

The loss of K, REE, Th, and U from a Martian and a terrestrial basalt by acidic leaching

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Abstract—The mobilization of K, rare earth elements (REE), Th, and U from Martian surface material upon contact with acidic solutions probably occurred extensively on Mars about 4 to 3.5 Ga ago and seems to have occurred locally in more recent times. We have studied the dissolution of these elements by leaching the basaltic shergottite Zagami and the terrestrial basalt BE-N at constant pH values ranging from 5 to 1 in the absence and presence of added salts. Potassium is nearly immobile in Zagami and mobilized readily from BE-N. The REE reside mostly in calcium phosphates and dissolve readily, with those in whitlockite of Zagami reacting slightly better than those in apatite of BE-N. Thorium and U also reside mostly in calcium phosphates. Both dissolve similarly for both basalts and less readily than the REE. The experiments indicate the extent of the mobilization of K, REE, Th, and U, when acidic water leached the surface of Mars. Potassium was released slowly and in a small relative amount. The REE, and particularly the LREE, became mobile readily and were possibly distributed over large areas before immobilization. Thorium and U dissolved more slowly than the REE and were distributed less widely.

INTRODUCTION

Flowing water shapes landforms and redistributes the constituent elements of soils and rocks. The extensive aqueous alteration of the Martian surface in the past was detected from space by satellites, on the surface by rovers, and on Earth by investigations of Martian meteorites. The Martian hydrologic cycle has left morphological features such as fluvial erosion in valleys (Jaumann et al. 2005) and in the northern plain the sediment covers of ancient craters (Watters et al. 2006), and the shoreline of the ancient ocean (Perron et al. 2007). Alteration products detected by satellite include clay minerals in Noachian outcrops that originated from weathering by neutral or alkaline water, see, e.g., Loizeau et al. (2007). One recent model suggests that the surface water became acidic during the late Noachian and early Hesperian eras about 4 to 3.5 Ga ago. After this time, liquid water disappeared from the surface and its evaporation left extensive sulfate deposits (Bibring et al. 2006). More recent aqueous alteration occurred only locally, see, e.g., Hurowitz et al. (2006). The aqueous alteration of the Martian surface has left veins filled with clay minerals or precipitated salts in various SNC meteorites, while Zagami has been enriched in deuterium; see the review by Bridges et al. (2001).

The past aqueous redistribution of elements on the Martian surface might still be detectable today. Concentrations of the incompatible elements K and Th, studied in our experiments, have been measured globally in the Martian near-surface by satellites. Their global concentrations are rather uniform. This could be due to similar compositions of the parent magmas and little mobilization during the past aqueous alteration of the surface material, but also due to aeolian and other physical processes in the last 3.5 Ga (Taylor et al. 2007). Impact gardening of at least the top 30 m also homogenized the surface materials (Hartmann et al. 2001), thereby diluting any evaporates not protected by covers of sediment or lava during most of this time.

The inferences on the redistribution of elements by early aqueous alteration from satellite observations are modified by detailed surface investigations done by the rovers Spirit and Opportunity. A common feature of their landing sites is the rather uniform presence of 10 to 15 wt% of olivine in the soil; see, e.g., Morris et al. (2006). This concentration is only moderately lower than in Martian basalt and is due either to an acidic alteration at a low water-to-rock ratio or to mixing of acid-altered and fresh basaltic soil (Yen et al. 2005; Wang et al. 2006). Past aqueous alteration of Gusev plain rocks apparently has left alteration rinds. These rinds are low in

olivine and rich in sulfate and chloride from interaction with acidic brines (Ming et al. 2006). Rocks of the Columbia Hills are older and more strongly altered (Squyres et al. 2006a). 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. 2006b).

To learn about the possible aqueous mobilization of lithophile incompatible elements on Mars, we have leached the shergottite Zagami, and for comparison the terrestrial basalt BE-N, in the laboratory. Trends of the mobilization of K, rare earth elements (REE), Th, and U in Martian surface material upon contact with acidic solutions can be deduced by combining the results from the olivine-free Martian basalt Zagami and the terrestrial alkali olivine basalt BE-N. We compare the results on the mobilization of K and Th with their measured global surface concentrations on Mars. Concentrations of REE and U in Martian surface materials have not been measured by satellites or rovers. Understanding the ease of REE or U loss from basalt is relevant to conclusions based on the differentiation of its parent magma and to age determinations, e.g., by the Sm-Nd method or U-Pb isotopic systematics.

EXPERIMENTAL

We have leached Zagami and BE-N. Zagami is a basaltic shergottite consisting mainly of a fine-grained lithology and a smaller volume of a coarse-grained one. Our sample originates from the fine-grained lithology, which consists by volume of about 76% of pyroxene (augite and pigeonite), 18% of maskelynite (glass from about equal amounts of albite and anorthite with 4% or less of orthoclase [Stolper et al. 1979]), 1.5% of titanium oxides, and 0.5% each of pyrrhotite, whitlockite, and shock melts (McCoy et al. 1992). The geochemical reference standard BE-N is an alkali olivine basalt and consists of phenocrysts of olivine and augite in a matrix mainly of augite and small amounts of iron oxides, melilite, and nepheline. The quantities of the minerals have not been determined (Govindaraju 1980). The composition from a CIPW norm calculation is 34 wt% of diopside, 30% of feldspars, 22% of Fe and Ti oxides, and 12% of olivine.

We leached the 46–75 μm size fractions of the crushed solids; the powders were not rinsed. We applied rock/solution ratios of 100 mg/25 ml in the majority of the leaching experiments. Because the dissolution of minerals like olivine consumes acid, we used 0.1 N buffer solutions to keep the pH value approximately constant during the reactions. The buffer solutions were prepared from sodium acetate with adjustment of the pH value by acetic acid (NaAc), from sodium formate and HCl (NaFor), and from glycine plus sodium chloride and HCl (Gly). These buffers do not enhance the dissolution of metals by forming stable complexes under the experimental conditions. In this

aspect, they resemble hydrochloric and sulfuric acid that leached the surface of Mars about 4 to 3.5 Ga ago. However, the latter acids and their alkali salts do not form buffer systems at the pH values of our experiments. The solids were stirred with buffer solutions for 4 h at ambient temperature. The reactions were initially fast, with about 90% of the final loss of weight reached after 2 h for BE-N. The solids were separated by centrifuging. Remaining suspended solids were filtered using 0.22 μm filters and added to the centrifuged solids by washing the filters with water (2.5 ml for Zagami, 5 ml for BE-N) which was also used to wash the solids. The solids were washed again and dried at 110 $^{\circ}\text{C}$.

The sample weight of Zagami in the leaching experiments was always 100 mg. Reactions were carried out with buffer solution, in the presence of 13 wt% Na_2SO_4 and 1.6 wt% NaCl, and in the presence of sulfate, chloride, and 1.6 wt% NaH_2PO_4 . Recovered Zagami ranged from 91 to 97 mg; there was no systematic change with experimental conditions, which were as follows:

Table 1. Experimental details for Zagami.

Starting pH value	5.0	4.0	3.0	2.0	1.0
Buffer, (vol. in ml)	NaAc, 25	NaAc, 25	NaFor, 25	Gly, 25	Gly, 40
Final pH	5.0	4.0	3.2	2.05	1.1
Final pH ^a	5.15	4.05	3.05	2.1 ^b	1.2 ^b
Final pH ^c	5.0	4.05	3.1	2.15 ^b	1.1 ^b

^aReactions with added sulfate and chloride.

