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ORIGINAL PAPER

Impact of Alkaline Earth Metals on Aqueous Speciation of Uranium(VI) and Sorption on Quartz

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Abstract The effect of Mg-, Ca-, and Sr–Uranyl-Carbonato complexes with respect to sorption on quartz was studied by means of batch experiments with U(VI) concentration of 0.126×10^{-6} M in the presence and absence of Mg, Ca, and Sr (each 1 mM) at pH from 6.5 to 9. In the absence of alkaline earth elements, 90% of the U(VI) sorbed on the quartz surface at all pH. In the presence of Mg, Ca, and Sr, the sorption of U(VI) on quartz decreased to 50, 10, and 30%, respectively. Sorption kinetics of U(VI) on quartz is faster in the absence of alkaline earth elements and reached equilibrium after 12 h, whereas in the presence of Mg, Ca and Sr, the kinetics of U(VI) sorption on quartz is pH dependent and attained equilibrium after 24 h. Aqueous speciation calculations for alkaline earth uranyl carbonates were carried out by using PHREEQC with the Nuclear Energy Agency thermodynamic database (NEA_2007) by adding constants for $MUO_2(CO_3)_3^{2-}$ and $M_2UO_2(CO_3)_3^0$ (M = Ca, Mg, Sr). This study reveals that alkaline earth elements can have a significant effect on the aqueous speciation of U(VI) under neutral to alkaline pH conditions and subsequently sorption behavior and mobility of U(VI) in aqueous environments.

Keywords Uranium(VI) · Alkaline earth elements · Sorption · Alkaline earth uranyl carbonates · Quartz

1 Introduction

Uranium is an ubiquitous element in rocks, soil, and water. Besides natural occurrence, it is distributed in the environment by means of fertilization (Barisic et al. 1992), coal combustion (Papp et al. 2002; Kumar et al. 2005), mining activities (Meinrath et al. 1999; Merkel et al. 2002; Merkel and Hasche-Berger 2005), and nuclear industry. According to the concept of disposing burnt nuclear fuel in deep waste repositories in suitable host rocks,

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the risk of migration of uranium back to the biosphere has to be investigated by means of risk assessment studies. Since the mobility of uranium in water is strongly dependent on uranium speciation, it is important to know the dominant uranium species, in order to predict the distribution and migration behavior. The major controlling factors of uranium speciation are pH, ionic strength, redox potential, availability of organic and inorganic ligands, formation of colloids, solubility product of limiting minerals, and kinds of interfaces during the interaction process of solved and sorbed complexes (Bernhard 2005). In circumneutral to alkaline pH, the mobility of U(VI) in aquifers is mainly determined by the formation of uranyl carbonate complexes, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Hsi and Langmuir 1985; Pabalan et al. 1996), if no alkaline earth metals are present.

However, ternary complexes of alkaline earth uranyl carbonates may play an important role in the environmental chemistry of uranium. The $Ca_2UO_2(CO_3)_3^0$ was first reported by Bernhard et al. (Bernhard et al. 1996). Further studies of the calcium uranyl carbonate complexes introduced the $CaUO_2(CO_3)_3^{2-}$ complex and showed that they play an important role in the aqueous chemistry of U(VI) at neutral to alkaline pH range (Kalmykov and Choppin 2000; Bernhard et al. 2001; Zheng et al. 2003). Kelly et al. (2007) noticed the limited and slow bioreduction of U(VI) in the presence of calcium and the formation of calcium uranyl carbonate complexes. In circumneutral pH range, U(VI) sorption in calcareous soils is strongly influenced by calcium uranyl carbonate complexes (Zheng et al. 2003). Because the concentration of Mg is high in many uranium mill tailing sites, especially in carbonate rich terrain (Abdelouas et al. 1998), the formation of magnesium uranyl carbonate complexes may have an impact on the uranium migration behavior as well. ^{90}Sr is a by-product of nuclear fission and is deposited in significant quantities in nuclear waste repositories. The beta emitter ^{90}Sr is a major pollutant together with U in the Hanford nuclear test site (USA), and other areas subjected by nuclear incidents (Standring et al. 2002; Smith et al. 2004).

