

Gain and loss of uranium by meteorites and rocks, and implications for the redistribution of uranium on Mars

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Abstract—Terrestrial alteration of meteorites results in the redistribution, gain, or loss of uranium and other elements. We have measured the maximum U adsorption capacity of a meteorite and two geochemical reference materials under conditions resembling terrestrial ones (pH 5.8). The basaltic eucrite Sioux County adsorbs 7 ppm of U. The result for the terrestrial granite AC-E is similar (5 ppm), while the basalt BE-N adsorbs 34 ppm of U.

We have also investigated U adsorption in the presence of phosphate (0.01 M or less) in imitation of conditions that probably occurred in the earlier history of Mars. Such a process would have altered Martian surface material and would be noticeable in Martian meteorites from the affected surface. The experiments demonstrated the counteracting effects of phosphate, which increases U adsorption, but decreases the quantity of dissolved U that is available for adsorption. U adsorption by AC-E increases to 7 ppm. The lowered value for BE-N of 8 ppm results from the low quantity of dissolved U in the volume of solution used.

The results from the adsorption experiments and from leaching the Martian meteorite Zagami and a terrestrial basalt imply that the aqueous redistribution of U on Mars was moderate. Acidic liquids mobilized uranium and other metals, but present phosphate impeded the dissolution of U compounds. Some mobilized U may have reached the global sinks, while most of it probably was transported in the form of suspended particles over a limited distance and then settled.

INTRODUCTION

The contact of terrestrial surface waters with meteorites results in alteration of meteorite finds, during which elements are lost, gained, or redistributed. Gain of terrestrial material is common for meteorite finds from hot deserts and is demonstrated visually by an efflorescent salt crust (“caliche”) surrounding the part of the meteorite in contact with the ground. The crust forms upon evaporation of surface water, which contains mainly calcium carbonate, but also typically 0.01–5 ppb of UO_2^{2+} and other trace elements. The uranyl ions form from U(IV) during weathering of rocks in an oxidizing atmosphere. Measured uranium concentrations of the deposited salt crusts are 1.78 ppm for Sayh al Uhaymir (SaU) 005 (Dreibus et al. 2000) and 1.9 ppm for Dar al Gani (DaG) 476 (Dreibus et al. 2001), which are olivine-phyric shergottites from the deserts of Oman and Libya. An increased U concentration of 0.12 ppm in surface material versus 0.09 ppm in interior material was noted for DaG 476 (Zipfel et al. 2000; Barrat et al. 2001). The interior of meteorites is accessible to surface waters through networks of fractures and

microcracks, and the terrestrial contaminants also fill cracks and veins inside the meteorites. The lunar meteorite DaG 262 from the Libyan Desert has a doubled to tripled U content in comparison to samples from Antarctica (Bischoff et al. 1998). Canyon Diablo iron oxides have gained 0.2–0.6 ppm of terrestrial U in 50,000 years (Hofmann 1992). Finds of Tatahouine from 1994 contain 1–2 ppb of U in contrast to <1 ppb in samples collected immediately after the fall in 1931 (Barrat et al. 1999). Measured terrestrial U in material close to the surface of chondrites from Oman has been used to calculate their terrestrial residence time (Stenger et al. 2006).

Terrestrial alteration of Antarctic meteorite finds is less general due to the scarcity of liquid water and the low temperature. However, white efflorescence or rust occurs on the surfaces of Antarctic meteorites for 4–54% of the specimens, depending on the meteorite group. Here, the evaporation deposits correlate with depletion of alkali and alkaline earth elements from meteorite interiors (Velbel 1988). Leaching of U from Antarctic eucrites has been mentioned in a recent review of terrestrial alteration of meteorites (Crozas et al. 2003). A considerable enrichment in

U has resulted for Frontier Mountain Range chondrites from contact on a few days per year with melt water containing U leached from a moraine consisting mostly of granite (Delisle et al. 1989).

The varying contamination of meteorites during terrestrial alteration has initiated our experimental investigation of the maximum U adsorption by a stony meteorite. The chosen experimental conditions preclude an enrichment in U by other mechanisms like co-precipitation. We have selected a eucrite fall, Sioux County, for our experiments. The U concentration in eucrites covers the range of 50–200 ppb, so that a terrestrial contamination might go unnoticed. The rather large range of La/U ratios of 15 to 50 in eucrites, compared to the chondritic ratio of 30, also is not a useful indicator of a contamination by terrestrial U. A better indicator is the Th/U ratio of 3.9 with a one-sigma error of 0.8. Experiments with two geochemical reference materials, a basalt and a granite, were done under the same conditions. The rocks supply reference data on adsorption properties under our experimental conditions. For the geostandards, we have extended our experiments to U adsorption in the presence of phosphate. This reaction does not occur under normal terrestrial conditions. It has been possible toward the end of the wet period of Mars when acidic solutions flowed on the surface and mobilized metals (see below). As the solutions on Mars became less acidic due to reactions with surface material, dissolved U was either adsorbed or formed sparingly soluble uranyl phosphate by reaction with phosphate of the Martian surface. We have studied the dissolution of U, Th, and K by leaching the basaltic Martian meteorite Zagami. The combined results from the adsorption experiments and leaching experiments on Zagami and a terrestrial basalt can be used to delimit the extent of the redistribution of U on Mars.

Acidic solutions needed for the effective mobilization of metal ions from rocks seem to have flowed on Mars during the late Noachian and early Hesperian eras ~4–3.5 Ga ago. The evaporation of water left extensive sulfate deposits found by mineralogical mapping from space (Bibring et al. 2006). This result from large-scale measurements is modified by detailed surface studies. Investigations by the rovers Spirit and Opportunity revealed complex interactions of the landing sites with water in the past. Both have in common the rather uniform presence of 10–15 wt% olivine in the soil (see, e.g., Morris et al. 2006). This moderate decrease with respect to Martian basalt is due either to an acidic alteration at a low water-to-rock ratio, or mixing of acidically altered and fresh basaltic soil (Yen et al. 2005; Wang et al. 2006). Additional traces of past aqueous alteration are for Gusev rocks alteration rinds low in olivine and rich in sulfate and chloride from interaction with acidic brines (Ming et al. 2006). Sandstones in Meridiani Planum formed from sands strongly altered by interaction with acidic solutions. Later alterations resulted from sandblasting and contact with acidic films (Squyres et al. 2006).