^bOnly 0.8 wt% NaCl were added because of NaCl in Gly.

^cReactions with added sulfate, chloride, and phosphate.

We used samples of 200 mg when leaching BE-N. Reactions were carried out with buffer solution and in the presence of added salts, 13 wt% Na_2SO_4 and 1.6 wt% NaCl; see Table 2 for details. For several experiments with BE-N, we isolated leached REE, Th, and U from the centrifuged and filtered solutions via coprecipitation with iron hydroxide (Goldberg et al. 1963). Results are summarized at the end of section BE-N.

The concentrations of K, REE, Th, and U in the leached basalts and iron hydroxide precipitates were analyzed via instrumental neutron activation analysis (INAA). Samples of about 40 mg were irradiated in the TRIGA Mark II reactor of Johannes Gutenberg University, Mainz, at a flux of 7×10^{11} neutrons per square centimeter per second. Results are listed in Tables 7 (Zagami) and 8 (BE-N). Measurement errors were usually 5% or better for BE-N and 10% or better for Zagami. Errors >10% are given with the experimental data.

The loss of soluble minerals during leaching is negligible for Zagami, but reaches 40 wt% for BE-N and increases the concentrations of the less reactive elements in the leached samples. Therefore, we have to correct the starting concentrations of K, REE, Th, and U for the weight loss before calculating their residual concentrations from their

Table 2. Experimental details for BE-N.

Starting pH value	5.0	4.0	3.0	2.0	1.0	0.5
Buffer (vol. in ml)	NaAc, 50	NaAc, 50	NaFor, 50	Gly, 75	Gly, 75	Gly, 50
Final pH	5.13	4.13	3.35	2.30	1.20	0.64
Residue (mg)	180	165	140	120	120	120
Final pH ^a	5.07	4.15	3.30	2.25	1.18 ^b	0.63 ^b
Residue (mg) ^a	185	175	160	120	120	115

^aReactions with added salts.

^bOnly 0.8 wt% NaCl were added because of NaCl in Gly.

concentrations by weight in the leached samples. We multiply their starting concentrations by factors derived from the increase in the concentrations of Sc and Hf in the leached samples with respect to their concentrations in the pristine ones. We use Sc and Hf, because their concentrations increase most upon leaching BE-N and also Zagami. The virtual immobility of Sc and Hf is probably due to their residence in (almost) resistant minerals like pyroxenes. For BE-N, we averaged the factors of the increased concentrations of Sc and Hf of each experiment. These values for each type of solution (buffer or buffer plus sulfate and chloride) at the various pH values were used to calculate the regression lines, which then yielded the factors used for the correction of the starting concentrations of K, REE, Th, and U. The contribution of these incompatible elements to the weight loss during leaching is negligible. Experimental concentrations of Sc and Hf and resulting factors are listed in Table 5. For Zagami, the average factors from the increase in Sc and Hf at each pH value were small and independent of the composition of the solution. We averaged the three experimental factors for the used solutions for each pH value. A regression calculation yielded the factors for the correction of the starting concentrations, see Table 5.

The patterns of residual REE in Zagami (Fig. 3) and BE-N (Fig. 4) also result from regression calculations. We selected experimental data with low measuring errors and used an exponential function.

RESULTS OF THE LEACHING EXPERIMENTS

We leached Zagami at pH 5 to pH 1 and BE-N at pH 5 to pH 0.5 to determine the pH dependence of the loss of the incompatible elements K, REE, Th, and U. Leaching at higher pH values is inefficient; the loss of incompatible elements was negligible in earlier experiments on U adsorption at pH 5.8 for up to two weeks (Dreibus et al. 2007). Leaching in the presence of added anions simulates possible conditions on the Martian surface and shows their influence on the mobilization of the incompatible elements. For Zagami, we used sulfate/chloride and sulfate/chloride/phosphate. Salts of the anions were applied in the molar ratio of 6.3 S : 1.7 Cl : P as found in Martian soils (Yen et al. 2005; Gellert et al. 2006). BE-N was leached in the presence of sulfate/chloride. See the experimental part for details. The deduced reactivity of the

minerals during leaching is based on their known chemical properties, but not on crystallographic studies of leached samples.

Zagami

The minerals of Zagami do not dissolve appreciably in the used acidic solutions. The weight loss of about 5% at pH 5 remains constant as the acidity of the solutions increases to pH 1. The concentrations of residual K, REE, Th, and U are given in Table 7.

The concentration of K in the fine-grained lithology of Zagami is 1100 to 1200 ppm. Maskelynite hosts about 90 wt% and the mesostases most of the rest (McCoy et al. 1992, 1999). About 5% of K dissolve at pH 5, this amount is within the range of the measuring error. The remaining 95% of K are not mobilized by increasing acidity of the solutions or added sulfate, chloride, or phosphate, confirming preliminary results (Dreibus et al. 1996a, 2007), see Fig. 1. We suppose that a part of the mesostasis is readily soluble. Maskelynite seems to be practically inert and to chemically resemble feldspar, from which it forms upon exposure to high shock pressure. The dissolution of feldspar in acidic media is very slow with rate constants in the range of 10^{-11} mol per m^2 per s, they increase slightly with increasing concentration of acid, see plotted literature data in Taylor et al. (2007).

The REE of our sample of Zagami are enriched to about $9 \times CI$ (Fig. 2), their pattern is flat with a small hump around Sm-Gd, see, e.g., Shih et al. (1982) for similar results. Two thirds to three quarters of REE reside in phosphates, mostly in whitlockite and to a smaller extent in rarer apatite. Their CI-normalized REE patterns are flat. The rest of the REE are bound mostly to augite and somewhat less to pigeonite. Their REE patterns are depleted in LREE. The REE concentration in maskelynite is low, its pattern shows a strong, positive Eu anomaly (McCoy et al. 1999).

The dissolution of REE depends strongly on the pH value of the buffer solution and also on added salts, especially phosphate. Average residual REE in % of the starting concentrations by weight are given in Table 3.

The dissolution of REE compounds by the buffer solution without added salts increases moderately with a change in pH from 5 to 4 and then strongly on going to pH 3. Adding sulfate and chloride decreases the dissolution of REE

Table 3. Average residual REE in Zagami in wt%.

Acidity of the used solution	pH 5	pH 4	pH 3	pH 2, pH 1
Buffer solution	90	70	25	25
Added sulfate and chloride	90	85	25	25
Added sulfate, chloride, and phosphate	95	95	50	25

at pH 4. Added phosphate impedes the dissolution of sparingly soluble phosphates of Ca and REE at pH 5 to 3 more strongly due to the law of mass action. At lower pH, however, the dissolving effect of the acid prevails, see also Fig. 3. The constant concentration of residual REE reached at pH 3 or less, and at pH 2 in the presence of phosphate indicates that all REE in readily soluble phosphate minerals have been dissolved. The change in the REE patterns from flat ones at pH 4 or more to HREE-enriched ones at pH 3 or less confirm that the phosphate minerals with their flat REE patterns have been leached, see Figs. 2 and 3. The average, residual REE concentration of about 25 wt% agrees with the volume-weighted concentrations of REE in acid-resistant augite and pigeonite. We observe a weak positive Eu anomaly of the leached samples only after reactions at pH 3 or less; it originates from the strong positive Eu anomaly of maskelynite; see Fig. 2.