Geipel et al. (2008) suggested the formation of $MgUO_2(CO_3)_3^{2-}$ as well as $Mg_2UO_2(CO3)_3^0$ on results using time-resolved laser-induced fluorescence spectroscopy (TRLFS) without, however, reporting formation constant for $Mg_2UO_2(CO3)_3^0$. Dong and Brooks (2006, 2008) determined formation constant for $MgUO_2(CO_3)_3^{2-}$ using an anion exchange method. The formation of strontium uranyl carbonates were investigated and discussed, and formation constants were reported using anion exchange method (Dong and Brooks 2006), respectively, TRLFS (Geipel et al. 2008).

In natural environments, migration of radionuclide is often controlled by sorption on minerals present along the seepage and groundwater flow path. Thus, it is important to know sorption behavior in the subsurface to evaluate the suitability of geologic repositories for nuclear waste materials or the long term behavior of uranium mining and milling sites. Sorption behavior of various metal ions can be modeled by surface complexation models (SCM) which is a valuable tool to simulate and predict radionuclide migration under natural conditions. SCM depicts the equilibrium between aqueous chemical species and the surface species formed at the mineral surfaces, surface complexes, using mass action equations and can be integrated within reactive transport models (Kohler et al. 1996; Curtis et al. 2006). Quartz is a common mineral phase present in the earth's crust as well as one of the essential minerals in granitic rock which is one of the possible host rocks for the construction of repositories for nuclear waste. The sorption of U(VI) on quartz as well as the formation and structure of uranyl surface species on silica were studied and discussed elsewhere (Lieser et al. 1992; Sylwester et al. 2000; Gabriel et al. 2001; Prikryl et al. 2001; Stamberg et al. 2003).

Objectives of this study were to test whether alkaline earth metals are influencing the sorption of U(VI) on quartz and whether this can be taken as an additional proof for the existence of alkaline earth uranyl carbonate complexes and the need to take these formation constants into account for future risk assessment studies. One side aspect was the investigation into the kinetics of the sorption behavior.

2 Materials and Methods

2.1 Solid and Solution Preparation

Quartz sand F32 was obtained from Quarzwerke Frechen, Germany. The sand has an average grain size of 0.24 mm and a specific theoretical surface area of 102 cm^2/g. The XRD characterization revealed 98.6 ± 0.26% quartz and 1.4 ± 0.26% calcite. Additional chemical analysis shows 99.7% SiO_2, 0.2% Al_2O_3, and 0.03% Fe_2O_3. Calcite and iron oxides were removed by washing several times with diluted (1:10) 65% nitric acid for more than 1 day, then thoroughly rinsed with deionized water and air-dried. An U(VI) stock solution (0.126×10^{-6} M) was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (Chemapol, Czech Republic) dissolved in deionized and purified water (TKA, Germany). To avoid precipitation or sorption of U(VI), the water was pre-acidified with HNO_3 to pH 2.5. Solutions of 1×10^{-3} M calcium chloride, strontium chloride, magnesium chloride, and sodium hydrogen carbonate were prepared by dissolving $CaCl_2 \cdot 6H_2O$ (Aldrich, Germany), $SrCl_2 \cdot 6H_2O$ (VEB, Germany), $MgCl_2 \cdot 6H_2O$ (Fluka, Germany), and $NaHCO_3$ (Merck, Germany) in appropriate volume of deionized and purified water. All chemicals used were of ACS reagent grade or better.

2.2 Batch Experiments

All experiments were conducted with 10 g quartz and 100 ml solution under normal laboratory conditions (temp. 23 ± 1°C) in 150 ml PTFE beakers, because a considerable amount of uranium sorption was noticed on glass wares during preliminary experiments at such low concentration of uranium at neutral to alkaline pH conditions. The PTFE beakers were covered with parafilm to prevent interaction with the atmosphere. Four sets of sorption experiments were performed with uniform uranium concentration of 0.126×10^{-6} M and 1×10^{-3} M NaHCO3 and 1.5×10^{-3} M NaCl as ionic strength buffer:

