$ cluster by H-bonds involving H_2O in the $[AuCl(H_2O)]^0$ cluster.

The simulations predict a decrease in first and second shell hydration with increasing CO_2 mole fraction (X_{CO_2}) at both 340 ºC and 800 ºC (Fig. 2); however, the 800 ºC simulations yielded less hydration than at 340 ºC at the same X_{CO_2}. The dry $[AuCl]^0$ cluster became the

dominant species for X_{CO_2} >0.8 at 340 ºC, and X_{CO_2}>0.6 at 800 ºC, showing that dehydration is easier at higher temperature (Fig. 2a). The first and second shell hydration illustrated in Fig. 2b indicates that the hydration number decreases with increasing X_{CO_2}, producing a good linear correlation for 340 ºC (R^2=0.90) and 800 ºC (R^2=0.88). The first and second shell hydration number at 800 ºC decreased significantly compared to that at 340 ºC. At 340 ºC, X_{CO_2}= 0.1, there were 3.7 water molecules (1 in the first shell and 2.7 in the second shell) surrounding Au (5 Å cutoff), whereas at 800 ºC, this number decreased to 1.8 (1 in the first shell, 0.8 in the second shell).

We also conducted simulations with the same number of water molecules but without CO_2 at 340 ºC to test for differences in $AuCl^0$ hydration. The same trend of increasing hydration with increasing number of H_2O molecules in the simulation box was found regardless of whether the simulation box contained only H_2O or a mixture of H_2O+CO_2 (Fig. 3a). Such a trend was described for low-density H_2O-only fluids in our previous study[18]. However, the hydration numbers were slightly larger in the CO_2-H_2O mixed systems than in the H_2O-only systems for the same numbers of H_2O in the simulation box (Fig. 3b). Although the non-polar CO_2 molecule plays a less active role in ion hydration than the polar H_2O molecule, the steric effects of the CO_2 molecule resulted in slightly larger hydration numbers for mixed CO_2-H_2O mixed fluids at similar 'water density'. In other words, CO_2 appears to increase the clustering of waters around the $AuCl_{(aq)}$ moiety.

3.2 Solubility experiments

The results of Au solubility measurements in HCl-CO_2-H_2O vapor with CO_2 mole fractions ranging from 0.4 to 0.84 are shown in Fig. 4. The measured solubility, expressed in terms of Au mole fractions, decreased with increasing CO_2 mole fraction (Table 2). The measured Au concentrations in our experiments, however, are very close to the detection

limit of 0.8 ppb and three data points are similar within quoted uncertainties (Fig. 4). The results are also plotted as a function of water fugacity together with the Au solubility data in CO_2-free HCl-H_2O vapor at 340 ºC reported by Hurtig and Williams-Jones[17]. These results show that, for similar water fugacity and pH conditions, our solubility results in CO_2 bearing vapor are similar to the values of CO_2-free water vapor by Hurtig and Williams-Jone[17] (Fig. 4b), suggesting that adding CO_2 does not enhance Au solubility.

4 Discussion and conclusions

Our MD simulations show that H_2O, a polar molecule, plays a much more active role than the non-polar CO_2 molecule in Au speciation in low-density H_2O-CO_2 fluids. The CO_2 molecule did not bind with the Au-Cl species, and the hydration number increased with increasing mole fraction of water in the vapor. The number of H_2O molecules reached a maximum of 3.7 in the first and second coordination shells of $AuCl_{(aq)}$ for the highest H_2O/CO_2 ratio (10:1) at 340 ºC. This is consistent with the range of hydration number (1-10) at the same temperature determined experimentally by Hurtig and Williams-Jones[17]. Our results also agree with those of a X-ray absorption study[11], which measured a 22% decrease in the hydration number of rubidium bromide in CO_2-bearing (up to 0.15 mole fraction) relative to CO_2-free solutions at 445 ºC. In our previous studies, we also demonstrated that hydration of Cu(I) and Au(I) chloride species is dependent on the density of water, *i.e.*, hydration decreases with decreasing fluid density[18].