The REE pattern of pristine Zagami on a “% left” basis naturally has a Lu/La ratio of 1.0. A similar value from CI-normalized concentrations results because of the flat REE pattern (Fig. 2). Their increasing LREE-depletion with decreasing pH of the leaching solutions results in the following Lu/La ratios, calculated from the data of the regression curves; results for BE-N are given for comparison (salt = sulfate plus chloride):

Table 4. Lu/La ratios of the leached basalts.

pH value	5	4	3	2	1	0.5
Zagami, buffer and buffer + salt ^a	0.97	1.08	8	8 ^b	8	–
Zagami, buffer + salt + P	0.97	1.01	1.40	8	8	–
BE-N, buffer and buffer + salt	1.10	1.09	1.12	1.8 ^c	2.10	2.21

^aFrom the reaction in the presence of salt only.

^bThe individual values differ only slightly.

^cIndividual values are 2.38 in buffer solution and 1.22 with present salt.

The final Lu/La ratio of 8 agrees with that of the LREE-depleted patterns of the acid-resistant augite and pigeonite. Our Yb/La ratio from the CI-normalized curves (Fig. 2) also is 8 and agrees with the ratio of 9 calculated from literature data for the volume-weighted sum of the REE in the pyroxenes of Zagami (Wadhwa et al. 1994; McCoy et al. 1999).

Earlier leaching experiments on Shergotty and the (olivine-phyric) basaltic shergottite Elephant Moraine (EET) A79001 with 1 M HCl for 10 min reduced the REE in the residue to about 15% of the initial concentrations. The patterns were depleted in LREE with CI-normalized Lu/La ratios of 11 and 21, respectively, and had large, positive Eu anomalies (Laul et al. 1986). The results indicate a noticeable attack on pyroxenes, in contrast to our experiments under milder conditions.

The flat REE patterns of the basaltic shergottite falls contrast with the steep ones of Antarctic finds and made us wonder if the latter might result from acidic leaching either on Mars or in Antarctica. We do not consider finds from hot deserts because of possible terrestrial REE contaminations, see Crozaz et al. (2003). Our lithology of Zagami has a REE concentration of $9 \times$ CI, that of Shergotty is $10 \times$ CI (Laul et al. 1986). Both have CI-normalized Lu/La ratios of 1.14. Basaltic shergottite finds from Antarctica have REE maxima of about $20 \times$ CI for Queen Alexandra Range (QUE) 94201 (Dreibus et al. 1996b) and $10 \times$ CI (lithology A) or $20 \times$ CI (lithology B) for EETA79001 (Burghel et al. 1983; Laul et al. 1986). Their LREE-depleted patterns have CI-normalized ratios Lu/La ~ 4 for EETA79001A and Yb/La ~ 9 for QUE 94201, see Fig. 2. The REE patterns of all four shergottites were attributed to the compositions of their parent magmas. Indeed, the arguments against acidic leaching as the origin of the steep REE patterns of the Antarctic shergottites prevail. The concentrations of the heavier REE in the Antarctic finds are considerably higher than in leached samples and in the range usually found for pristine basaltic shergottites. Their patterns show the typical hump between Gd and Ho. The patterns of the leached samples of Zagami here are flat. The hump is also missing in leached samples of Shergotty and EETA79001, see Laul et al. (1986).

About 90% of Th and U reside in the scarce phases of Zagami that dissolve in 2 M HCl. More detailed investigations of the very similar Martian meteorite Shergotty have shown that these phases are phosphates and mesostasis, both also host REE. Concentrations of Th/U in the most abundant and acid-resistant minerals maskelynite (0.16/0.05 ppm) and in pyroxene (0.07/0.02 ppm) are low (Chen et al. 1986). Uranium is enriched in Fe and Ti oxides of Zagami (Borg et al. 2005). The total concentrations of Th and U in whole rock samples of pristine and leached Zagami are low. Our measured data are incomplete and occasionally have large uncertainties, see Table 7. The differences in the concentrations of residual Th and U in % of the starting values and the influences of added sulfate, chloride, and phosphate are smaller than the uncertainties of the measurements. Therefore, instead of plotting individual curves of residual Th and U as a function of the pH value, we have used the data to delimit the range of residual Th and U, see Fig. 1. The solubility of Th and U is lower than that of the REE. Dissolution is moderate at pH values down to 3, where the dissolution of the main host

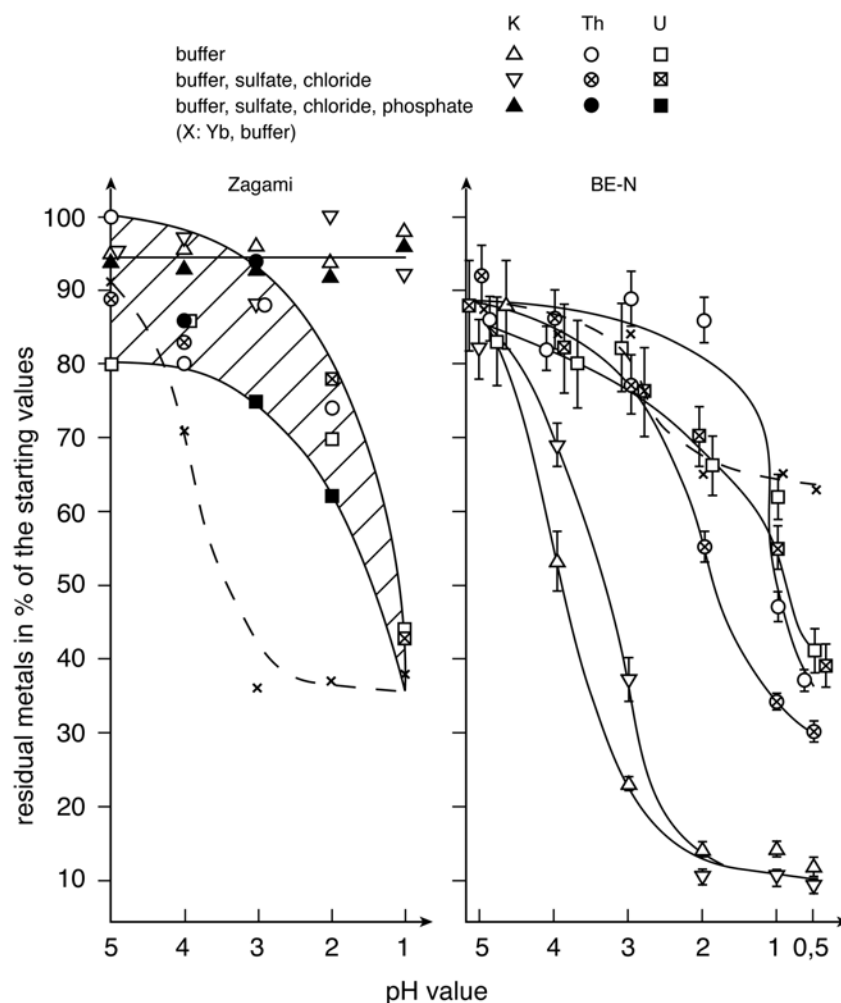


Fig. 1. Residual K, Th, and U in leached Zagami and BE-N in % of the starting concentrations. For Zagami, the errors of the measurements of K are 7% or less, see section Zagami and Table 7 on errors for Th and U. Error bars are shown for the measurements of BE-N.

mineral whitlockite is complete in the absence of phosphate. The dissolution of Th and U increases at pH 2, and becomes still larger at pH 1. Thorium in Zagami decreases from 0.33 to about 0.15 ppm and U from 0.076 to about 0.035 ppm, about 50% of the starting values.