MATERIALS AND METHODS

We have used the 46–75 μm size fractions of the ground eucrite Sioux County and the geochemical reference materials AC-E and BE-N in our uranium adsorption experiments. The ferroan basaltic eucrite Sioux County is a monomict breccia. Modal abundances of constituent minerals are 56% of pigeonitic pyroxene, 41% of plagioclase (90% anorthite), and 2% of silica (Duke et al. 1967). The U concentration is about 0.07 ppm (Barrat et al. 2000). The microgranite AC-E is composed of alkali feldspars and quartz with less than 10 wt% of amphibole, pyroxene, and other minerals (Potts et al. 1987). The basalt BE-N consists of phenocrysts of olivine and augite in a matrix of augite and small amounts of iron oxides, melilite, and nepheline (Govindaraju 1980). Uranium concentrations are 4.6 ppm in AC-E and 2.4 ppm in BE-N (Govindaraju 1995).

All sorption experiments were done in 0.1 N sodium acetate buffer solutions at ambient temperature and pH 5.8. This resembles the physical conditions in terrestrial surface waters except for the increased ionic strength. Buffer solutions saturated with uranyl phosphate were prepared by stirring with the precipitated salt for about 6 h. After sedimentation over the weekend, the solutions were filtered. Inductively coupled plasma (ICP) measurements gave an average U concentration of 3.1×10^{-6} mol/L (0.74 $\mu\text{g}/\text{mL}$) in the saturated solution. Mixing saturated solution and pure buffer solution gave solutions of lower U concentration. Solutions more highly concentrated in U were obtained by adding the calculated volumes of dissolved uranyl nitrate to the buffer solutions. The actually obtained concentrations were measured by ICP.

Buffer solutions containing phosphate were prepared by adding the required amount of phosphate buffer of pH 5.8 to buffer solutions more highly concentrated in sodium acetate so that a final concentration of 0.1 N in sodium acetate resulted. Then the solutions were saturated with uranyl phosphate, as described above. An ICP analysis gave 6.7×10^{-7} mol/L (0.16 $\mu\text{g}/\text{mL}$) of U in the solution with 0.0001 mol/L of phosphate. The solution with 0.01 mol/L of phosphate contained 2×10^{-8} mol/L (0.0048 $\mu\text{g}/\text{mL}$) of U. This value was measured by instrumental neutron activation analysis (INAA) of the evaporation residue. The increase in phosphate by a factor of 100 leads to a decrease in U by a factor of 35 and suggests that more than one uranyl orthophosphate species determines the U solubility (see, e.g., Schreyer et al. 1954).

The sorption experiments were carried out as described earlier (Dreibus et al. 2004): the solution rose slowly through the crushed rock, placed on a sintered-glass filter in a glass apparatus. The solution was returned at least once per day to the external beaker, and more often on the first days of the reactions. Sample weights were 100 mg for Sioux County, 150 mg for the geostandards in absence of phosphate, and

Table 1. Measured U content and calculated amount of adsorbed U in ppm as a function of U concentration in the solution and reaction time. See the Materials and Methods section for experimental details. The analytical uncertainty of U is better than 5%.

| Dissolved U ($\mu\text{g/mL}$) | | 0.19 | 0.37 | 0.74 | 1.7 |
|----------------------------------|------------|-------------|---------------|----------------|-----------------------------|
| Reaction time (d) | | 3/7/14 | 3/7/14 | 3/7/14 | 3/7/14 |
| AC-E | | | | | |
| | Measured U | | -/6.0/6.3 | -/7.3/7.6 | 10.0/10.1/10.6 |
| | Adsorbed U | | -/1.2/1.5 | -/2.3/2.6 | 4.0/4.1/4.6 |
| Other granites | | GS-N | GA | | |
| | Adsorbed U | 0.6/0.8/1.1 | 0.8/2.2/2.0 | | |
| BE-N | | | | | |
| | Measured U | 8.5/8.7/9.1 | 8.8/15.5/13.4 | 27.6/26.1/30.3 | 42.0/29.9/39.3 ^a |
| | Adsorbed U | 6.0/6.2/6.6 | 6.2/12.9/10.8 | 24.8/23.3/27.5 | 38.2/26.1/35.5 |
| Sioux County | | | | | |
| | Measured U | -/3.0, 3.2 | -/4.7, 5.5 | -/5.8, 5.9 | -/7.7, 7.5/7.7, 8.8 |
| | Adsorbed U | -/2.8, 3.0 | -/4.5, 5.3 | -/5.5, 5.6 | -/6.4, 6.2/6.4, 7.5 |

^aSolution with 2.7 $\mu\text{g U/mL}$.

Table 2. Measured U and P contents and calculated amounts of adsorbed U in ppm and sorbed P in wt% as a function of reaction time from solutions saturated with uranyl phosphate. See the Materials and Methods section for starting U and P concentrations in the geostandards and for analytical uncertainties.

| Phosphate | | 0.0001 mol/L | 0.001 mol/L | 0.01 mol/L |
|---------------|------------|-----------------------------|-----------------------------|-------------------------|
| Dissolved U | | 0.16 $\mu\text{g/mL}$ | n.d. | 0.0048 $\mu\text{g/mL}$ |
| Reaction time | | 3/7/14 d | 3/7/14 d | 3/7/14 d |
| AC-E | | | | |
| | Measured U | 7.5/6.7/6.9 | 10.5/7.9/9.2 | 10.3/8.1/14.2 |
| | Adsorbed U | (2.9) ^a /2.1/2.3 | (5.9) ^a /3.3/4.6 | 5.7/3.5/9.6 |
| | Measured P | 0.282/0.251/0.280 | 0.102/0.145/0.152 | 0.288/0.310/0.301 |
| | Sorbed P | 0.055/0.044/0.073 | 0.074/0.117/0.124 | 0.068/0.090/0.081 |
| BE-N | | | | |
| | Measured U | 4.7/10.6/6.9 | 9.2/11.9/9.1 | 8.8/6.2, 10.6/7.4, 15.3 |
| | Adsorbed U | 2.3/8.2/4.7 | 6.8/9.5/6.7 | 6.4/3.8, 8.2/5.0, 12.9 |
| | Measured P | 0.86/0.86/0.90 | 0.83/0.89/0.89 | 0.95/1.03/1.35 |
| | Sorbed P | 0.34/0.34/0.38 | 0.31/0.37/0.37 | 0.41/0.50/0.81 |

^aValues in parentheses were not used in calculations of the regression lines.