The new MD simulations explain the solubility behavior of Au in both the CO_2-bearing vapor of this study, and previous CO_2-free vapor experimental studies[16-17]. The simulations demonstrate that hydration is the key control of Au speciation and solubility in CO_2-HCl-H_2O vapor, and that CO_2 has a negative effect on Au solubility as Au(I)-Cl species in high T-P vapors, *e.g.*, volcanic gases, because of the dehydration of the $AuCl_{(aq)}$ complex. The negative

trend in solubility with increasing CO_2 mole fraction has been reported for the solubility of AgCl in dense H_2O-CO_2 mixtures at 400 ºC and 600-100 bar[8], and for Au in H_2O-CO_2 mixtures at 450 ºC and 600-700 bar[15].

Normally, the changes in hydration around Au, Cu and Ag chloride species are attributed to the decrease in the dielectric constant with increasing CO_2 mole fraction, following the Born equation that relates solvation energy to the dielectric constant of the solvent[8]. However, this simple macroscopic approach does not account for the increase in solubility of Fe, Zn and Sn minerals in CO_2-bearing aqueous fluids relative to CO_2-free aqueous fluids[14]. We propose that, at the molecular level, the change in translational entropy is the driving force behind the hydration number change as a function of CO_2 mole fraction in the vapor, similar to hydration behavior of Au(I) and Cu(I) complexes in low density water[18], and that this explains the different solubility behavior of Au and base metals such as Zn. Consider the dehydration reaction for Au-chloride (Eq 1) and Zn-chloride complexes[23] (Eq 2a, b):

$$[AuCl(H_2O)_n]^0 = [AuCl(H_2O)_{n-m}]^0 + mH_2O \quad (1)$$

$$[Zn(H_2O)_4]^{2+} + [Cl(H_2O)_6]^- = [Zn(H_2O)_3(Cl(H_2O)_5)]^+ + 2H_2O \quad (2a)$$

$$[Zn(H_2O)_3(Cl(H_2O)_5)]^+ + [Cl(H_2O)_6]^- = [Zn(H_2O)_2(Cl(H_2O)_5)_2]^0 + 2H_2O \quad (2b)$$

With an increase in the proportion of CO_2, the fugacity of water decreases and therefore water is released from both the Au and Zn chloride complexes. As a result, the entropy of the system increases, driving both reactions (Eq 1 and 2) towards the right hand side. For the Au system (Eq. 1), this causes Au solubility to decrease, as shown experimentally for Au[17], Ag[34] and Cu[12] in HCl-bearing vapor. In contrast, for Zn(II) (Eq. 2), this transition of the dehydration and replacement of water by chloride causes an increase in the stability constants

for the higher order chloride complexes (see data compiled for many transition metals[35]) and there is a corresponding increase in Zn mineral solubility.

Ultimately, the fundamental difference in the behavior of the univalent metals (*e.g.*, Au, Cu and Ag) and the divalent transition metals (*e.g.*, Zn, Fe and Ni) lies in the different electronic configurations of Au(I)/Cu(I)/Ag(I) and the first-row divalent metal ions. We attribute this contrasting behavior to the differences in coordination chemistry and affinity of chloride/bisulfide ligands for different coordination geometries. With a $d^{10}s^{1}$ configuration for Cu/Ag/Au, the linear structure of Cu(I)/Ag(I)/Au(I) complexes remains unchanged and involves a maximum of two first-shell ligands (e.g., the linear L-M-L complex, where M = Cu^{+}, Ag^{+}, Au^{+}; L = Cl^{-}, HS^{-}, H_2O) over a wide range of P-T conditions, salinity, and CO_2 contents[20, 32-33, 36-38]. A decrease in density or increase in CO_2 content will not change the geometry and the number of ligands in the first shell. In contrast, the complexes of other first-row divalent transition metal ions (*e.g.*, Zn(II)[22-23, 39], Fe(II)[40], Ni(II)[41], Mn(II)[42]) undergo entropy-driven geometric changes (octahedral to tetrahedral/trigonal planar) with increasing T, decreasing pressure or density, or decreasing water activity[38]. Adding CO_2 to high-density chloride solutions will promote a decrease in coordination number, which will promote the solubility of the minerals of these first-row divalent metals (as observed by Kokh et al[14]). The decrease in coordination number promotes the solubility of the minerals of these first-row divalent metals because of the increased stability of the corresponding tetrahedral/trigonal planar metal-chloride complexes.

