Cation-exchange properties of pumice: Taking a sip from a volcanic cocktail

J. H. Sterba,* G. Steinhauser, M. Bichler

Atominstitut der Österreichischen Universitäten, Vienna University of Technology, Vienna, Austria

The search for the telltale signs of volcanic eruptions in easily dateable (biological) material like tree rings or speleothems has been going on for a very long time. Even though the reactions of tree rings to cataclysmic events are fairly well understood, there has not been a satisfactory method to distinguish volcanic from other climatically active events. Recent findings of differing Ba-contents in soil and the unexpected mobility of Ba during volcanic eruptions strongly suggest that tephra changes the concentrations of trace elements in the surrounding topsoil. To better understand the mechanics of this enrichment, leaching experiments with volcanic ashes have been performed that show that pumice acts as a cation-exchanger. Neutron activation analysis (NAA) with its reasonably simple sample preparation and the possibility to distinguish volcanic ashes from contamination of solvents by using activated ashes offers a hands on approach to the problem above. Several samples of known composition of volcanic ashes have been activated and leached with different solvents and solutions, aiming to both recreate a realistic situation comparable to natural leaching due to rain fall and obtain quantifiable results.

Introduction

Large scale volcanic eruptions present drastic incidents that had and have climatic influence. Due to the dispersion of large quantities of ash[1–5] during such eruptions, tephra horizons are widely used as time and synchronization marks in sedimentary sequences,[6,7] ice-,[8] and drill cores.[9]

Tree rings and speleothems, especially stalagmites that offer reliable dating information and record climatically active events, like volcanic eruptions, have been used to try to chronologically arrange large scale volcanic eruptions.[10,11] However, no method has yet been found to clearly distinguish volcanic from other climatically active events.

There are some studies on the effects of freshly fallen tephra on pastures and livestock[12–15] but no information on the influence of old tephra on soil exists, except the common knowledge that volcanic soil is considered rather fertile.

The special research program SCIEM2000 of the Austrian Academy of Sciences[16] has been set up to synchronize the civilizations of the Eastern Mediterranean in the 2nd Millennium BC and relies heavily on the dating of the so-called 'Minoan' eruption of Santorini (Thera, Greece) that happened sometime between the 15th and the 17th century BC. Single tephra shards found in the GRIP ice-core could stem either from the 'Minoan' eruption,[17,18] giving a date of 1645 BC, but Ba and Sr values do not correlate with the values from the Minoan eruption. Another study[19] shows that the shards could also belong to an Aniakchak-eruption (Alaska, USA).

Thus, the aim of this study was to find out what reactions, if any, occur during the several thousand years of washing due to rainfall between old tephra and soil.

This includes the search for useable chemical (primary) markers that the natural leaching of volcanic ashes can produce in plants or speleothems, with special attention payed to Ba.

Experimental

For this study, all leached pumice samples came from the same batch of Santorini Upper Pumice (Bo), called 'SAT-5', that has been in use as an in-house standard for several years. The batch was created from approximately 250 g of pumice that was ground to a grain size of less than 3 μm in an agate mortar and homogenized. After homogenization the batch has been dried to constant weight.

Santorini Bo was used, since a sufficiently large amount of already homogenized pumice was available and the elemental composition of the 'SAT-5' batch is known very well.[20,21]

Using ground and homogenized pumice instead of naturally occurring grain sizes offers larger surfaces for leaching as well as better suitability for irradiation in Suprasil™ quartz glass vials.

Leached pumice

Two series of experiments have been performed. In the first, 5 samples of approximately 1 g (Table 1) each of pumice have been sealed in Suprasil™ quartz glass vials. Those vials were irradiated in the central irradiation tube of the Triga Mark II reactor of the Atominstitut der Österreichischen Universitäten (Stadionallee 2, 1020 Vienna, Austria) for approximately 30 hours at a neutron flux density of $1 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$.

* E-mail: jsterba@ati.ac.at

Table 1. Samples and leaching solution for the first series

Sample	Mass, g	Leachate	Concentration, mol/l	Volume, ml
G1	1.172	H_2O dest		48.7
G2	1.420	H_2SO_4	0.1	48.4
G3	1.088	CsCl	0.01	46.8
G4	1.105	Tap water		47.0
G5	1.193	Rb_2SO_4	0.01	47.8

After irradiation and a necessary cooling time of 4 days, the vials were opened and mixed with 50 ml of the respective leaching solutions (H_2O dest.; Viennese tap water; H_2SO_4 Merck™, Darmstadt, suprapur, 0.1 mol/l; CsCl AnalR™, The British Drug Houses Ltd., 0.01; Rb_2SO_4 Merck™, Darmstadt, Suprapur, 0.01 mol/l; see Table 1). Distilled water, tap water, and H_2SO_4 have been used to simulate normal rainfall, surface water and acidic rainfall after a volcanic eruption,[22] respectively. Rb_2SO_4 and CsCl were used to investigate the cation-exchange properties of pumice, since alkali metals are absorbed following Na<K<Rb<Cs in cation-exchangers.