450 mg for the geostandards in presence of phosphate. We started with about 400 mL of buffer solution in each experiment. Equilibration always was allowed to proceed for 7 and 14 days. Reactions were also run for 1 or 3 days in some cases, but only the results after 3 days of reaction are given in Tables 1 and 2. The low adsorption values after 1 day of reaction were used only as tests of the internal consistency of the data sets. Solutions of experiments running for 1 or 2 weeks were replaced by fresh ones after about half of the reaction time. At the end of the reaction, the solutions were sucked from the samples. Residual buffer solution in the moist samples amounts to about 0.05 mL at a sample weight of 100 mg, 0.07 mL at 150 mg, and 0.2 mL at 450 mg. The samples were dried at 110 °C.

Uranium in the samples was determined by INAA. The samples were irradiated in the TRIGA Mark II reactor of Johannes Gutenberg University, Mainz, at a flux of 7×10^{11} neutrons per square centimeter and second. The activities of U and other elements were measured by gamma spectroscopy. Phosphorus was determined in samples from experiments in

the presence of phosphate by precipitating ammonium phosphomolybdate (see Dreibus et al. 2004 for details). Sorbed U and P were calculated from the raw results by subtracting the literature values for U and our experimental starting values for P (0.21 wt% for AC-E and 0.52 wt% for BE-N); see Tables 1 and 2 for results. Our starting values for P are higher than in the literature due to the co-precipitation of impurities. However, we consider only relative changes in P. We also subtracted U and P gained by the samples from the residual buffer solutions during drying. Total analytical uncertainties are better than 5% for U and better than 20% for P.

Leaching experiments were done with the Martian meteorite Zagami and a terrestrial basalt, an olivine-melilite from the Rhoen Mountains in Germany. About 0.2 g of each sample was stirred for 12–16 h with 15 mL of an acidic solution (pH 4 to 5) containing 20 wt% of $\text{MgSO}_4 \times 7 \text{H}_2\text{O}$. The centrifuged and filtered solids were dried and analyzed by INAA. Results for K, Th, and U are given in Table 3; those for rare earth elements are described in Dreibus et al. 1996.

Table 3. Mobilization of incompatible elements by leaching with a 20 wt% $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ solution (pH 4 to 5) for the Martian meteorite Zagami and a basalt from the Rhoen Mountains in Germany.

| Element | Zagami | | Rhoen basalt | |
|---------|------------------------|----------------------------|------------------------|----------------------------|
| | Original content (ppm) | Loss by leaching (ppm [%]) | Original content (ppm) | Loss by leaching (ppm [%]) |
| U | 0.100 | 0.076 (76) | 1.320 | 0.634 (48) |
| Th | 0.340 | 0.214 (63) | 5.040 | 1.613 (32) |
| K | 1100 | 50 (4) | 9700 | 3395 (35) |

RESULTS OF THE ADSORPTION EXPERIMENTS AND DISCUSSION

The aim of our study is to determine the maximum U adsorption capacity of a eucrite and, for comparison, of typical terrestrial materials. For the latter, we have investigated the influence of phosphate on the reaction. Adsorption of U can happen during terrestrial alteration of meteorites. Adsorption of U in the presence of phosphate does not occur under terrestrial conditions because of the low surface concentration of phosphate due to the formation of apatite and scavenging by plants. However, this reaction simulates a process that may have occurred in the earlier history of Mars. The use of ground materials speeds up equilibration and imitates geologic time scales.

Exchange reactions leading to sorption of U, or U and P, are initially rapid (Tables 1 and 2). Samples of 150 mg frequently sorb 80% or more of the equilibrium value in 3 days. Equilibration for 450 mg samples, used in reactions with phosphate, is slower. The standard model of metal adsorption assumes the presence of strong and weak adsorption sites. At low concentrations of dissolved metals, equilibration with strong adsorption sites predominates and a high percentage of the dissolved metal is adsorbed. As the concentration of dissolved metal increases, the percentage of adsorbed metal decreases due to the increasing equilibration with weak adsorption sites. Our results agree with this model (Fig. 1).

It seems that U substitutes protons or alkali ions. Evidence for this is missing because liberated protons equilibrate with the buffer solution and additional alkali ions in the solution are negligible with respect to those of the used buffer solution. The acetate buffer solution does not extract measurable amounts of Fe, Al, or other metals from the starting materials; this was verified by INAA of the solids as well as ICP analyses of the solutions. Other buffers like citrate are more reactive. The pH value of the solution increases from 5.8 to 6.0 during equilibration with 450 mg of BE-N, smaller increases result for AC-E and Sioux County, and for smaller amounts of the starting materials.

Reactions with U

General Observations

In our experimental setup, the concentration of U does not drop below 75% of the starting value during the reactions.

Measured U concentrations in samples of AC-E, BE-N, and Sioux County after equilibration for up to two weeks with solutions of various U concentrations are listed in Table 1. Net amounts of adsorbed U are also given; they were calculated as described in the experimental section. Plots (not shown) of net amounts of adsorbed U versus duration of reaction were of the type usually found for adsorptions: for each concentration of U, the initially rapid gain in U during the first days of reaction slows down later and approaches a maximum value after 3–7 days. The calculated regression lines show that there is at most a small increase in gained U during the second week of the reactions. The values given by the regression lines for two weeks of reaction represent the equilibrium value of U adsorption at the concentration of U in the used solution (ignoring the possibility of an increase by perhaps a few percent when doubling or tripling the duration of the reaction). Below saturation, the adsorption equilibrium value increases with the concentration of U in the solution. The increase in adsorbed U slows down, as the adsorption capacity of the used solid is approached. When all adsorption sites are in equilibrium with the dissolved metal ions, a further increase in the concentration of U in the solution does not result in an increased adsorption. Plotted regression lines of these equilibrium values of adsorbed U versus U concentrations in the solutions are shown in Fig. 1. In these plots, too, the initially rapid increase of the equilibrium value with the concentration of U in the solution levels off at higher concentration of U and approaches a maximum value, which is the U adsorption capacity of the used material. Results are 5 ppm for AC-E, 34 ppm for BE-N, and 7 ppm for Sioux County. Equilibrium values of U adsorption (see Table 1) of the geochemical reference granites GS-N and GA (Govindaraju 1995) confirm the results for AC-E by approximately falling on the same curve. From the shapes of the curves in Fig. 1, we are confident that our materials gain U exclusively by adsorption. The onset of an additional gain of U by competing reactions like a precipitation of U compounds would result in inflections in the approximately horizontal parts of the curves.