1. Only uranium and quartz
2. Uranium, calcium (1×10^{-3} M), and quartz
3. Uranium, strontium (1×10^{-3} M), and quartz
4. Uranium, magnesium (1×10^{-3} M), and quartz

All experiments were conducted at a pH range from 6.5 to 9. The pH was adjusted from 6.5 to 9 using 0.1 M NaOH/HCl, respectively. The pH electrode (EGA 142/TFK, Meinsberger, Germany) combined with pH meter (WTW GmbH, Germany) was calibrated using analogous buffer solutions. All experiments were modeled in advance using the geochemical speciation code PHREEQC (Parkhurst and Appelo 1999) with the Nuclear Energy Agency thermodynamic database NEA_2007 (Grenthe et al. 2007) with the intention to avoid over-saturation of any mineral phases during the experiments.

The experiments were performed for a period of 48 h using a magnetic stirrer (IAK, Germany) to obtain steady contact of the solution with the solid throughout the experiments. Samples were collected at a time interval of 1, 3, 6, 12, 24, and 48 h and at the same intervals pH were read. Uranium was determined immediately after sampling by differential pulse adsorptive cathodic stripping voltammetry (797 Va Computrace, Metrohm, Switzerland) using a hanging mercury drop electrode (HMDE) as reference electrode (Benedikt 2007). The detection limit of the method is 0.1 μg/L.

The percentage of U(VI) sorption on quartz was calculated from the difference between initial and final U(VI) concentration using the Eq. 1:

$$\text{Sorption}\,(\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \tag{1}$$

where Ci and Cf are the initial and final U(VI) concentrations in the solution. All the experiments were carried out in duplicates, and the percentage of error was less than ±5.

Apart from the above said four main sets of experiments, we conducted supplementary experiments in the absence of uranium and thus containing only Mg/Ca/Sr (1×10^{-3} M) with quartz to investigate the sorption behavior of alkaline earth elements on quartz. The experimental procedure was as above and the collected samples were analyzed for alkaline earth elements using ICP-MS (XSeries 2, Thermo Fisher Scientific).

2.3 Data Evaluation

A couple of studies about the formation and evaluation of alkaline earth uranyl carbonate complexes have been performed and published. Dong and Brooks (2006, 2008) suggested the formation constants for $M_2UO_2(CO_3)_3^0$ (M = Ca, Ba) and $MUO_2(CO_3)_3^{2-}$ (M = Mg, Ca, Sr, Ba) using anion exchange method. Instead of anion exchange method, Bernhard et al. (2001) and Geipel et al. (2008) used TRLFS to determine the formation constants of $M_2UO_2(CO_3)_3^0$ (M = Ca, Sr, Ba) and $MUO_2(CO_3)_3^{2-}$ (M = Mg, Ca, Sr, Ba). The latter research group was able to calculate log K value for $Sr_2UO_2(CO_3)_3^0$. In order to compare the aqueous speciation calculation of anionic or zero-valent complexes of Mg, Ca, and Sr, calculations were done using PHREEQC with NEA_2007 database and the log K values added either from Dong and Brooks (2006) or Bernhard et al. (2001) and Geipel et al. (2008) and plotted in Fig. 1a–f. Figure 1a and b comprises the aqueous speciation of magnesium uranyl carbonate complex and is showing similar behavior for both results. But there is a little difference in the nature of formation of calcium uranyl carbonate complexes as shown in (Fig. 1c, d). The major difference can be noticed in the formation of strontium uranyl carbonate complexes (Fig. 1e, f). While Bernhard and Geipel reported formation and log K values of both $Sr_2UO_2(CO_3)_3^0$ and $SrUO_2(CO_3)_3^{2-}$, Dong and Brooks reported only the formation of $SrUO_2(CO_3)_3^{2-}$.

Aqueous speciation and log K values of the aforementioned studies are summarized in Table 1. Nevertheless, the differences between the log K values suggested for the same species are negligible in the above studies (see Table 1). However, there is no valid reference for the formation constant of $Mg_2UO_2(CO_3)_3^0$ so far in the literature. The aqueous speciation calculation for the further study was performed by PHREEQC using NEA_2007 database adding formation constants taken from Dong and Brooks (2006) for ternary complexes of uranyl and carbonate with the alkaline earth elements Ca, Mg, and Sr.