Hence, the contrast between the coordination structure of Cu(I)/Ag(I)/Au(I) and that of the divalent metals (Fe(II) and Zn(II)) helps explain why Cu/Au/Ag behave differently from other transition metals in magmatic hydrothermal fluids. In the case of Au, the subject of this paper, the linear coordination structure of the Au-Cl species ensures that hydration and thus

Au solubility will decrease with increasing X_{CO_2}. Thus the main role of CO_2 addition to an auriferous fluid will be to reduce Au solubility and, for porphyry-epithermal systems, the episodic fluxing of CO_2 from a degassing magma into the overlying hydrothermal system could be a key control of gold ore deposition, as recently demonstrated for copper[13].

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Table 1. Simulation details for $AuCl^0$ in CO_2-H_2O and H_2O-only fluids. Each simulation was performed in a 30 x 30 x 30 $Å^3$ cubic box.

Temperature and composition	No. of CO_2	No. of H_2O	X_{CO_2}	fH_2O (bar)	No. of $AuCl^0$	Density (g/cm^3)	Simulation time (ps)	Pressure (bar)	1st shell* hydration	2nd shell* hydration
340 ºC 1 $AuCl^0$, CO_2+H_2O	45	5	0.9	10.5	1	0.1273	31.03	152.9[a]	0.04	0.20
	43	7	0.86	14.7	1	0.1241	30.88	151.9[a]	0.10	0.18
	40	10	0.8	20.9	1	0.1194	31.17	150.5[a]	1.00	1.09
	35	15	0.7	31.4	1	0.1114	31.17	147.6[a]	1.02	2.09
	25	25	0.5	51.1	1	0.0954	29.22	140.1[a]	1.01	2.80
	15	35	0.3	68.4	1	0.0794	29.79	130.5[a]	1.01	3.40
	5	45	0.1	82.7	1	0.0634	29.04	118.9[a]	1.04	3.73
800 ºC 1 $AuCl^0$, CO_2+H_2O	45	5	0.9	28.0	1	0.1273	29.58	291[c]	0.01	0.07
	35	15	0.7	81.0	1	0.1114	30.15	284[c]	0.18	0.49
	30	20	0.6	107	1	0.1034	29.24	281[c]	0.51	0.96
	25	25	0.5	132	1	0.0954	29.55	279[c]	1.01	1.50
	15	35	0.3	181	1	0.0794	30.11	271[c]	1.02	1.69
	5	45	0.1	231	1	0.0634	29.41	265[c]	1.02	1.75
340 ºC 1 $AuCl^0$, H_2O only	0	50	0	88.3	1	0.0554	32.07	112.4[b]	1.02	3.35
	0	45	0	83.9	1	0.0499	30.63	104.8[b]	1.02	3.57
	0	35	0	73.2	1	0.0388	31.78	87.7[b]	1.03	3.14
	0	25	0	58.6	1	0.0277	32.18	67.0[b]	1.02	1.97
	0	15	0	39.4	1	0.0166	31.20	42.9[b]	1.02	1.77

[a,b,c]Pressure was calculated from: a. the equation of state for H_2O-CO_2 mixtures of Hu *et al.*[27]; b. the NIST water chemistry database[28]; and c. Duan and Zhang[26].

*Distance cutoffs for the 1st and 2nd shell hydration were set at 3.0 Å and 5.0 Å, respectively[18].