Preliminary results on leaching Zagami and an alkali olivine basalt at about pH 4 using a commercial citrate buffer gave residual concentrations of around 30% for Th and U in Zagami (Dreibus et al. 2007). We now find about 90% of residual Th and U using a sodium acetate buffer. We assign the increased solubility in the preliminary experiments to the used buffer. It could enhance dissolution of Th and U by forming chelate complexes; see, e.g., Pasilis et al. (2003).

BE-N

The mineralogical composition of BE-N indicates that K resides preferentially in nepheline and also in melilite. Apatite contains most of the REE, Th, and U. Weak acids dissolve melilite and apatite, and stronger ones dissolve also

nepheline. Olivine also dissolves readily in acids. The dissolution of minerals consumes acid and causes the pH values in reactions of BE-N to increase more strongly than in those of Zagami, see the experimental section. It also gives the weight losses during leaching; they reach about 40 wt% at pH 2 and remain nearly constant upon increasing the acidity to pH 0.5. Measured concentrations of residual K, REE, Th, and U are listed in Table 8.

Potassium in BE-N mainly resides in acid-soluble minerals. Residual K decreases smoothly with the pH value, about 80 wt% being left at pH 5, less than 50% at pH ~3.5, and 15% at pH 2. The increase in acidity to pH 0.5 decreases remnant K to about 10%; see Fig. 1. We attribute the loss of K to an initial attack on melilite, followed by an attack on nepheline at lower pH values. The presence of sulfate and chloride reduces the liberation of K at pH 4 and pH 3. At pH 4, the concentration of residual K in BE-N (~60%) is similar to the concentration (65%) in the alkali olivine basalt used in preliminary experiments (Dreibus et al. 2007).

The quantity of residual REE decreases to about 70% of

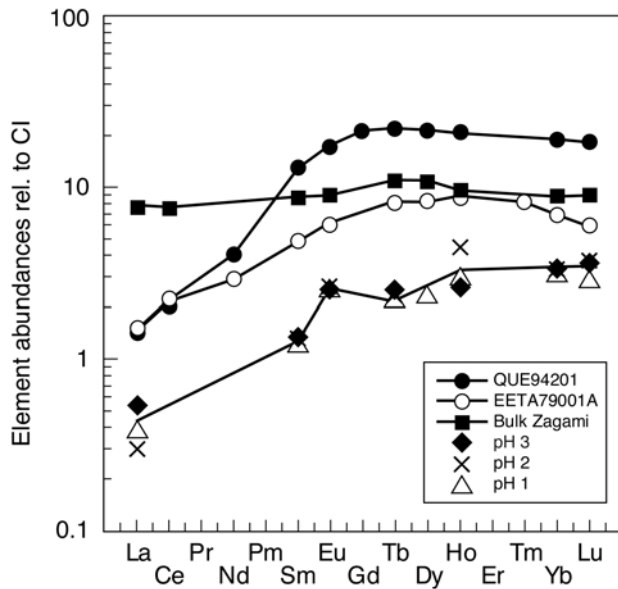


Fig. 2. CI-normalized REE patterns of pristine Zagami, of basaltic shergottite finds from Antarctica, and of Zagami leached with solutions containing sulfate and chloride.

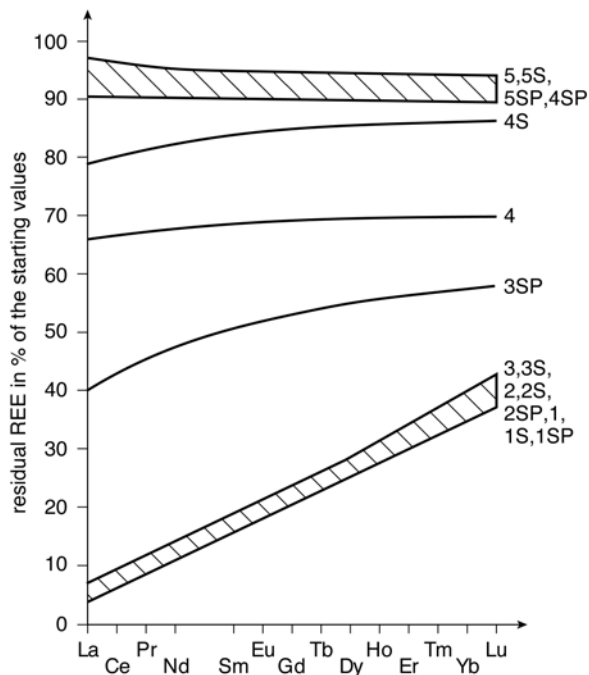


Fig. 3. Regression curves of residual REE in leached Zagami in % of the starting concentrations. The ciphers give the pH value of the solution; S indicates added sulfate and chloride, P indicates added sulfate, chloride, and phosphate.

the initial concentration, as the pH value of the solution decreases to 3. The almost complete dissolution of readily mobilized REE with about 40% left ($15 \times$ CI) requires pH 2 without added salts and pH 1 in the presence of sulfate and

chloride. A further decrease of the pH value sets free only small additional quantities of REE, see Fig. 4 (residual REE in % left) and Fig. 5 (CI-normalized REE). The patterns of residual REE in “% left” change from almost flat at pH 5 to HREE-rich at pH 2, and pH 1 in the presence of sulfate and chloride. The patterns become slightly steeper at lower pH. The resulting Lu/La ratios are listed with the ratios for Zagami; see above. Residual REE probably are hosted mostly in augite.

Phosphates of Th and U react similarly, as they become accessible to acid by dissolution of apatite; see Fig. 1. The better solubility of U at pH 5 and 4 with respect to Th, though in the range of the measuring error agrees with the behavior of the elements during terrestrial weathering; see, e.g., Keppler et al. (1990). As the pH value decreases, the solubilities of Th and U continue to increase similarly. About 80% are left at pH 3, where most of the apatite matrix is dissolved. Thorium seems to become more soluble than U at pH 1 and less. Leaching BE-N at pH 0.5 decreases Th from 10.4 to 3.6 ppm and U from 2.4 to 1.0 ppm (about 40%) after inclusion of the loss of soluble minerals. The curves of residual Th and U do not approach constant concentrations at low pH value, indicating the incomplete dissolution of potentially soluble minerals, in contrast to the curves of K and REE. Added sulfate and chloride do not change the amount of dissolution within the limits of the measuring error for U. For Th, added salts seem to increase its mobilization at pH 3 or less.

To ensure that we can account for REE, Th, and U missing from BE-N after leaching, we coprecipitated them with ferric hydroxide (Goldberg et al. 1963) from the filtered buffer solutions of experiments at pH 4 and pH 3. We measured the concentrations of REE, Th, and U in the dried precipitates by INAA and calculated the weights of the elements from the sample weights. The added weights of the elements in the leached samples and the dried precipitates were 85 to 98% of their weights in pristine BE-N, except for Tb, where we always found only around 80%.