Mean energies of the reactions resulting in U adsorption were obtained by plotting the linearized Dubinin-Radushkevich (D-R) isotherms (see, e.g., Ames et al. 1982 or Aksoyoglu 1989 for mathematical details). Used data are the equilibrium values of U adsorption for solutions with 0.74 $\mu\text{g}/\text{mL}$ of U or less, where adsorbed U increases about

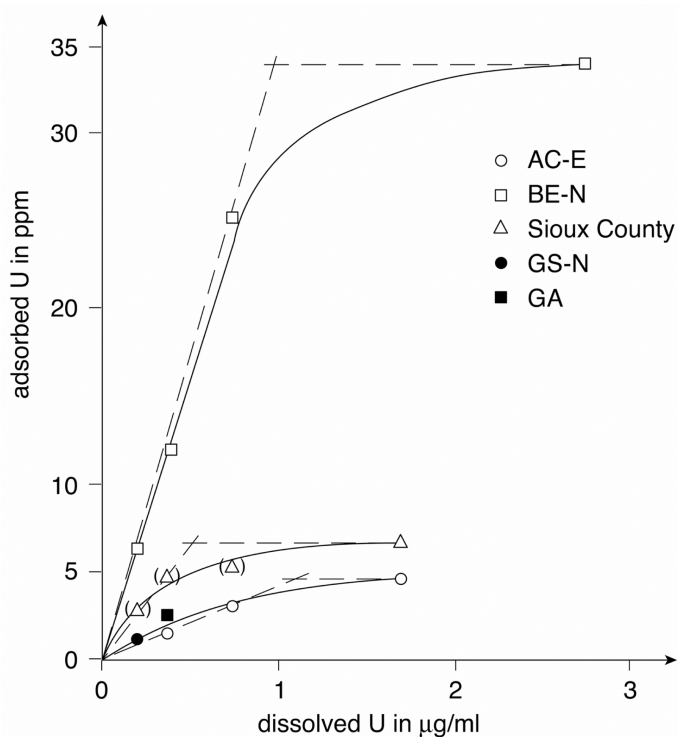


Fig. 1. Equilibrium values of U adsorption as a function of the U concentration in the solutions. Values for AC-E and BE-N are from plots of adsorbed U versus time (3 to 14 days); those for Sioux County in parentheses are the averaged results after 14 days of reaction. The dashed lines show extrapolations for low and high concentrations of U.

proportionally with the concentration of U in the solution. The slopes of the lines give energies for the reactions with U. Results are 10.0 kJ/mol for AC-E, 9.0 for BE-N, and 10.5 for Sioux County, all well within the range of 8–16 kJ/mol typically found for exchange reactions. The intercept of the D-R plots with the ordinate theoretically gives the maximum adsorption capacity via ion exchange. However, U adsorption in our experiments reaches only about 10% of the theoretical maximum. The same was found for U adsorption in earlier experiments, whereas Cs ion exchange led to experimental values close to the theoretical ones (Ames et al. 1982).

Investigations of the sites of U adsorption by the direct methods Rutherford backscattering, particle-induced X-ray emission (Alonso et al. 2003), and secondary ion mass spectrometry (Berry et al. 1994) demonstrate that adsorbed U on rock surfaces correlates with Fe(III) and Ti, but not with Si, Al, and K. Identified Ti minerals are rutile, sphene, and ilmenite. The silicates biotite, chlorite, epidote, and augite contain Fe(III) and adsorb U. Quartz and feldspars adsorb little or no U. An ion microprobe study showed that qualitatively the same minerals adsorb U leaking from the Oklo natural reactor zone (Bros et al. 2003). The direct studies confirm conclusions from earlier U adsorption experiments with individual minerals without identification of the adsorption sites by direct methods (see, e.g., Ticknor 1994). Adsorption of U on Fe-bearing minerals increases when the equilibration of the U solution is accompanied by

oxidation of Fe(II) to Fe(III) oxyhydrate, which is a preferred adsorption site. It forms in the presence of water from Fe(II) via mobilization, diffusion of ferrous iron toward the surface, and oxidation by aerated water (Arnold et al. 1998; Krawczyk-Bärsch et al. 2004). An increased adsorption of U after oxidation of Fe(II) also was found in experiments with olivine rock containing 28 wt% of Fe(II) (Rovira et al. 2000).

Adsorption of U by Sioux County

Sioux County is a eucrite of basaltic texture. The maximum U adsorption of 7 ppm therefore seems to be surprisingly low, when compared to the high U adsorption found for the terrestrial basalt BE-N. The adsorption capacity resembles that of a granite and agrees with the Fe(III) content in Sioux County of about 2.5 wt% after two weeks of reaction: AC-E has 2.53 wt% of Fe(III) and adsorbs 5 ppm of uranium. Sioux County is initially free of Fe(III) and contains 18.25 wt% of FeO, 0.45 wt% of FeS, and 0.05 wt% of Fe (Duke et al. 1967). An analysis of our sample of Sioux County gave 19.8 wt% of Fe(II), which includes contributions by FeS and Fe to the oxidizable matter and agrees reasonably well with the literature value. The Fe(II) content decreases to 18.8 wt% at the end of the first week of reaction and to 17.7 wt% after two weeks. ICP measurements show that Fe(III) is not lost to the solution, but remains in the solid. If we assume that the adsorption equilibrium has been

established already after one week of reaction, we can correlate the increase of 0.55 ppm in adsorbed U during the second week at the highest U concentration used with the decrease in Fe(II) by 1.1 wt%. From the increase in Fe(III) during the equilibration, we deduce possible U adsorption values of 6 ppm for absent Fe(II) oxidation or 17 ppm for complete Fe(II) oxidation. Considering the maximum possible Fe(III) content of 20.3 wt% in Sioux County, which is larger by half than the total iron content of BE-N (13 wt%), even the deduced maximum adsorption value of Sioux County is far below what would be expected from the results for the terrestrial basalt. We suppose that only a part of formed Fe(III) in Sioux County is available for adsorption. The reason for this seems to be that most pores in stony meteorites are occluded due to the increased volume of the products, after ~15 wt% of the initially present Fe(0) and Fe(II) have been oxidized (see, e.g., Lee et al. 2004). Accessible adsorption sites are therefore fewer than formed ones. This mechanism and the roughly similar chemical composition of differentiated achondrites suggest that their capacity of U adsorption is similar to that of Sioux County. Exact values depend on mineralogy and grain size as well as the porosity of an individual meteorite and on the pH value of the solution in contact with it.