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Table 2. Results of Au solubility experiments in CO_2-HCl-H_2O fluids at 340 ºC. Density was estimated using the measured cell volume and total sample weight. Pressure was calculated with the equation of state for CO_2-H_2O mixtures[26]. Mole fractions (X) refer to the ratio of the subscripted component to the total number of moles of H_2O + CO_2 + HCl. The H_2O fugacity was calculated using the fugacity coefficients from the HCh database[31].

X_{CO_2}	log $f$$H_2O$ (bar)	Density (g/cm^3)	Pressure (bar)	$logX_{HCl}$	Au (ppb)	logX_{Au}
0.84	1.22	0.1358	174.0	-4.39	2.0	-9.41
0.67	1.43	0.0713	105.5	-4.11	2.9	-9.32
0.54	1.48	0.0481	79.35	-3.99	4.2	-9.20
0.44	1.46	0.0320	58.09	-3.92	12.4	-8.78

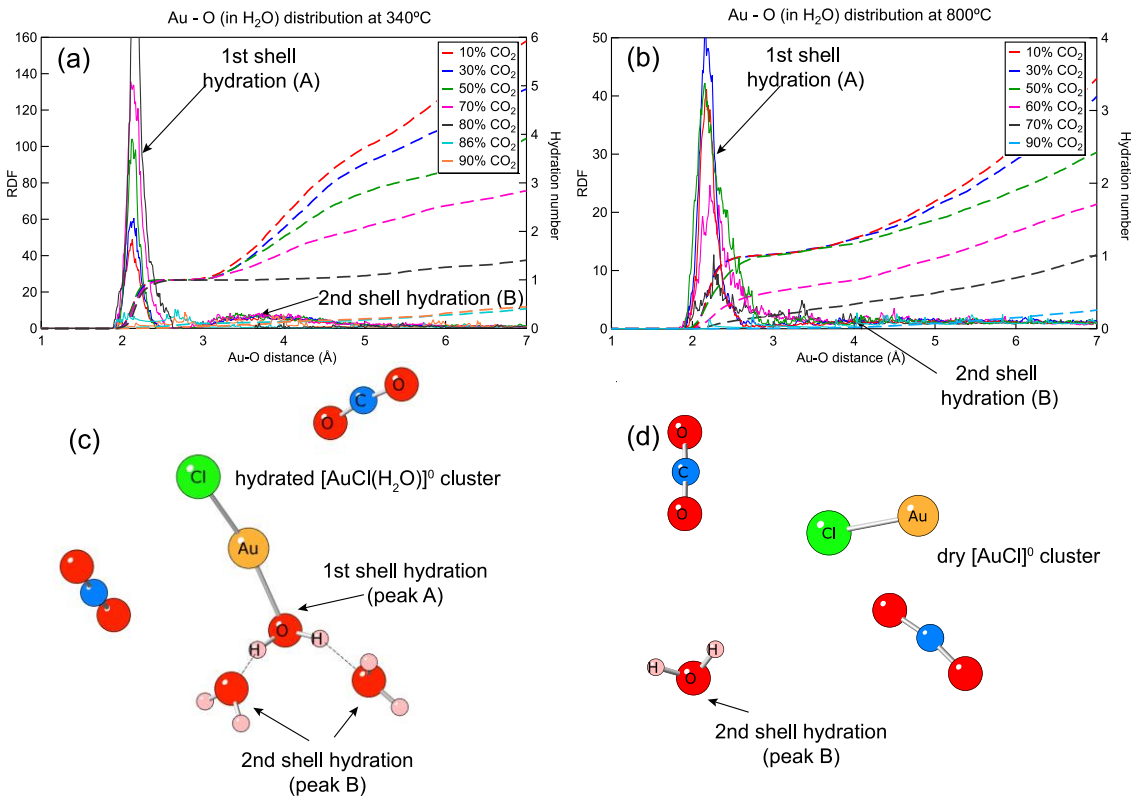

Figure 1. Radial distribution function (RDF, solid lines) and the hydration number (dash lines) of the Au-O pair at (a) 340 ºC and (b) 800 ºC with different X_{CO_2}; the snapshots of MD simulations (c) at 340 ºC, X_{CO_2} = 0.5 and (d) at 800 ºC, X_{CO_2} = 0.9 show the $AuCl_{(aq)}$ and the hydration shell.