Factors Determining the Mobilization of K, REE, Th, and U from Both Basalts

The loss of incompatible elements from both basalts upon contact with acidic solutions is almost identical for Th and U, similar for REE, and completely different for K. The different dissolution properties of K result from its prevalent residence in insoluble maskelynite of Zagami (1150 ppm) and in soluble minerals of BE-N (11500 ppm), presumably melilite and nepheline. Leaching at pH 1 results by chance in similar residual concentrations of about 1150 ppm in both basalts.

The basalts host REE, Th, and U mostly in calcium phosphates and the smaller part in minerals that are practically inert. The acidic dissolution of phosphates mobilizes REE, Th, and U. While the dissolution equilibria of REE in calcium phosphates are established rapidly and

Table 5. Measured concentrations of Sc and Hf in leached Zagami and BE-N and resulting factors of their relative increase.

pH value (pristine Zagami: Sc = 56,0, Hf = 1,55 ppm)	5	4	3	2	1	0,5
Measured Sc/Hf in buffer	59,7/1,54	60,0/1,62	60,7/1,61	59,2/1,64	61,2/1,63	
Average factor of increase	1,03	1,06	1,06	1,06	1,07	
In buffer + sulfate + chloride	60,6/1,63	60,5/1,68	59,2/1,65	60,7/1,71	59,4/1,66	
Average factor of increase	1,065	1,08	1,06	1,09	1,065	
In buffer + sulfate + chloride + phosphate	59,8/1,62	59,7/1,66	60,4/1,70	60,0/1,60	60,9/1,65	
Average factor of increase	1,06	1,07	1,075	1,05	1,075	
Average of average factors of increase	1,05	1,07	1,065	1,07	1,07	
Resulting factor from the regression calculation (pristine BE-N: Sc = 22, Hf = 5,6 ppm)	1,057	1,061	1,065	1,069	1,073	
Measured Sc/Hf in buffer	23,5/6,20	27,7/7,19	30,4/7,83	33,8/9,36	35,6/8,90	34,3/9,02
Average factor of increase	1,09	1,275	1,385	1,605	1,605	1,585
Resulting factor from the regression calculation	1,12	1,26	1,39	1,53	1,66	1,73
In buffer + sulfate + chloride	23,2/6,10	26,2/6,78	27,1/7,34	34,2/8,90	35,6/8,89	35,7/9,08
Average factor of increase	1,08	1,16	1,27	1,57	1,605	1,62
Resulting factor from the regression calculation	1,04	1,2	1,36	1,53	1,69	1,77

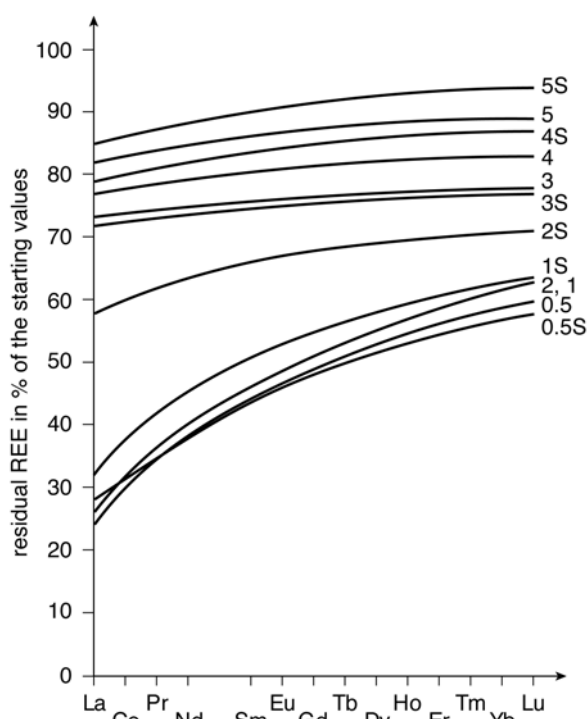


Fig. 4. Regression curves of residual REE in leached BE-N in % of the starting concentrations. The ciphers give the pH value of the solution; S indicates added sulfate and chloride.

simultaneously with that of their matrix, Th and U react slower and incompletely, indicating different mechanisms of dissolution. Calcium phosphate and leachable REE of Zagami dissolve completely at pH 3. The dissolution of leachable REE of BE-N is complete at pH 2 (and at pH 1 in the presence of added sulfate and chloride). The quantities of mobilized REE here are about three times larger than for Zagami. A

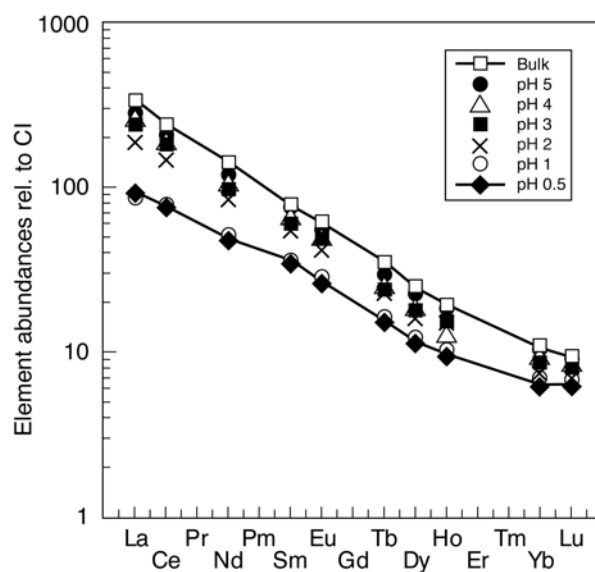


Fig. 5. CI-normalized REE in pristine BE-N and in samples leached by solutions containing sulfate and chloride.

matrix effect controls the mobilization of the REE. Dissolution experiments have demonstrated that whitlockite dissolves slightly faster than apatite in acidic solution, the rates of both increase with acidity (Gregory et al. 1974). The more ready dissolution of REE from whitlockite of Zagami than from apatite of BE-N suggests that the dissolution rate of the matrix material determines the relative amount of REE dissolution. There may also be a contribution by the higher phosphate concentration in BE-N (1.05 wt% P_2O_5) than in Zagami (0.48 wt%) (Shih et al. 1982).

The dissolution of Th and U in % of the starting values is similar for both elements and basalts and less extensive and

slower than that of the REE. It is independent of the host minerals of Th and U and of their differing concentrations in the pristine materials and increases with decreasing pH value of the solution. The Th/U ratio probably remains constant for Zagami and decreases slightly for BE-N. The curves of the concentrations of residual Th or U versus pH do not approach constant values and indicate that the dissolution of their potentially soluble minerals from Zagami and BE-N is incomplete. This behavior cannot result from the establishment of the dissolution equilibrium, because the solubility products of Th or U phosphates are constants at each pH value. Equal concentrations of dissolved Th or U would result for both basalts and different residual concentrations of Th or U in % of the starting values which are by a factor of 30 lower in Zagami than in BE-N. Instead, the mobilization of Th and U phosphates is determined by the kinetics of dissolution. It causes at each pH value the dissolution of the same relative percentage of Th and U with respect to their concentrations in the pristine basalts. The reaction constants are similar for the phosphates of both elements and increase with increasing acidity. The same was observed in the slow and incomplete acidic dissolution of Th phosphate. The concentration of Th ions in the solution was determined by the dissolution kinetics of $\text{Th}(\text{HPO}_4)_2$ and at $\text{pH} > 4$ also to some degree by that of $\text{Th}(\text{OH})_4$. Establishing the dissolution equilibrium would require about one year due to the low solubility (Fourest et al. 1999).