Stony meteorites gain elements from aqueous solution purely by adsorption only under laboratory conditions. Competing reactions occur during the aqueous alteration of meteorites in hot and cold deserts. In both environments, water leaks into the meteorites via cracks and oxidizes meteoritic iron and troilite, yielding precipitates of Fe(III) oxyhydrates. At weakly acidic conditions, they are excellent adsorption sites for uranyl ions (see the previous section) and also adsorb lanthanide ions (Rabung et al. 1998). The water that alters the meteorites is weakly acidic due to dissolved carbon dioxide or sulphuric acid from troilite oxidation. This liquid dissolves phosphates which are the main carriers of uranium and lanthanides (REE) (see, e.g., Lee et al. 2004). Mobilized metal ions are adsorbed, precipitated upon evaporation of water, or lost by leaching. Details on the fate of mobilized metal ions are often ignored in descriptions of the terrestrial alteration of meteorites.

The chance to identify effects of adsorption in weathered meteorites from hot and cold deserts is better for Antarctic ones because of the fewer chemical and physical processes involved. Alteration occurs mostly after exhumation of the meteorites from the glacial ice. Insolation heating at temperatures around 0 °C results in contact with water containing carbon dioxide, but usually no dissolved terrestrial salts (Schultz 1986; Jull et al. 1988). The main visible alteration product is rust. A minority of stony meteorites form white evaporite minerals on their surface. They consist of redistributed meteoritic compounds like gypsum or calcite, and of magnesium carbonates from weathering of olivine in the presence of dissolved carbon dioxide (Velbel 1988; Jull

et al. 1988). Abnormal REE patterns are observed in the majority of Antarctic eucrites. Light lanthanides (LREE) reside preferentially in phosphates; their dissolution leads to LREE loss. An exception is Ce, which is oxidized to Ce(IV) and is less soluble in this oxidation state (see, e.g., Mittlefehldt et al. 1991). The mobilized REE become redistributed within the meteorite along cracks and defects. In a study of an Antarctic eucrite, they were found not to enter minerals, but to “fix themselves on other minerals” (Floss et al. 1991). We infer that they do so due to adsorption. However, a possible trapping of REE in microcracks was also mentioned without giving details (Crozzaz et al. 2003). Adsorption seems to have played an important role in the gain of up to 2 ppm of U by Antarctic chondrites from the Frontier Mountain Range during their residence time on top of the ice. U stems from contact on a few days per year with streams of melt water that leach terrestrial elements from a granitic moraine (Deslisle et al. 1989).

In hot deserts, water from dew or occasional showers dissolves terrestrial compounds, among them those of REE and U, which behave similarly. Contact of the solutions with meteorites mobilizes meteoritic compounds. The dissolved ions are immobilized by competing adsorption and co-precipitation; the latter results as the water evaporates. The formed terrestrial contaminant on the surface and in cracks inside the meteorites is mainly calcium carbonate containing coprecipitated other compounds; see the Introduction. Terrestrial trace elements incorporated by meteorites during weathering in hot deserts are LREE, U, Pb, Sr, and Ba (Crozzaz et al. 2003). The relative shares of adsorption and co-precipitation in the terrestrial contamination by LREE and U depend on the details of weathering. The processes might become separable by ion microprobe measurement of concentration profiles of U or other trace elements in thin sections of weathered meteorites containing cracks filled by precipitated terrestrial contaminations.

Terrestrial alteration via adsorption or co-precipitation leads to problems with U-Pb, Rb-Sr, and Sm-Nd isotopic systematics (Crozzaz et al. 2003). A contamination is identified readily in the case of ordinary meteorites, where the age has to be similar to that of the solar system. Moreover, gain or loss of U does not affect Pb-Pb isochrones. The abnormal REE patterns of Antarctic eucrites have been mentioned above. Terrestrial REE contaminations have been found in acid extracts of hot desert SNC meteorites, leading to young Sm-Nd ages. Their residual phases have not been affected and have yielded correct Sm-Nd ages (Jagoutz et al. 2001).

Adsorption of U by Terrestrial Granite and Basalt

Our results on U adsorption by AC-E and BE-N agree qualitatively with literature data on maximum U adsorption on granites and basalts at ambient temperature. Differences in materials and experimental conditions prevent an exact agreement. For example, the amount of U adsorbed by rocks

and minerals depends on the pH value and reaches a maximum at about pH 6.5–7.5 (see, e.g., Baik et al. 2003 or Arnold et al. 1998). In addition, literature data on U adsorption by granites and basalts were calculated from the lowered U concentrations of the solutions after the reactions, but not from analyses of the solids.

Our maximum U adsorption of 5 ppm for AC-E at pH 5.8 seems small when compared to 23 ppm found for a Swiss granite at pH 8 (Aksoyoglu 1989) and 15 ppm (pH 5.5) to 20 ppm (pH 7.0) for a Korean granite (Baik et al. 2003). However, these granites contain 10 wt% or more of biotite and other minerals with a high affinity for U, while the content of those minerals in AC-E is markedly lower; see the experimental section. We do not expect additional adsorption of U by AC-E upon longer reaction or with solutions of higher U concentrations.

Our U adsorption value of 34 ppm for BE-N at pH 5.8 seems to represent the maximum amount of U that can be adsorbed under our experimental conditions. Our value is similar to two values for Columbia River basalts, which adsorb 42 and 50 ppm of U at pH 7.7 to 7.9 (Ames et al. 1982). We attribute the differences to our result to the differing experimental conditions; the iron contents of the basalts are similar, although this does not necessarily mean equal accessibility to U adsorption. A third Columbia River basalt adsorbed 102 ppm of U. There is no obvious reason in the mineralogical or chemical composition of this basalt for this surprisingly high value, which also was derived from the loss of U from the solution, but not from a measurement of adsorbed U in the basalt. Possible explanations include a small number of highly effective adsorption sites or an unnoticed precipitation of U compounds from the solution.