After vigorous shaking and 15 minutes in an ultrasonic bath the samples were centrifuged for 20 minutes at 3000 s^{-1}. The liquid was decanted and filtered with Schleicher and Schuell™ blue ribbon filters.

The clear liquids were then measured at a fixed geometry of 4 cm from a 222 cm^3 HPGe γ-detector (1.78 keV resolution at the 1332 keV ^{60}Co-peak, 48.2% relative efficiency) for 3600 seconds and, after three weeks of additional decay time for 10,000 seconds. The first measurement was used to determine the contents of ^{153}Sm, ^{177}Lu, ^{239}Np, ^{140}La, ^{24}Na, and ^{82}Br in the samples. In NAA, ^{239}Np is usually used to measure uranium contents of the sample, since ^{239}Np is the decay product of ^{239}U, the activation product of ^{238}U, and can be detected more sensitively. Since this study investigates chemical properties, ^{239}Np content does not represent uranium content.

Br$^-$ as an anion is not relevant to this study, investigating the cation-exchange capabilities of pumice. However, its presence gives rise to the speculation that pumice can also act as an anion-exchanger.

The second measurement provided data on ^{141}Ce, ^{169}Yb, ^{177}Lu, ^{233}Pa, ^{181}Hf, ^{131}Ba, ^{147}Nd, ^{134}Cs, ^{160}Tb, ^{86}Rb, ^{59}Fe, ^{65}Zn, ^{46}Sc, ^{60}Co, ^{152}Eu, ^{124}Sb, and ^{85}Sr. As in the case of ^{239}Np, ^{233}Pa as the decay product of ^{233}Th, which itself is the activation product of ^{232}Th, cannot be used as a representative for thorium contents of the sample.

Adsorption of Ba

Since the first series of experiments clearly showed that the reactions responsible for the mobilization of different elements from the pumice matrix are cation-exchange reactions, a second series of experiments was performed, investigating the mechanisms of adsorption and remobilization of Ba on pumice. For this second series of experiments, 4 samples of approximately 1 g Santorini Bo (from the same 'SAT-5' batch as before) were used.

119.85 mg of $BaCl_2 \cdot 2H_2O$ (Loba-Chemie, Wien-Fischamend, pro analysi) were weighed into a PE-vial and irradiated in one of the dry irradiation tubes of the Triga Mark II reactor at a neutron flux of $1.7 \cdot 10^{12}$ n·cm^{-2}·s^{-1} for approximately 6 hours. The barium chloride was then dissolved in 5 ml of H_2O creating a stock solution.

Four samples of about 1 g pumice were mixed with 1 ml of the stock solution. Different amounts of H_2SO_4 and water were added to each sample, creating volumes of 50 ml each at different pH-values. The samples were shaken and put into an ultrasonic bath for 15 minutes. After centrifugation for 20 minutes at 3000 s^{-1} the liquids were decanted into PE-vials. Both, before and after decantation, the samples were measured at a fixed geometry with a HPGe γ-detector (see above) for 400 seconds each.

Ba-adsorption rates were calculated from the change in concentration between the two measurements.

To make sure that no Ba-containing solution remained in the vials with the pumice, the samples were filled with 50 ml of H_2O, shaken lightly, centrifuged and decanted. The decanted solution was measured again to monitor the washing. After the second washing, Ba concentration in the decanted liquid was higher than explainable by remaining Ba-solution. Thus it was concluded that instead of merely removing the remaining stock solution from the sample, the second washing already removed some of the adsorbed Ba from the samples.

After washing, the samples were leached with 50 ml of solutions of NaCl (Merck™, Darmstadt, pro analysi, ~3.5% corresponding to sea water), $La(NO_3)_3 \cdot 6H_2O$ (Riedel-de Haën AG, Germany, 0.001 mol/l), H_2SO_4 (pH 2), and tap water, respecively (Table 2). For leaching, the same procedure as in the washing procedure described above was used.

Results and discussion

Results for the leached pumice samples are presented in Table 3, showing all values in counts·s^{-1}·g^{-1}. Since the aim of this study was to explore the mechanisms of the mobilization of different elements in naturally leached old pumice, it was not deemed necessary to produce absolute values for the leached substances.

Additionally to the elements presented in Table 3, the leaching with H_2SO_4 showed ^{153}Sm, ^{177}Lu, ^{239}Np, ^{140}La, ^{141}Ce, ^{169}Yb, ^{181}Hf, ^{147}Nd, ^{160}Tb, ^{65}Zn, ^{152}Eu, and ^{124}Sb.

Table 2. Sample masses, leaching solutions, and results for the Ba-adsorption experiments

Sample	Mass, g	pH	Ba adsorbed, mg/g	Leachate	Concentration	Ba leached, %
GK1	1.242	1.5	0.34	NaCl	3.5%	30.8
GK2	1.032	4.5	0.57	$La(NO_3)_3$	0.001 mol/l	21.9
GK3	1.015	4.5	0.90	H_2SO_4	0.1 mol/l	1.6
GK4	0.927	4.5	0.57	Tap water		25.0

Errors due to counting statistics are below 1% for adsorption values and below 5% for leaching values.