The influence of added sulfate and chloride on the dissolution equilibria of K, REE, Th, and U varies. Uncertainties given in Fig. 1 for K, Th, and U in BE-N are from the concentration measurements, the total uncertainties of the data are probably twice as large. With the latter uncertainties, we find that added sulfate and chloride decrease the mobilization of K at pH 4 and 3. This might be due to the precipitation of jarosite. However, we do not find a reduced liberation of K at lower pH values, where we expect the same reaction. Hardly any K is mobilized from Zagami; there is no influence of added salts. Added sulfate and chloride impede the loss of REE from Zagami only at pH 4. For BE-N, the effect occurs in experiments at pH 5, pH 4, and pH 2. Equilibration of dissolved REE with sparingly soluble REE sulfates might explain this, if the effect was not absent at pH 3. Data on the loss of Th and U from Zagami are too uncertain and incomplete to show if there is an influence of added salts. For BE-N, the solubility of Th increases at pH 2 or less in the presence of sulfate and chloride. The reason for this is obscure. The influence of added salts on the solubility of U is smaller than the uncertainty of the measurements. In conclusion, some of the observed effects of added sulfate and chloride might be artifacts; others may result from the precipitation of secondary minerals. The influence on the dissolution is but of minor importance with respect to the influence of a change in the pH value of the solution used for leaching.

IMPLICATIONS FOR THE SURFACE CHEMISTRY OF MARS

The mineralogical composition of the Martian surface has been studied globally by satellites and locally by rovers. Satellite observations from the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) in the IR range (Bandfield et al. 2000; Rogers et al. 2007) and in the VNIR range from the Mars Express OMEGA spectrometer (Bibring et al. 2006; Poulet et al. 2007) are complementary. Prevailing minerals on the surface of Mars are pyroxene (OMEGA) and feldspar (MGS-TES). The concentration of olivine is 10% or more (OMEGA). The Mars rovers analyzed the Martian soil chemically and mineralogically by X-ray (APXS), IR (Mini-TES), and Mössbauer spectroscopy. The soil is similar at both landing sites, with a deduced composition of 35 to 45 wt% of pyroxene, 35 to 40% of plagioclase, and 10 to 15% of olivine (Yen et al. 2005). CIPW norms calculated from the chemical compositions of Gusev (McSween et al. 2006b) and Columbia Hills rocks (McSween et al. 2006a) indicate that they consist mainly of plagioclase, slightly less pyroxenes, and some olivine, with iron and titanium oxides and calcium phosphates as accessory minerals. The rocks are similar to olivine-phyric shergottites.

Acidic leaching of minerals probably was extensive on Mars about 4 to 3.5 Ga ago, see the Introduction for details. We use our leaching experiments with Zagami (crystallization age ~200 Ma) to qualitatively deduce the acidic mobilization of K, REE, Th, and U from the older basalts (>3 Ga) of the Martian surface. This is possible, because the mantle source regions for SNC meteorites were differentiated early and changed only little due to absent crustal recycling until remelted to form the SNC parent magmas (McSween 2003). Experiments with synthetic Martian materials showed that moderately acidic solutions readily attack olivine and apatite; their dissolution leads to an increase in the pH value of the solutions. Titanium and Fe oxides react incompletely at pH 1, plagioclase is quite unreactive at this pH value, and pyroxene even more so (Tosca et al. 2004; Hurowitz et al. 2005). A slightly different sequence resulted from model calculations (Zolotov et al. 2007). A plot of collected literature data (Taylor et al. 2007) shows that the rate constants of feldspar dissolution are by three to four orders of magnitude slower than that of apatite.

Upon contact with acidic solutions, elements can remain practically immobile either due to their residence in virtually inert minerals or precipitation into secondary minerals like jarosite. A retarded mobilization of K did occur on Mars. In Meridiani Planum, mobilized K (and Na) was scavenged from acidic solutions via precipitation of jarosite. It is still abundant in outcrops, although part of it later was hydrolyzed at higher pH values yielding hematite and dissolved K (McLennan et al. 2005; Morris et al. 2006). We do not detect a mobilization of elements via this mechanism in our experiments at constant pH

value. However, the similar mobilization of elements in reactions in absence and presence of added sulfate and chloride suggests that the formation of secondary minerals requires special conditions and has a limited influence on the mobilization of the studied elements under conditions resembling Martian ones. Possible reasons might be a slow rate of formation or an insufficient concentration of one of their constituent components. Under our experimental conditions, the formation of jarosite is possibly limited by the availability of Fe, which is relatively immobile at the used pH values, and also by available K for Zagami.

Our experiments demonstrate that the liberation of K from its host mineral maskelynite in Zagami is not noticeable at pH 1 or higher. As feldspars are abundant on Mars, this suggests a similarly slow reaction there. An extrapolation based on the acidic dissolution of terrestrial rocks predicts that after 0.5 Ma of weathering only 15% of mobilized K originates from feldspar, which hosts 84% of initially present K (Harlavan et al. 2002). Dissolved K precipitates as a salt only upon the evaporation of the solution. A prolonged aqueous alteration should have led to high concentrations of K in global sinks. Studies by satellite and by rovers suggest that the mobilization of K on Mars was moderate at most. The GRS measured the following concentrations of K in ppm:

- Global average 3300, range 2600–3800 (Taylor et al. 2007);
- Southern basalts 3200, northern basalts 4300 (Karunatillake et al. 2006).

Evaluations for individual areas yield an enrichment of K in dust and soil relative to local bedrock (Newsom et al. 2007). The differences in concentrations of K generally were attributed to the compositions of the parent magmas, with later modest modifications by aqueous alteration or aeolian erosion. The rovers measured the following concentrations of K in ppm:

- Meridiani soil 3700–4200, outcrops 4600–5000 (Yen et al. 2006);
- Gusev soil 3200–3700, basalts 600–1300 (Gellert et al. 2006);
- Columbia Hills rocks 2900–5000 (Gellert et al. 2006).

The data also suggest a limited mobilization at most. The enrichment in Gusev soil is not necessarily due to precipitated K, because the local origin of the soil is uncertain. The concentration of K in the evaporation deposit Paso Robles in the Gusev plain is the same as in the soil (Gellert et al. 2006).

Whitlockite and also apatite host most of REE, Th, and U in Zagami. The interaction with moderately acidic solutions readily mobilizes the REE, and particularly the LREE. Compounds of Th and U dissolve more slowly than those of the REE. Dissolved phosphate lowers the solubility of sparingly soluble phosphates of REE, Th, and U via the law of mass action in moderately acidic solution. Phosphate is abundant in Martian soils (0.8–0.9 wt% of P_2O_5) and rocks (0.5 wt% or more) (Yen et al. 2006). The results of the leaching experiments in the absence and presence of phosphate probably bracket the dissolution of REE, Th, and U

on Mars about 4 to 3.5 Ga ago. The more readily dissolved REE probably were distributed more extensively than Th and U, before the pH value of the solution increased by reaction with olivine or other minerals. The ions of REE, Th, and U then formed sparingly soluble compounds or were adsorbed. The deduced moderate mobilization of Th agrees with data measured by the GRS. The global average is 0.62 ppm with a range of 0.37 to 0.95 ppm (Taylor et al. 2007). The average concentration is 0.63 ppm in the southern basalts and 0.94 ppm in the northern, possibly andesitic, basalts (Karunatillake et al. 2006). GRS data of individual areas indicate an enrichment of Th in dust and soil relative to the local bedrock (Newsom et al. 2007). The differences in the concentrations of Th, as for K, were attributed principally to differing compositions of the parent magmas, with later modest modifications by aqueous alteration or aeolian erosion. Concentration measurements of REE and U on Mars are missing, except for early U measurements at very low spatial resolution by the Phobos-2 mission (Surkov et al. 1994).