Reaction with U and P

Samples of 450 mg were used for the reactions in order to have enough material for the phosphorus analysis. An investigation of the dependence of U adsorption on sample weight demonstrated the limits of our experimental setup. Samples of 450 mg after 2 weeks had adsorbed only 75–80% of the amount of U adsorbed by samples of 150 mg or less. The weight effect becomes larger when reactions are run only for a few days. We assign the weight effect to the limited speed of U diffusion to adsorption sites. We assume that the extent of the effect does not depend on the presence of phosphate.

Addition of phosphate to solutions of UO_2^{2+} has two counteracting effects. The presence of phosphate enhances the adsorption of U by minerals (Payne et al. 1998). At the same time, the low solubility products of uranyl orthophosphates decrease the amount of U dissolved in a fixed volume of solution; see the experimental section for measured concentrations.

Experimentally, however, the uptake of U by the geostandards increases at low concentrations of phosphate in the solutions in spite of the decreasing U concentrations; see Table 2 for data and Fig. 2 for plotted results. The included regression lines were calculated from the listed data in order to determine the equilibrium adsorption values. The limited number of data makes the lines tentative. However, the differing effect of increasing concentrations of phosphate is obvious: there is a regular increase of adsorbed U with the concentration of phosphate for the granite, whereas a limiting value is approached for the basalt.

The enhancement of U adsorption by AC-E is marked even at a low concentration of phosphate. A 450 mg sample adsorbs 2.5 ppm of U from a solution with 0.16 $\mu\text{g}/\text{mL}$ of U and 0.0001 M phosphate. In absence of phosphate, a 150 mg sample adsorbs the same amount of U from a solution containing 0.74 $\mu\text{g}/\text{mL}$ of U (see Tables 1 and 2 and Figs. 1 and 2). U adsorption increases steadily with phosphate concentration up to 0.01 M in spite of the decreasing concentration of U. The maximum adsorption of U by AC-E in the presence of phosphate (7 ppm) is markedly higher than in its absence (4.5 ppm). Including the weight effect of our experiments, the maximum U adsorption almost doubles in the presence of phosphate. A substantial further increase in adsorbed U at higher concentrations of phosphate seems unlikely because of the accompanying decrease in dissolved U in the used standard volume of solution.

A more exact understanding of the reactions results from the molar P/U sorption ratios. They were calculated from the equilibrium sorption data by weight (% for P, ppm for U), given by the regression lines in Figs. 2 and 3. Division by the atomic masses yields sorbed moles of P and U per gram of rock. The molar P/U sorption ratio is 1800 ± 350 for all experiments, with a slight increase with phosphate concentration. The almost constant value indicates that for AC-E no deficits in sorbable P or U impede the reactions and that an increase in sorbed P results in a proportional increase in adsorbed U in the studied range of phosphate concentrations.

We also find an increased adsorption for BE-N at phosphate concentrations of 0.0001 M and 0.001 M (Fig. 2). In 0.0001 M phosphate solution with 0.16 $\mu\text{g}/\text{mL}$ of U, the adsorption of U (6.5 ppm from the regression line) is the same as in the solution with 0.19 $\mu\text{g}/\text{mL}$ of U in absence of phosphate (Fig. 1). Including the influence of the sample weights, this means an increase in adsorption by more than a quarter due to the presence of phosphate. When the phosphate concentration increases to 0.001 M, U adsorption increases by nearly 2 ppm, which is similar to the increase found for AC-E, but smaller than expected, considering the better adsorption properties of BE-N. The resulting U gain of about 8 ppm seems to be the adsorption maximum in presence of phosphate under the experimental conditions. A further increase in the concentration of phosphate to 0.01 M does not

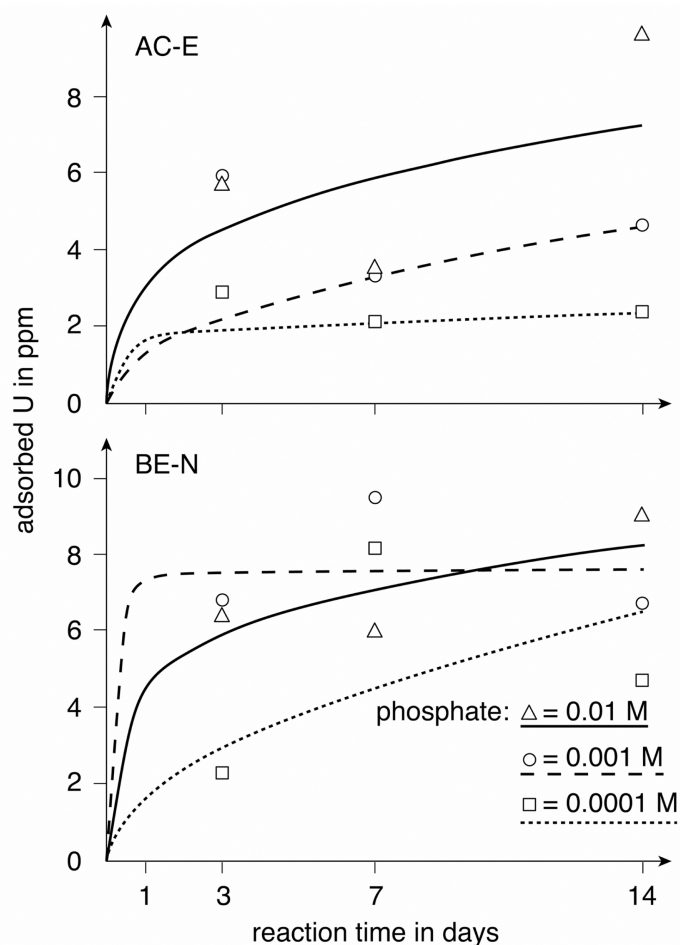


Fig. 2. Adsorption of U from buffer solutions 0.1 N in sodium acetate as a function of reaction time. The solutions are saturated with uranyl phosphate and contain additional phosphate. Experimental results and calculated regression lines are shown.

increase U adsorption. This is caused by the low quantity of dissolved U ($0.005 \mu\text{g/mL}$) in the volume of solution. The used solution, 400 plus about 350 mL, contains $3.6 \mu\text{g}$ of U, of which $3.47 \mu\text{g}$ are adsorbed. Nevertheless, phosphate enhances U adsorption by more than a factor of 8; the curve for BE-N in Fig. 1 predicts an adsorption of only about 1 ppm at this concentration of U in the absence of phosphate instead of 8 ppm (10 ppm for a 150 mg sample) adsorbed in its presence. A repetition of the experiment confirmed the initial values of U uptake within the limits of data scatter, which is linked to the presence of phosphate. In dilute phosphate buffer solutions, the scatter of the U adsorption results prevented the identification of any systematic change with the concentrations of U and P.