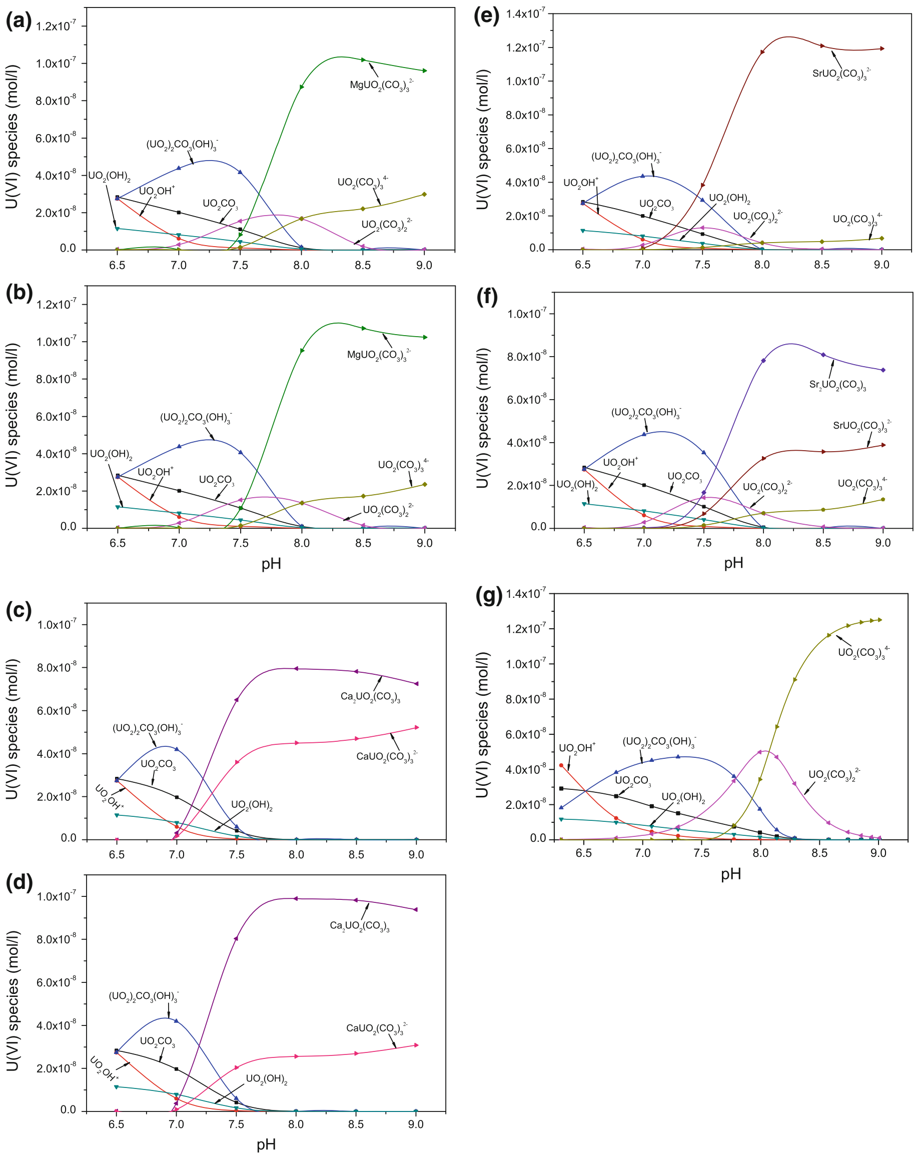

Fig. 1 Aqueous speciation calculation of Magnesium uranyl carbonate species in relation to pH using Phreeqc with NEA_2007 database and **a** log K from (Dong and Brooks 2006) and **b** log K from Geipel et al. (2008). (0.126×10^{-6} M U, 1×10^{-3} M Mg, 1×10^{-3} M $NaHCO_3$, 1.5×10^{-3} M NaCl, temperature: 23°C, pCO2: $10^{-3.5}$ hPa). Aqueous speciation calculation of Calcium uranyl carbonate species in relation to pH using Phreeqc with NEA_2007 database and **c** log K from (Dong and Brooks 2006) and **d** log K from Bernhard et al. (2001). (0.126×10^{-6} M U, 1×10^{-3} M Ca, 1×10^{-3} M $NaHCO_3$, 1.5×10^{-3} M NaCl, temperature: 23°C, pCO2: $10^{-3.5}$ hPa). Aqueous speciation calculation of strontium uranyl carbonate species in relation to pH using Phreeqc with NEA_2007 database and **e** log K from (Dong and Brooks 2006) and **f** log K from Geipel et al. (2008). (0.126×10^{-6} M U, 1×10^{-3} M Sr, 1×10^{-3} M $NaHCO_3$, 1.5×10^{-3} M NaCl, temperature: 23°C, pCO2: $10^{-3.5}$ hPa). **g** Calculated U(VI) species distribution (Phreeqc with NEA_2007 database) in relation to pH (0.126×10^{-6} M U, 1.5×10^{-3} M NaCl, 1×10^{-3} M $NaHCO_3$, temperature: 23°C, pCO2: $10^{-3.5}$ hPa)

Table 1 Aqueous speciation of U(VI) with alkaline earth metals and stability constants

Aqueous reactions	log K
1. $Mg^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = MgUO_2(CO_3)_3^{2-}$	26.11[a]
	26.24[b]
2. $2Ca^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = Ca_2UO_2(CO_3)_3^{0}$	30.7[a]
	30.79[b]
3. $Ca^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = CaUO_2(CO_3)_3^{2-}$	27.18[a]
	26.93[b]