Table 3. Results of the leached pumice samples. All values are given in counts·s^{-1}·g^{-1}

Leachate	^{24}Na	^{233}Pa	^{131}Ba	^{134}Cs	^{86}Rb	^{85}Sr	^{59}Fe	^{46}Sc	^{60}Co
H_2O	14184	0.264	BDL	BDL	BDL	BDL	0.090	0.303	0.060
H_2SO_4	29268	BDL	0.655	0.191	0.583	0.063	2.251	5.072	0.565
CsCl	21159	0.058	0.282	0.116	0.277	0.053	0.027	0.072	0.037
Tap water	17529	BDL	BDL	BDL	BDL	BDL	0.372	0.068	0.181
Rb_2SO_4	22490	0.095	0.566	0.116	0.560	0.082	0.072	0.157	0.201

BDL marks the values where the detection limit was not exceeded. Errors due to counting statistics are less than 10% except for ^{233}Pa and ^{59}Fe where error does not exceed 15%.

No other leachate showed any of the above elements, so the leaching is attributed to the acidic dissolution of the phenocrysts, like sulfides or apatite, contained in the glass matrix of the pumice. Thus, for the comparison of the results, the leaching with H_2SO_4 is ignored.

Since no other sample showed any of the above elements typical for apatite (REE)[23] in pumice, it was concluded that the leaching reactions of the other leachates are limited to the surface of the glass phase of the sample. It can be assumed that, contrary to crystalline matter, irradiation did not significantly change the physical and chemical properties of the glass fraction.

When the data for the leaching with distilled water, tap water, CsCl (c_{Cs^+}=0.01 mol/l), and Rb_2SO_4 (c_{Rb^+}=0.01 mol/l) is compared, the values for ^{24}Na, ^{134}Cs, ^{86}Rb, ^{85}Sr, and ^{131}Ba indicate strongly that the mobility of the cations is due to an ion-exchange reaction. The large values for ^{59}Fe, ^{46}Sc, and ^{60}Co leached with tap water are probably caused by unusually high Fe-contents of the tap water due to construction works on the plumbing of the Atominstitut during the time of experiments.

It is somewhat surprising though, that the amounts of nearly all elements leached with Rb^+ are higher than the corresponding values for the leaching with Cs^+, even though the ionic radius of Cs^+ is larger (r_{Cs^+}=1.88 Å, r_{Rb^+}=1.72 Å).[24] A normal ion-exchange resin would react differently. It can be argued that since the glass phase of pumice, in contrast to ion-exchange resins, does not have a regularly structured surface, the slightly smaller ion can penetrate further into the pores and thus contact a larger surface. That Rb and Cs both mobilize the same amount of Cs further supports this interpretation.

Additionally, those results correspond strongly to recently published findings[25] on the adsorption of different elements on pumice samples, where the adsorption of Rb on pumice is significantly larger than the adsorption of Cs. Especially Ba^{2+} showed higher mobility than expected.

Thus, to further understand the process of adsorption and ion-exchange, radioactively marked Ba was adsorbed on several pumice samples. The results for those Ba-adsorption experiments are shown in Table 2.

Ba was used since recent findings showed unexplained but pumice-related anomalies in the Ba-contents of cave sediments.[25] The analysis of volcanic tephra particles in the GRIP ice core associated with the so-called 'Minoan' eruption show overabundant Ba and Sr values.[18]

The adsorption of Ba on the pumice shows only a slight dependence on pH values. The different leachates were chosen to try out different processes of ion-exchange. As expected, H_2SO_4 produces the insoluble $BaSO_4$ (solubility product constant $K_{sp(BaSO4)}$= $1.08 \cdot 10^{-10}$ mol^2/l^2)[26] and thus cannot mobilize the adsorbed Ba.

Due to the law of mass action, leaching with a 3.5% NaCl solution detaches over 30% of the adsorbed Ba, the typical reaction used to regenerate ion-exchangers. Similarly, tap water, containing significant amounts of Na, Mg, and Ca (6–11 °dH) releases 25% of the adsorbed Ba. Since the trivalent La^{3+} ion has a higher affinity to ion-exchanging surfaces than the divalent Ba^{2+} ion, almost 22% of the adsorbed Ba were mobilized when treating the Ba-loaded pumice samples with solutions of La^{3+}.

Conclusions

Natural leaching of pumice deposits can mobilize several cations such as Na, Ba, Cs, Sr, and Rb by ion-exchange. K probably shows the same characteristics but due to the relatively short half-life of its activation product (^{42}K, 12.36 h) and the comparatively high detection limit (1000 ppm) it was not detected in any of the samples used in this study. Strongly acidic rain (H_2SO_4) as it occurs during or shortly after volcanic eruptions can intensify this process by dissolving crystals contained in the pumice.

Sea water also can mobilize several ions due to the law of mass action, again evidencing the pumice's cation-exchange capabilities.

Thus, it seems reasonable to attribute Ba anomalies in speleothems, soils or tree rings to volcanic activity. Ba, Cs, Sr, and Rb should further be investigated for their usability as primary markers, tagging volcanic eruptions in dateable biological materials.

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