The calculation of the molar P/U sorption ratios for BE-N confirms the different course of the reactions of AC-E and BE-N, indicated by the curves of adsorbed U as a function of dissolved phosphate in Fig. 2. While the decrease of the concentration of dissolved U with the increasing concentration of phosphate does not affect the reactions of AC-E, the increasing deficit in dissolved U is obvious in the

reactions of BE-N. Its molar P/U sorption ratio increases from about 2400 for the solution containing 0.0001 M of phosphate to 4600 at 0.001 M and 5600 at 0.01 M. The decreasing supply of dissolved U in the used volume of solution therefore prevents BE-N from reaching saturation with respect to adsorbed U in the presence of increasing concentrations of phosphate. When a larger volume of solution is used and availability of dissolved U is not the limiting factor, we predict a maximum U adsorption of 19 ppm. This value is based on a molar P/U sorption ratio of 2400 and the phosphorus sorption of 0.6 wt% from a solution 0.01 M in phosphate and $2 \times 10^{-8} \text{ M}$ ($0.005 \mu\text{g/mL}$) in U. At this concentration, BE-N adsorbs about 1 ppm of U from the solution in the absence of phosphate (see Fig. 1).

The improved adsorption of U in the presence of phosphate might result from the formation of a ternary surface complex, formed by P, U, and iron oxyhydrate or other sorption sites. Alternatively, a secondary phase, formed from sorption sites and phosphate, might adsorb U better than the original sorption sites (Payne et al. 1998). Our experiments do not indicate which mechanism is to be

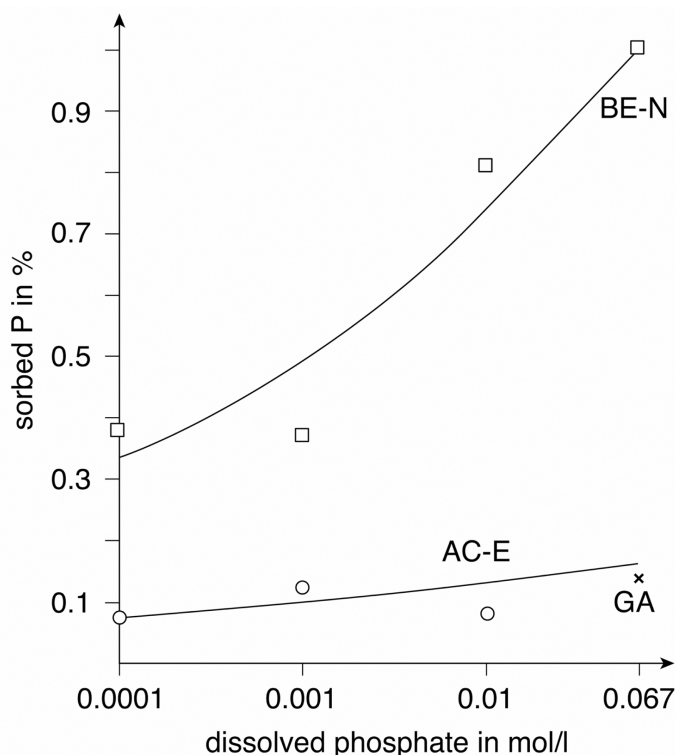


Fig. 3. Sorption of P after two weeks of reaction from buffer solutions 0.1 N in sodium acetate (pH 5.8) and containing phosphate. Earlier results for the geochemical reference granite GA and basalt BE-N (Dreibus et al. 2004) using 0.067 mol/L of phosphate are also shown and were included in the calculations of the regression lines.

preferred, because the concentration of P in the solution is much higher than that of U. Sorption of P prevails, as indicated by the large and, for BE-N, variable molar P/U sorption ratios.

Data on P sorption are included in Table 2. The basalt BE-N sorbs P much more readily than the granite AC-E. There is a strong initial sorption for both at low P concentration in the solution. BE-N in buffer solution containing 0.0001 M of phosphate sorbs almost all of the phosphorus present. The increase in P sorption levels off at higher concentrations of phosphate, when the maximum sorption capacities are approached. The results obtained here at phosphate concentrations of 0.01 mol/L or less match our earlier results (Dreibus et al. 2004) for BE-N and the geochemical reference granite GA in phosphate buffer solutions more highly concentrated in P. The curves of sorbed P versus the concentration of dissolved phosphate resemble those for U adsorption (Fig. 1), when they are plotted using an abscissa with a linear scale. As our phosphate concentrations span three orders of magnitude, we have used a logarithmic abscissa in our plots of the experimental data and calculated regression lines on phosphorus sorption in Fig. 3. These plots better resolve the results on P sorption at low concentrations of dissolved phosphate, but the approach of phosphorus saturation is not recognizable.

RESULTS OF THE LEACHING EXPERIMENTS

Solutions containing dissolved, adsorbable U(VI) form in an oxidizing atmosphere upon contact of acidic solutions with the rocks containing uranium compounds. In order to find out about the mobilization of U and the other lithophile elements K and Th from Martian basalts, we have leached the crushed Martian basaltic meteorite Zagami, using weakly acidic magnesium sulfate brine. A terrestrial basalt, HST, was leached for comparison. The acidic solution mobilizes U and Th from both basalts in roughly similar relative amounts via dissolution of phosphates (whitlockite for Zagami, apatite for HST); see Table 3. K is mobilized significantly only from feldspar in HST. K in Zagami mostly resides in maskelynite and K-rich mesostases (Stolper et al. 1979; McCoy et al. 1999) which react more slowly than feldspar.