4. $2Sr^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = Sr_2UO_2(CO_3)_3^{0}$	29.73[c]
5. $Sr^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = SrUO_2(CO_3)_3^{2-}$	26.86[a]
	26.07[c]
6. $2Ba^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = Ba_2UO_2(CO_3)_3^{0}$	29.75[a]
	29.76[c]
7. $Ba^{2+} + UO_2{}^{2+} + 3CO_3{}^{2-} = BaUO_2(CO_3)_3^{2-}$	26.68[a]
	26.16[c]

[a] Dong and Brooks (2006), [b] Bernhard et al. (2001), [c] Geipel et al. (2008)

3 Results and Discussion

3.1 Aqueous Speciation

Figure 1(a, c, e, g) shows the calculated aqueous speciation of 0.126×10^{-6} M U(VI) as a function of pH in the presence and absence of Mg, Ca, and Sr at a concentration of 1×10^{-3} M with a background electrolyte of 1.5×10^{-3} M NaCl and 1×10^{-3} M $NaHCO_3$ equilibrated with atmospheric partial pressure of CO_2 ($_PCO_2 = 10^{-3.5}$ hPa). The calculated U(VI) speciation without alkaline earth metals is shown in Fig. (1g). In equilibrium with atmospheric CO_2, uranyl carbonate complexes $(UO_2)_2CO_3(OH)^{3-}$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are the most dominant carbonate U(VI) species under neutral to alkaline pH conditions. Figure 1a illustrates the calculated effect of Mg on uranium speciation. The most dominant species in alkaline pH range is now $MgUO_2(CO_3)_3^{2-}$. Because of the uncertainty of the existence of the $Mg_2UO_2(CO_3)_3^0$ species, this complex was not taken into account for further evaluation. However, the proposed $Mg_2UO_2(CO_3)_3^0$ complex (Dong and Brooks 2006; Geipel et al. 2008) would not change (Fig. 1a) significantly because it would become significant only at high Mg concentrations.