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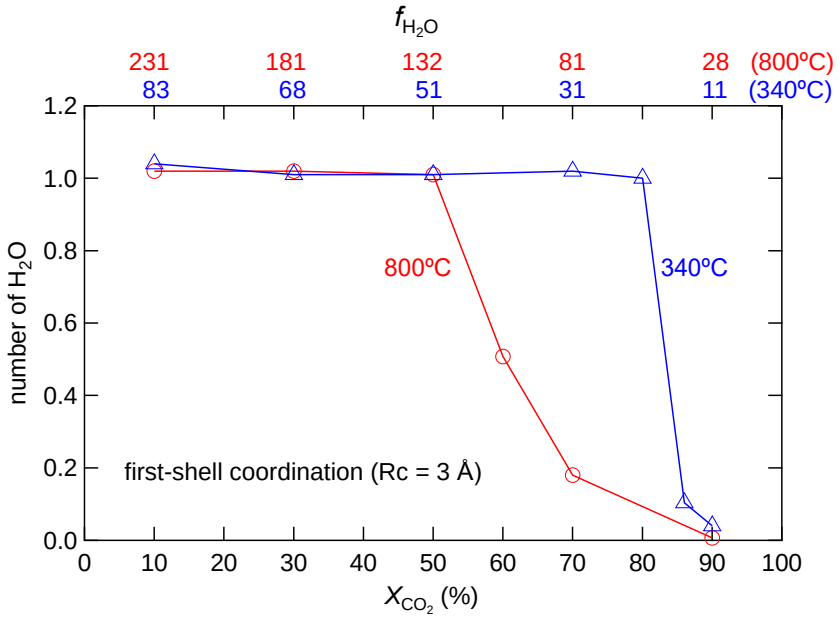
(a)



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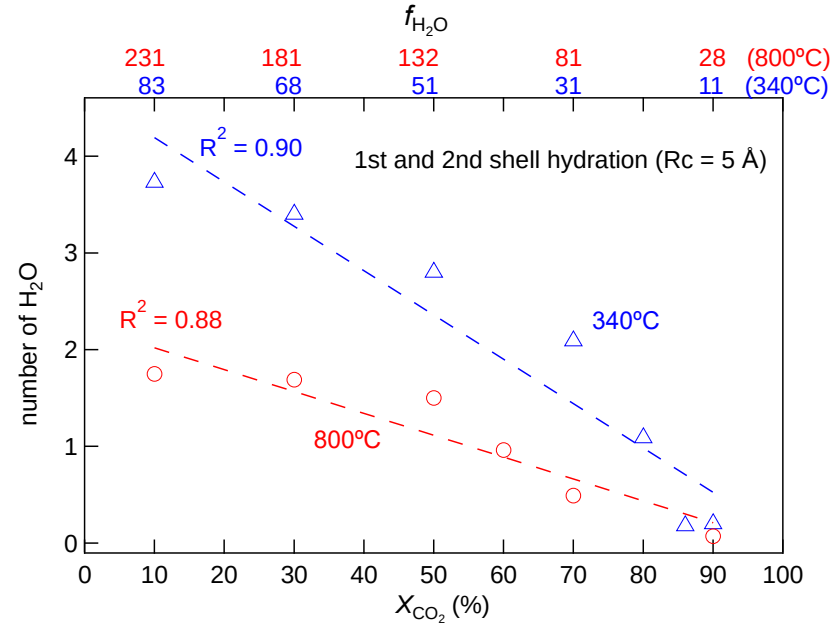

Figure 2. First shell (a) and second shell (b) hydration of Au-Cl clusters as a function of X_{CO_2} and X_{H_2O} at 340 ºC (blue, triangles) and 800 ºC (red, circles). The solution compositions are reported in Table 1.