IMPLICATIONS FOR THE REDISTRIBUTION OF U, AND ALSO K AND TH, ON MARS FROM THE LEACHING AND ADSORPTION EXPERIMENTS

Our adsorption and leaching experiments in the presence of phosphate are similar to conditions on Mars more than 3.5 Ga ago (see the Introduction), when part of its surface interacted with acidic brines, which mobilized metals including U. Our experimental results suggest that a

redistribution of dissolved U over large distances did not occur, because the concentration of U in basalts was low, and dissolved phosphate impeded its dissolution. The concentration of U in Martian basalts, derived from the composition of the less than 200 Ma old basaltic Martian meteorites, is 0.05–0.15 ppm. We use these values because the mantle source regions for basalts were differentiated early in the history of Mars and then remained virtually unchanged until remelted to form magmas (McSween 2003). Dissolved phosphate originating from the Martian soil and basalt decreases the dissolution of U on Mars via the law of mass action because of the low solubility of uranyl phosphate; also see the Materials and Methods and the Reaction with U and P sections for our experiments on U adsorption in the presence of phosphate. The soil contains 0.3–0.4 wt% P in the form of phosphate, which is mostly bound to calcium. Other anions present are abundant sulfate and chloride (Gellert et al. 2006). The phosphorus concentration in Martian basalts, as known from SNC meteorites, is in the same range (Lodders 1998). As the acidity of the solutions decreased during the contact with basalts via reactions with metal compounds, conditions became favorable for the adsorption of any dissolved U on minerals. Its maximum occurs at pH 6.5–7.5; see the Adsorption of U by Terrestrial Granite and Basalt section. The abundant iron oxyhydrate of the soil or the basalts probably adsorbed dissolved ions of U readily, present phosphate increasing the adsorption. An enrichment of U should readily be noticeable in Martian basalts. However, all Martian basalts sampled by meteorites have crystallization ages of less than 200 Ma and do not seem to be enriched in U. We assume that in contrast to Earth, the dissolution of U was probably too limited for the hydrothermal formation of deposits of U compounds.

The limited solubility of U suggests that during the acidic alteration of rocks the U compounds were mobilized mostly as suspended particles. The particles were carried away by flowing liquid and settled on the way to global sinks, the distance of transport depending on local conditions. The chemically similar Th compounds behaved similarly, thereby preventing a significant aqueous fractionation of U from Th. The deduced restrictions of the mobilization of U and Th are compatible with the observed global distribution of Th and the inferred one of U (see below). A sedimentary transport mechanism has also been used to explain the mineral fractionation of Fe and Ti in samples studied during the Pathfinder mission (McLennan 2000). A third lithophile, K, is as incompatible as Th and U in igneous rocks. However, any K set free from feldspars is highly soluble and mostly accumulates in oceans and inland seas.

The distribution of U on the Martian surface has not been measured either directly by Mars rovers or from space by the Mars Odyssey Gamma-Ray Spectrometer (GRS). However, the U distribution can be inferred from GRS data on K and Th. The GRS measurements with an analysis depth of the top

third of a meter gave Th concentrations of 0.5–0.7 ppm in the southern highlands and 0.7–1.0 ppm in the northern plains. A similar trend has been found for K with values of 0.3 and 0.4 to 0.5 wt% (Wänke et al. 2005; Taylor et al. 2006); see also the earlier Phobos-2 results (Surkov et al. 1994). The K/Th ratio for most areas differs by 50% or less from the global average across the Martian surface (Taylor et al. 2006). The moderate fractionation of K from Th and the similar dissolution properties of Th and U compounds suggest that the U distribution resembles that of Th. From the Th data and the Th/U ratio of 4 in SNC meteorites, we estimate U concentrations of 0.1–0.15 ppm in the southern highlands and 0.15–0.25 ppm in the northern plains. These values for the Martian surface are slightly higher than the typical U concentrations in basaltic Martian meteorites. The same was found for the concentrations of K measured by GRS and also for the Th data, from which we have deduced the U concentrations. It appears that the basaltic Martian meteorites are not representative of the Martian surface (Taylor et al. 2006).

Arguments for a modest mobilization of lithophile elements, followed by an aqueous fractionation of K from Th (and also U) are lower K/Th ratios for sites of deposition of sediments and higher ratios in basins, they suggest leaching of K and deposition from evaporating solutions. However, the modest variations of the K/Th ratios can also be due to igneous processes (Taylor et al. 2006). Additional effects that today might obscure an initially larger fractionation are combined impact gardening and homogenization of soil by aeolian processes during the last 3.5 Ga of dry Mars (see, e.g., Rieder et al. 2004).

SUMMARY

In experiments simulating terrestrial weathering conditions, solutions containing U have yielded maximum U adsorptions of 5 ppm for the granite AC-E, 34 ppm for the basalt BE-N, and 7 ppm for the basaltic eucrite Sioux County. As the adsorption capacity of Sioux County possibly increases with oxidation of Fe(II), adsorption values up to 17 ppm cannot be excluded in case of complete oxidation. Our experiments have demonstrated that a magmatically differentiated meteorite can potentially adsorb considerable amounts of U from surface water without the simultaneous growth of crystals of terrestrial contaminants in cracks and voids. We assume that the measured U adsorption value for Sioux County, around 7 ppm, also gives the order of magnitude of U adsorption by differentiated achondrites, and possibly by stony meteorites in general. We have identified examples where adsorption seems to explain observations on the terrestrial alteration of Antarctic meteorites. During weathering of meteorites in hot deserts, co-precipitation of terrestrial calcium carbonate and trace elements obscures gains of the latter by adsorption.

Counteracting effects determine the adsorption of U from solutions containing added phosphate. While sorbed phosphate increases the adsorption capacity, dissolved phosphate reduces the amount of dissolved U. Its adsorption rises to a maximum of 7 ppm for AC-E (and 8.5 ppm after correcting for the weight effect of our experiments). The decrease to 8 ppm for BE-N results from our used standard solution-to-rock ratio. Higher adsorption values require contact with larger volumes of solution.

Our experimental results suggest that the aqueous fractionation of U from Th and the enrichment of Martian rocks and soils via adsorption of dissolved U probably were low. The deduced small differences in U distribution on the surface on Mars prevalingly seem to result from processes, which generate particulate matter by aqueous alteration or physical weathering of rocks. The particles were then distributed by flowing water in the past or for the last 3.5 Ga are still redistributed by combined impact gardening and wind.

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Editorial Handling—Dr. Christine Floss

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