From Fig. 1c, it becomes evident that according to the thermodynamic data of Dong and Brooks (2006), $Ca_2UO_2(CO_3)_3^0$(aq.) is the predominant complex at neutral to alkaline pH followed by $CaUO_2(CO_3)_3^{2-}$. Uranyl carbonate complexes like $(UO_2)_2CO_3(OH)^{3-}$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are considerably unimportant under the given experimental boundary conditions. The impact of Sr on uranium aqueous speciation is plotted in Fig. 1e. The $SrUO_2(CO_3)_3^{2-}$ is the most dominant species under alkaline pH conditions if the proposed $Sr_2UO_2(CO_3)_3^0$ complex (Geipel et al. 2008) is not taken into account. Using the supposed log K for $Sr_2UO_2(CO_3)_3^0$, this would become the most dominant complex (see Fig. 1f).

3.2 Kinetics

The kinetic experiments were conducted for 48 h at a pH range 6.5–9. Figure 2a–d illustrates the adsorption of U(VI) onto quartz in the presence and absence of Mg, Ca, and

Sr at the above given experimental conditions. In the absence of alkaline earth elements, rapid sorption of U(VI) onto quartz and equilibrium after 12 h more or less independent from pH (Fig. 2a) was obtained. On contrary, U(VI) sorption on quartz in the presence of Ca, Mg, and Sr is pH dependent and shows a dynamic progress. In the presence of Mg, the sorption of U(VI) reaches equilibrium after 24 h except for pH 7 and 9 showing slight desorption (Fig. 2b). In the presence of Ca, the system is less dynamic, when compared to Mg and Sr, and reaches equilibrium after 24 h (Fig. 2c). But in the presence of Sr, the system is more dynamic for the first 24 h and stable for the remaining period (Fig. 2d). Huber and Lützenkirchen noticed the dissolution of silica during sorption experiments in the alkaline pH range (Huber and Lützenkirchen 2009) which could be an explanation for this observation. On contrary, it is as well reported that dissolved or released Si do not have a major influence on the sorption of U(VI) in the pH range of 7–8.75 for the first 168 h. (Fox et al. 2006).

3.3 Sorption

Apart from the minor kinetic effects, we see a distinct pH dependency for all experiments with Mg, Ca, or Sr, while in the pure U-CO_3-system, the pH dependency is minor and