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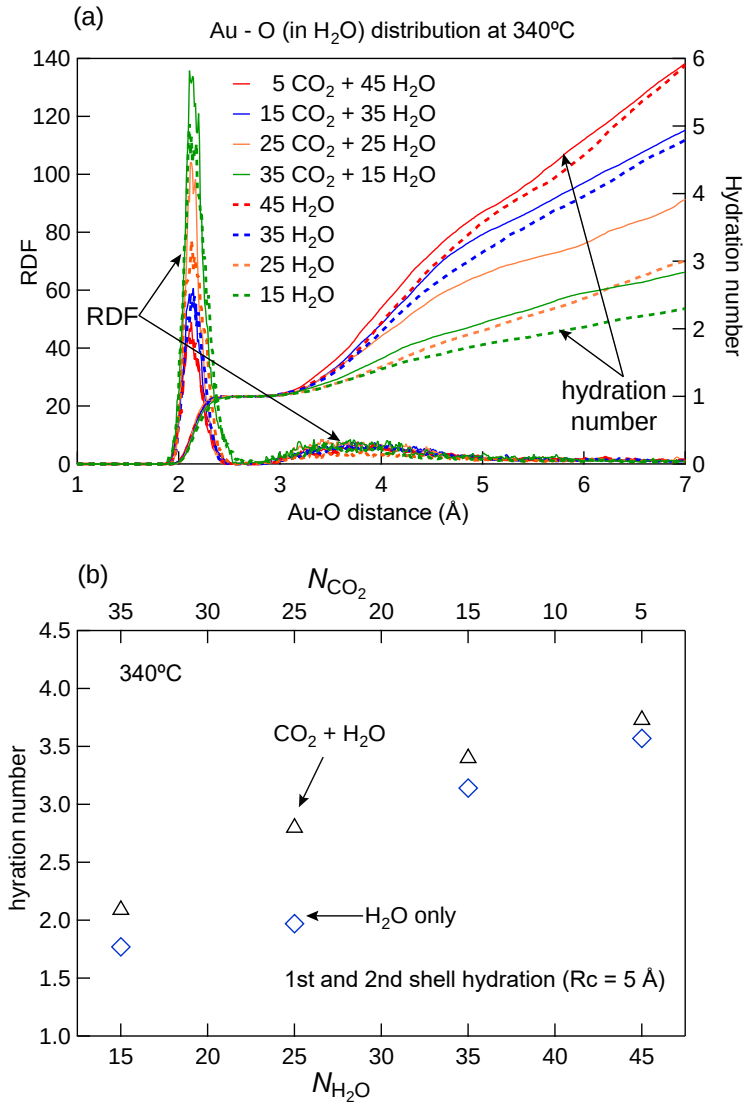

Figure 3. (a) RDF plots and (b) hydration number of $AuCl_{(aq)}$ for MD simulations of mixed CO_2-H_2O and H_2O-only systems at 340 ºC and a box size of 30 $Å^3$.