The K/Th ratio is potentially useful for the identification of an aqueous alteration of surface material. The interaction with approximately neutral solutions preferentially removes K, while Th is immobile; the K/Th ratio of the leached rock decreases. Leaching by acidic solutions for limited time preferentially removes Th residing in calcium phosphates and increases the K/Th ratio of the leached rock. The K/Th ratio of pristine Zagami is lower than that of the Martian surface, because the concentration of Th is slightly and that of K much lower. This prevents a direct comparison of the K/Th ratios, but indicates general trends. Upon contact of Zagami with acidic solutions, the concentration of K remains constant and only that of Th decreases as the acidity of the solution increases. The average values from the concentration ranges for Th and U in Fig. 1 yield the following K/Th ratios:

Table 6. Change of the K/Th ratio of Zagami upon acidic leaching.

	pH of the solution					
	Pristine	5	4	3	2	1
K	1130	1070	1070	1070	1070	1070
Th	0,330	0,297	0,294	0,281	0,234	0,132
K/Th	3420	3600	3640	3810	4570	8110

In our experiments, an acidic alteration becomes noticeable in the K/Th ratio only at pH values <3. The small range of the K/Th ratio from the GRS measurements suggests for Mars aqueous alterations at moderate acidity. The K/Th ratios range from 4000 to 7000 for 95% of the studied surface; the global average is 5330. The K/Th ratios tend to be higher in sinks (Taylor et al. 2007). The K/Th ratios of the southern highland basalts (5080) are higher than those of the northern plains (4570) (Karunatillake et al. 2006). The differences were attributed to igneous origins, perhaps with later, modest aqueous alteration. We suppose that the ions ultimately yielding the extensive sulfate deposits detected by the

Table 7. Concentrations of incompatible elements in leached Zagami in ppm^a.

Element	K	Th	U	<i>La</i> ^b	Ce	<i>Sm</i>	<i>Eu</i>	Tb	Dy	<i>Ho</i>	<i>Yb</i>	<i>Lu</i>
Untreated solid	1130	0,33	0,076	1,86	4,80	1,33	0,51	0,40	2,73	0,55	1,43	0,22
pH 5, (factor 1,057) starting value	1194	0,35	0,08	1,97	5,07	1,41	0,54	0,42	2,89	0,58	1,51	0,23
Buffer, measured	1140	0,36 (20)	0,064 (20)	1,91	5,00	1,31	0,49	0,38	2,50	0,59	1,38	0,20
Residue in %	95	100	80	97	99	93	91	90	87	100	91	87
Buffer + S ^c + Cl, measured	1130	0,31 (20)	n. d.	1,79	3,60	1,29	0,48	0,38	2,50	0,62	1,37	0,21
Residue in %	95	89		91	71	91	89	90	87	100	91	91
Buffer + S + Cl + P, measured	1120	n. d.	n. d.	1,92	5,40	1,34	0,52	0,39	2,70	0,55	1,49	0,22
Residue in %	94			97	100	95	96	93	93	95	99	89
pH 4, (factor 1,061) starting value	1199	0,35	0,081	1,97	5,09	1,41	0,54	0,42	2,90	0,58	1,52	0,23
Buffer, measured	1150	0,28 (20)	0,07 (30)	1,32	3,60 (15)	0,95	0,37	0,28 (15)	1,90 (20)	0,42 (15)	1,08	0,16
Residue in %	96	80	86	67	71	68	68	67	66	72	71	70
Buffer + S + Cl, measured	1160	0,29 (15)	n. d.	1,57	4,80 (15)	1,16	0,44	0,36	2,40	0,50	1,31	0,21
Residue in %	97	83		80	94	82	81	86	83	86	86	91
Buffer + S + Cl + P, measured	1120	0,30 (12)	n. d.	1,86	5,00 (20)	1,30	0,52	0,40	2,80	0,55	1,50	0,21
Residue in %	93	86		94	98	92	96	95	97	95	99	91
pH 3, (factor 1,065) starting value	1203	0,351	0,081	1,98	5,11	1,42	0,54	0,43	2,91	0,59	1,52	0,23
Buffer, measured	1160	0,31 (12)	n. d.	0,14 (30)	< 1.5	0,24	0,17 (15)	0,11 (20)	< 1	0,18 (15)	0,55	0,09
Residue in %	96	88		7		17	31	26		31	36	39
Buffer + S + Cl, measured	1060	<0,15	<0,06	0,13	<0,6	0,22	0,16	0,10	<1	0,16 (25)	0,57	0,10
Residue in %	88	<43	<75	7	<12	15	29	23	<30	27	38	41
Buffer + S + Cl + P, measured	1120	0,33 (15)	0,06 (25)	0,82	2,3 (20)	0,69	0,32	0,22 (15)	1,34 (20)	0,29 (12)	0,94	0,15
Residue in %	93	94	75	41	45	49	59	51	46	49	62	65
pH 2, (factor 1,069) starting value	1208	0,353	0,081	1,99	5,13	1,42	0,55	0,43	2,92	0,59	1,53	0,24
Buffer, measured	1140	0,26 (20)	0,057 (30)	0,01 (45)	<0,8	0,21	0,16	0,13 (25)	<1,2	0,20	0,57	0,10
Residue in %	94	74	70	1	<15	15	29	30	<41	34	37	43
Buffer + S + Cl, measured	1220	<0,18	0,063 (30)	0,078 (20)	1,10	0,21	0,16	0,096 (20)	2,0 (25)	0,27	0,58	0,096 (12)
Residue in %	100	<51	78	4	21	15	29	22	69	46	38	42
Buffer + S + Cl + P, measured	1110	<0,15	0,05 (30)	0,12 (20)	n. d.	0,22	0,16	0,11 (20)	0,83 (20)	0,18	0,62	0,098 (15)
Residue in %	92	<42	62	6		15	29	26	28	13	41	43
pH 1, (factor 1,073) starting value	1212	0,354	0,082	2,00		1,43	0,55	0,43	2,93	0,59	1,53	0,24
Buffer, measured	1190	<0,15	0,036 (30)	0,083 (25)	n. d.	0,21	0,16 (15)	0,1 (20)	<1,5	0,17	0,59	0,09
Residue in %	98	<42	44	4		15	29	23	<50	29	38	38
Buffer + S + Cl, measured	1120	<0,18	0,035 (35)	0,095 (25)	n. d.	0,205	0,156 (15)	0,085 (25)	0,63 (30)	0,18 (20)	0,53	0,08 (15)
Residue in %	92	<51	43	5		14	29	20	22	31	35	33
Buffer + S + Cl + P, measured	1160	<0,15	<0,03 (5)	0,1 (20)	n. d.	0,21	0,14 (15)	0,082 (25)	<0,8	0,17 (15)	0,57	0,09
Residue in %	96	<42	<44	5		15	26	19	<25	29	37	38

^aMeasuring errors >10% are given in parentheses.

^bResults for elements in italics were used in calculations of the regression curves.