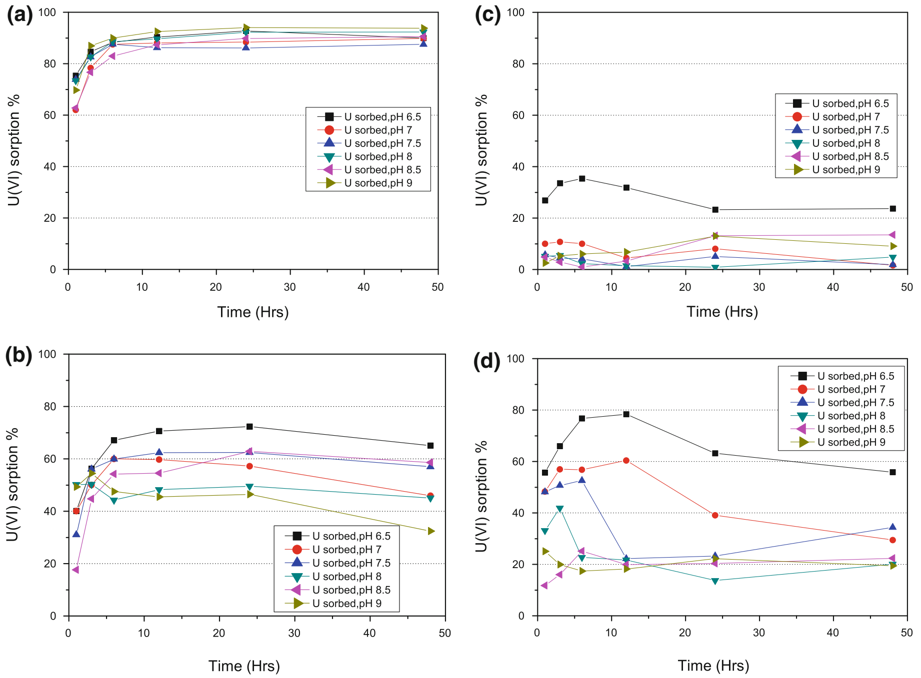

Fig. 2 **a** Kinetics of U(VI) sorption on quartz at pH 6.5–9 (0.126 × 10^{-6} M U, 1.5 × 10^{-3} M NaCl, 1 × 10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **b** Kinetics of U(VI) sorption on quartz in the presence of Mg at pH 6.5–9 (0.126 × 10^{-6} M U, 1 × 10^{-3} M Mg, 1.5 × 10^{-3} M NaCl, 1 × 10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **c** Kinetics of U(VI) sorption on quartz in the presence of Ca at pH 6.5–9 (0.126 × 10^{-6} M U, 1 × 10^{-3} M Ca, 1.5 × 10^{-3} M NaCl, 1 × 10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **d** Kinetics of U(VI) sorption on quartz in the presence of Sr at pH 6.5–9 (0.126 × 10^{-6} M U, 1 × 10^{-3} M Sr, 1.5 × 10^{-3} M NaCl, 1 × 10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa)

about 90% of the uranium is sorbed to quartz. The high sorption behavior of U(VI) independent from pH is in contradiction with previous studies (Fox et al. 2006; Davis et al. 2004; Prikryl et al. 2001) who found a decline in sorption behavior from pH 8. This difference in behavior, when compared with the above studies, is due to the very low uranium concentration (0.126×10^{-6} M) and the higher solid to solution ratio (100 g/L silica) in this study. Moreover, Stamberg et al. (2003) observed similar sorption behavior for uranium–silica system under alkaline pH conditions. For all experiments with alkaline earth metals present, the sorption is significantly less than in the absence of alkaline earth metals: about 50% for Mg, 30% for Sr, and 10% for Ca in the system (Fig. 3a–c). Competitive sorption with the alkaline earth metals can be excluded as proved by sorption experiments with solutions containing only alkaline earth metals in the absence of uranium. From Fig. 3d, it is clear that under neutral to alkaline pH conditions, the sorption of alkaline earth metals on quartz is negligible. The average sorption percentage (over all pH) for Mg, Ca, and Sr is 3, 4, and 5%, respectively. Moreover, Fox et al. (2006) noticed as well low affinity of Ca to quartz in the pH range 6–8. Thus, the formation of the anionic and zero-valent complexes of the alkaline earth metals with uranyl and carbonate explain the reduction in sorption of U(VI) on quartz. Following the argumentation of Dong and Brooks (2006, 2008) that only for Ca but not for Mg and Sr, the formation of a zero-valent