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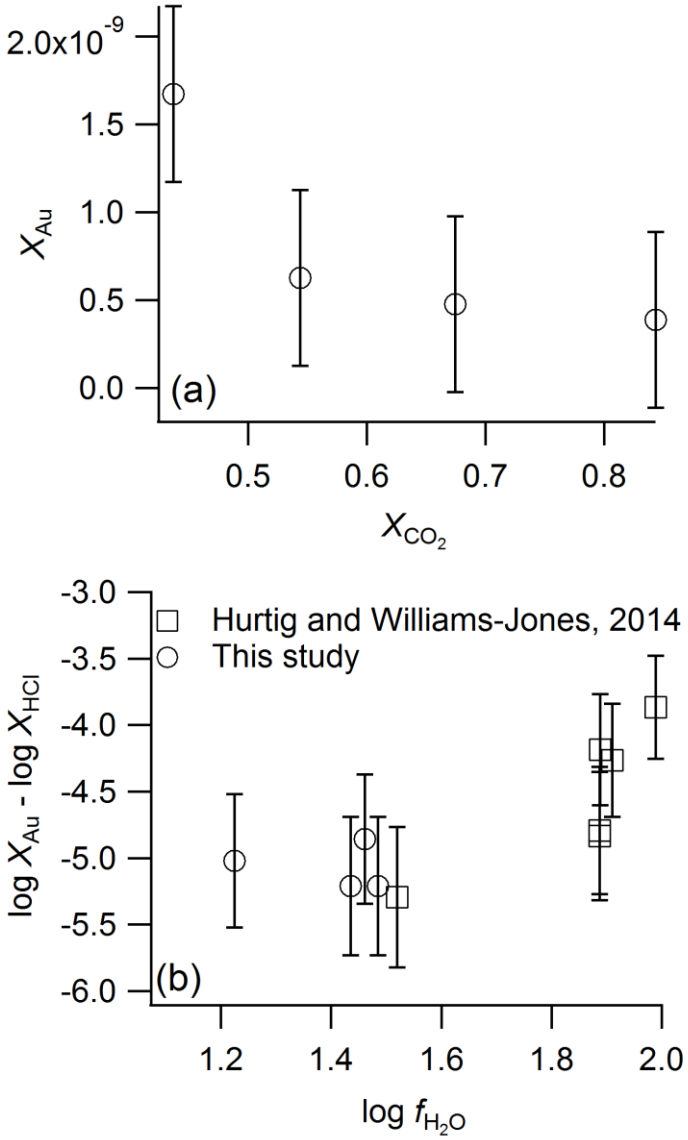

Figure 4. (a) Mole fraction of dissolved gold as a function of CO_2 mole fraction in CO_2-HCl-H_2O vapor at 340 ºC. (See Table 1 for solution compositions). (b) Gold solubility normalized to HCl mole fraction as a function of the logarithm of water fugacity. Values of gold solubility in HCl-H_2O vapor[17] are plotted for comparison.

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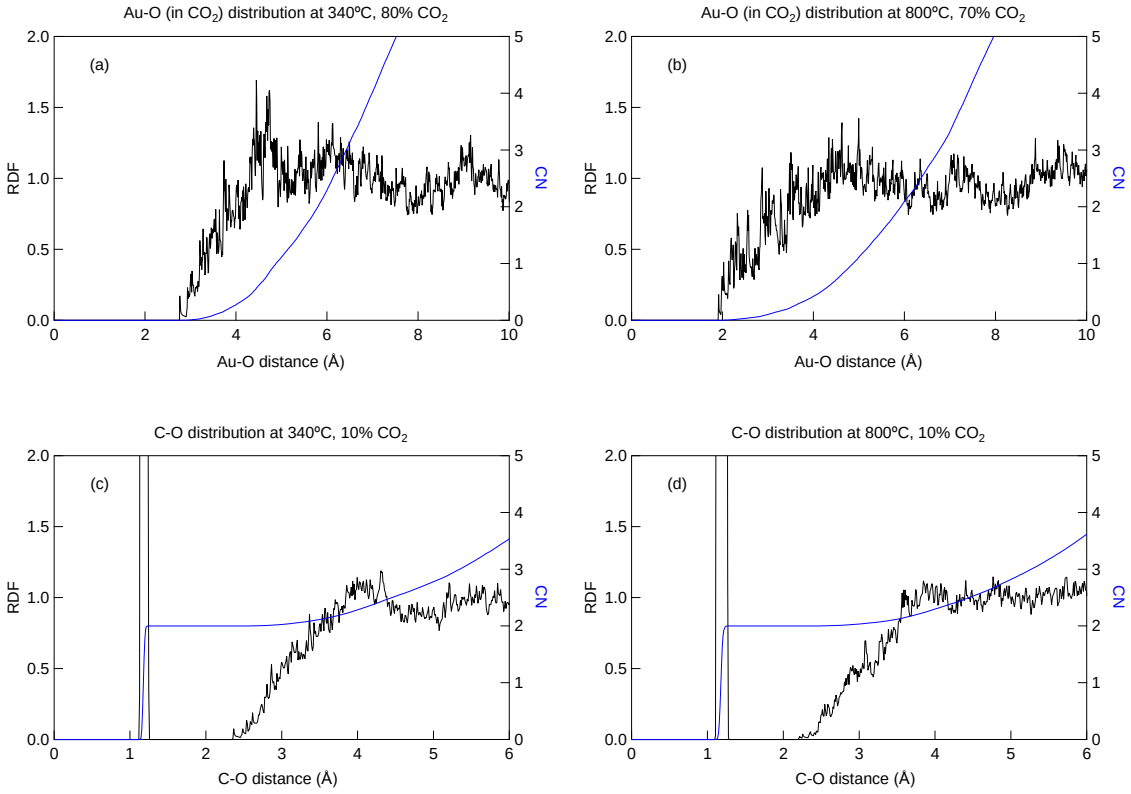