^cS, Cl, and P indicate added sulfate, chloride, and phosphate.

Table 8. Concentrations of incompatible elements in leached BE-N in ppm.^a

Element	K	Th	U	<i>La</i> ^b	Ce	Nd	<i>Sm</i>	<i>Eu</i>	Tb	Dy	<i>Ho</i>	<i>Yb</i>	<i>Lu</i>
Untreated solid	11540	10,4	2,4	82	152	67	12,2	3,6	1,3	6,4	1,1	1,8	0,24
pH 5, (factor 1,12) starting value	12925	11,6	2,7	92	170	75	13,7	4	1,46	7,17	1,23	2	0,27
Buffer, measured	10200	9,97	2,23	74	145	57	12,3	3,4	1,2	5,8	1,1 (12)	1,75	0,25
Residue in %	79	86	83	80	86	76	90	85	82	81	89	88	93
pH 5, (factor 1,04) starting value	12002	10,8	2,5	86	158	70	12,7	3,7	1,35	6,66	1,14	1,87	0,25
Buffer + S ^c + Cl, measured	9790	9,9	2,2	71,9	137	59	12,1	3,31	1,14	6,0	1,1 (15)	1,73	0,24
Residue in %	82	92	88	84	87	84	96	89	84	90	96	93	96
pH 4, (factor 1,26) starting value	14540	13,1	3,0	103	192	84	15,4	4,5	1,64	8,06	1,39	2,30	0,30
Buffer, measured	7740	10,7	2,4	79,1	152	64	12,5	3,6	1,18	6,20	1,1 (15)	1,94	0,26
Residue in %	53	82	80	77	79	76	81	80	72	77	79	84	87
pH 4, (factor 1,20) starting value	13848	12,5	2,9	98	182	80	14,6	4,3	1,56	7,68	1,32	2,16	0,29
Buffer + S + Cl, measured	9520	10,7	2,38	77,5	147	61	12,5	3,5	1,1 (15)	5,6	0,88 (25)	1,91	0,26
Residue in %	69	86	82	79	81	76	86	81	71	73	67	88	90
pH 3, (factor 1,39) starting value	16041	14,5	3,3	114	211	93	17,0	5,0	1,81	8,9	1,53	2,5	0,33
Buffer, measured	3730	12,9	2,7	81,9	162	67	13,6	3,82	1,35	6,77	1,20	2,11	0,29
Residue in %	23	89	82	72	77	72	80	76	75	76	78	84	88
pH 3, (factor 1,36) starting value	15694	14,1	3,3	111,5	207	91	16,6	4,9	1,77	8,7	1,50	2,45	0,33
Buffer + S + Cl, measured	5800	10,8	2,5	79,3	157	64 (12)	12,7	3,8	1,2 (15)	6,30	1,2 (15)	1,94	0,28
Residue in %	37	77	76	71	76	70	77	78	68	72	80	79	85
pH 2, (factor 1,53) starting value	17656	15,9	3,7	125,5	233	102,5	18,7	5,5	1,99	9,79	1,68	3,1	0,41
Buffer, measured	2700	13,6	2,44	46	99	49 (12)	10,5	3,0	1,10	5,15	1,10	2,0	0,27
Residue in %	15	86	66	37	42	48	56	55	55	53	65	65	66
pH 2, (factor 1,53) starting value	17656	15,9	3,7	125,5	233	102,5	18,7	5,5	1,99	9,79	1,68	3,1	0,41
Buffer + S + Cl, measured	2120	8,71	2,61	69,8	146	62	12,7	3,67	1,3 (12)	6,27	1,30	2,18	0,31
Residue in %	12	55	70	56	63	60	68	67	65	64	77	70	76
pH 1, (factor 1,66) starting value	19156	17,3	4,0	136	252	111	20,3	6,0	2,16	10,62	1,83	3,0	0,41
Buffer, measured	2680	8,06	2,48	34,7	82,8	41,0	9,24	2,76	1,02	5,20	0,98	1,96	0,29
Residue in %	14	47	62	26	33	37	46	46	47	49	54	65	71
pH 1, (factor 1,69) starting value	19503	17,6	4,1	139	257	113	20,6	6,1	2,20	10,82	1,86	3,0	0,41
Buffer + S + Cl, measured	1950	5,97	2,26	44,6	96,4	44,4	10,4	2,98	1,06	5,21	0,99	2,01	0,29
Residue in %	10	34	55	32	38	39	50	49	48	48	53	67	71
pH 0,5, (factor 1,73) starting value	19964	18,0	5,8	142	262	116	21,1	6,2	2,25	11,07	1,90	3,1	0,42
Buffer, measured	2490	6,74	2,38	33,6	80,4	39,6	8,98	2,72	0,99	5,20	0,90	1,94	0,29
Residue in %	12	37	41	24	31	34	43	44	44	47	47	63	69
pH 0,5, (factor 1,77) starting value	20426	18,4	5,8	145	269	119	21,6	6,4	2,30	11,33	1,95	3,2	0,425
Buffer + S + Cl, measured	1940	5,61	2,25	40,2	88,3	42,0	9,86	2,84	1,05	5,32	1,00	1,88	0,390
Residue in %	9	30	39	28	33	35	46	44	46	47	51	59	68

^aMeasuring errors >10% are given in parentheses.^bResults for elements in italics were used in calculations of the regression curves.^cS and Cl indicate added sulfate and chloride.

OMEGA spectrometer (see the Introduction) were leached at pH 3 or more. These conditions would not have changed significantly the K/Th ratio of the Martian surface material.

SUMMARY

We leached the Martian basalt Zagami and the terrestrial basalt BE-N at pH 5 to pH 1 using buffer solutions and studied the mobilization of K, REE, Th, and U. Feldspar glass hosts 95 wt% of K in Zagami and is inert in our experiments, while 90 wt% of K in BE-N reside in soluble minerals and become mobile. Sixty percent or more of REE, Th, and U reside in calcium phosphates and become accessible to mobilization upon its dissolution. Whitlockite and also apatite of Zagami contain about 75 wt% of the total REE. The pH-dependent dissolution equilibria of phosphates of Ca and REE are established rapidly. Calcium phosphate dissolution and that of incorporated REE is complete at pH 3. Adding phosphate to the buffer solutions impedes the dissolution; the complete mobilization of soluble REE then requires pH 2. The complete dissolution of apatite and incorporated REE of BE-N requires pH 2 in the absence of dissolved phosphate. Surprisingly, the slower dissolution of Th and U in % of the starting concentrations is similar for both elements and basalts. This result is due to the kinetic control of the dissolution of the Th and U phosphates. About half of Th and U are still immobile at pH 1.

The experiments delimit the possible mobilization of K, REE, Th, and U from soil and rocks about 4 to 3.5 Ga ago, when acidic water flowed on the surface of Mars. Since most K resides in feldspar, our results suggest that only a small relative amount of K became mobile. The conditions for the mobilization of the REE, and particularly of the LREE, via dissolution of calcium phosphates probably were more favorable despite dissolved phosphate, which decreases the solubility of the sparingly soluble phosphates of Ca, REE, Th, and U. A higher percentage of the more readily mobilized REE dissolved compared to Th and U. The REE were also distributed more widely before becoming immobile again at an increased pH value of the solution. The conclusions from the leaching experiments agree for K and Th with their global distributions measured on Mars by satellite. The rather uniform concentrations suggest a very limited aqueous mobilization of the elements.

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