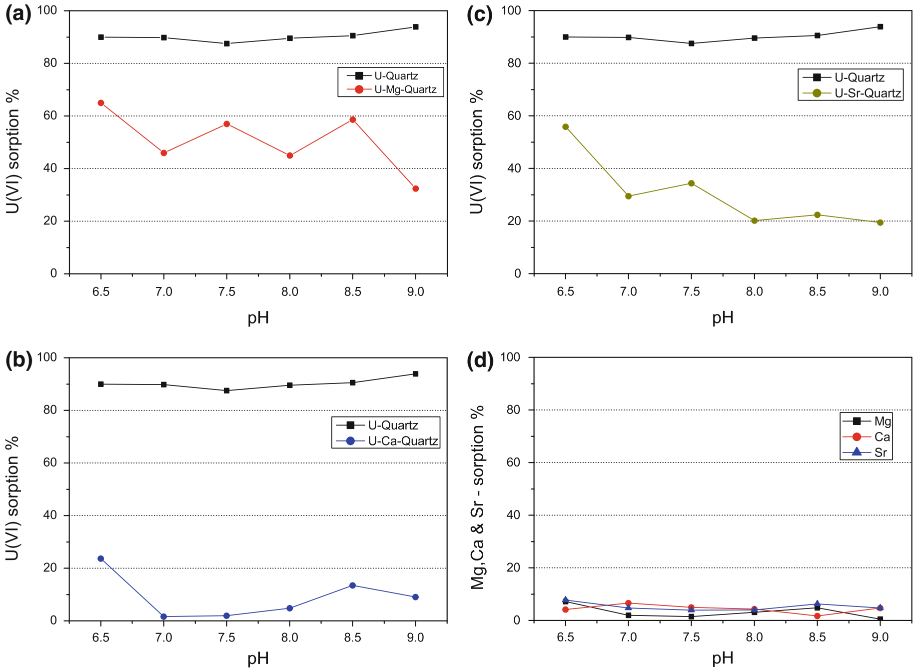

Fig. 3 **a** U(VI) sorption onto quartz as a function of pH, with and without Mg.(0.126×10^{-6} M U, Mg (1×10^{-3} M), 1.5×10^{-3} M NaCl, 1×10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **b** U(VI) sorption onto quartz as a function of pH, with and without Ca. (0.126×10^{-6} M U, Ca (1×10^{-3} M), 1.5×10^{-3} M NaCl, 1×10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **c** U(VI) sorption onto quartz as a function of pH, with and without Sr. (0.126×10^{-6} M U, Sr (1×10^{-3} M), 1.5×10^{-3} M NaCl, 1×10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa). **d** Sorption of Mg, Ca, and Sr onto quartz as a function of pH, without U(VI) (Mg, Ca, Sr (1×10^{-3} M each), 1.5×10^{-3} M NaCl, 1×10^{-3} M $NaHCO_3$, period: 48 h, 23°C, pCO2: $10^{-3.5}$ hPa)

complex is proved and this would explain that the biggest impact can be observed for Ca. In comparison at pH 9, only about 10% of Uranium is sorbed in case Ca is present and about 20% with Sr and 40% with Mg present.

In the presence of Ca, the sorption of U(VI) is reduced to 26% at pH 6.5 and to near zero at pH 7.5 and 10% at pH 9. As shown above in Fig. 1c, thermodynamic calculations suggest that the addition of Ca changes the aqueous speciation of U(VI) with the $Ca_2UO_2(CO_3)_3^0$(aq.) species which is predominant in the alkaline pH range. Retardation of U(VI) sorption in the presence of Ca at near neutral to alkaline pH range in soils are well documented (Zheng et al. 2003; Fox et al. 2006) and supports these findings.

In the presence of Mg, the U(VI) sorption on quartz decreased from 65% at pH 6.5 to 32% at pH 9 and shows varying values through out the pH range. The sorption retardation of U(VI) is due to the formation of $MgUO_2(CO_3)_3^{2-}$ (Fig. 1a) that is dominant in the alkaline pH range. In addition to this, Dong and Brooks (2008) reported the decrease in U(VI) sorption even on anion exchange resin in the presence of $MgUO_2(CO_3)_3^{2-}$, which is having less affinity to resin than $UO_2(CO_3)_3^{4-}$. Sorption of U(VI) on quartz decreased from 58% at pH 6.5 to 20% at pH 9 in the presence of Sr. From Fig. 1e, it is evident that $SrUO_2(CO_3)_3^{2-}$ is the dominant aqueous species in the alkaline pH range and thus causing the retardation in U(VI) sorption behavior.

4 Conclusions

U(VI) sorption on quartz is affected by the presence of alkaline earth elements. In the absence of alkaline earth elements, 90% of the U(VI) sorbed on the quartz surface at a pH range 6.5–9. In the presence of Mg, Ca, and Sr, the sorption of U(VI) on quartz decreased significantly. This sorption retardation is an indication of the influence and the existence of alkaline earth uranyl carbonate complexes. Moreover, the aqueous speciation calculation of U(VI) using PHREEQC with Nuclear Energy Agency thermodynamic database NEA_2007 enforced by data from Dong and Brooks (2006) in the presence of Mg, Ca, and Sr revealed that alkaline earth uranyl carbonate complexes are dominating in neutral to alkaline pH condition under our experimental conditions. The formation constant values of alkaline earth uranyl carbonate complexes from the literature are quite sensitive to the speciation calculations. From experimental results and aqueous speciation calculations, it is evident that Mg, Ca, and Sr are playing a major role in the aqueous speciation of U(VI) under neutral to alkaline pH conditions. Further studies are recommended to learn more about the alkaline earth uranyl carbonate complexes, especially the formation and existence of $Mg_2UO_2(CO_3)_3^0$ and $Sr_2UO_2(CO_3)_3^0$ complexes.

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