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446 Figure A1. RDF plot (black lines, left axis) and coordination number (CN, blue lines, right
447 axis) of (a) Au-O (O in CO_2) pair at 340ºC, 80% CO_2; (b) Au-O (O in CO_2) pair at 800ºC,
448 70% CO_2; (c) C-O pair at 340ºC, 10% CO_2; (d) C-O pair at 800ºC, 10% CO_2. Figs a,b show
449 that there is no bond between Au and O in CO_2 as there is no obvious peak between 2-3 Å.
450 The CN curves in Fig a,b show that within 3Å, there are less than 0.1 oxygens from CO_2
451 molecules surrounding Au (less than 0.05 CO_2 surrounding Au), indicating that there was no
452 complexation between Au and CO_2. As shown in Figs c,d, the CN of the C-O pair within 2 Å
453 is two; indicating that CO_2 is the only carbon species, and there is no $H_2CO_3/HCO_3^-/CO_3^{2-}$ in
454 the simulation.

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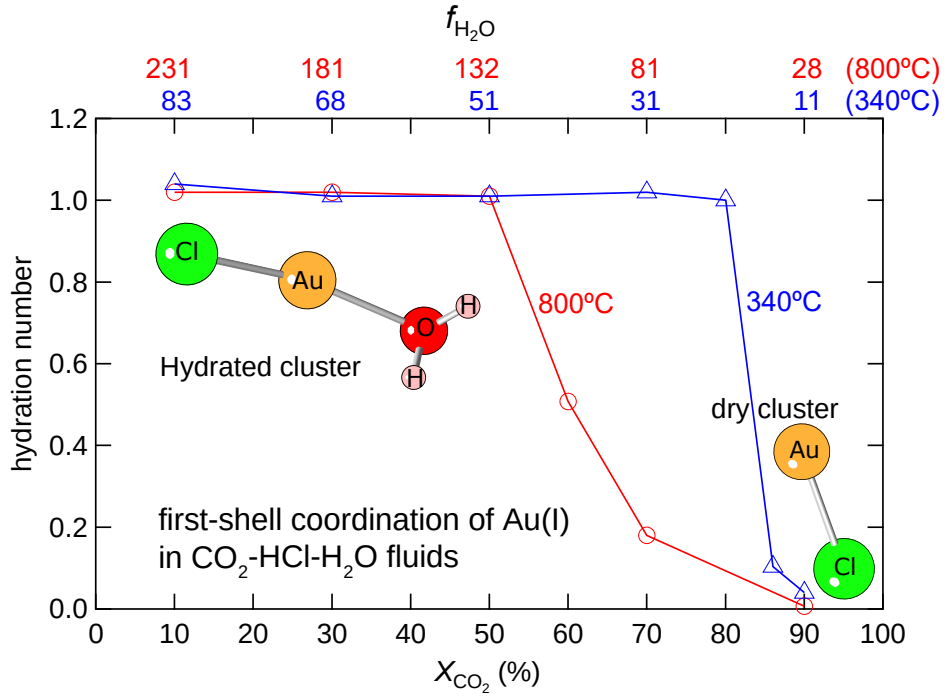

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