

ARGILLATION OF THREE SILICATE ROCKS EXPRESSED IN TERMS OF ION TRANSFER

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ABSTRACT

The transfer of ions during the weathering of a Medford diabase, a granite from British Guiana, and of the Cheto Arizona tuff is traced by recasting the analyses of the fresh rocks and their altered counterparts into 160-oxygen rock cells, and by comparing algebraically the products of the weathering reaction with the original reactants.

Hydrolysis and hydration are the first steps in the reaction. H ions were added in the weathering environment of the diabase and granite, but Mg ions were added in the change of tuff to bentonite.

Silica and alkali metal ions are dissolved and removed during weathering of the diabase and granite, presumably under acid conditions, but it appears that the Cheto tuff was formed under a non-acid environment where Mg was added. During the hydrolysis of silicate rocks, H ions are concentrated temporarily in the clay minerals on land, while OH ions go to the ocean.

More examples of ion transfer during weathering than the three given herein are needed to define the reactions occurring in the many environments of alteration which rocks encounter.

INTRODUCTION

Silicate rocks and minerals may be altered to rocks rich in clay minerals by ordinary surface weathering; by the action of shallow ground water, artesian water, hydrothermal fluids; and by halmoysis. In the processes, certain ions (participating elements will be referred to as ions for convenience, although covalent bonding may be important) may be removed from the reactant parent rocks, some may be added from the outside to form the products, and others may be rearranged in their association and bonding with neighboring ions.

The addition or subtraction of material is commonly inferred by comparing the chemical composition of the parent material with that of the products in terms of an assumed static oxide or mineral. Alumina (Leith and Mead, 1915, *et al.*), titanium oxide and "iron" (Harrison, 1933, p. 17), and zircon (Haseman and Marshall, 1945) have been assumed as remaining constant during the alteration process, and the loss and gain of other oxides computed. It is also possible to compute the loss and gain of ions, rather than oxides, during the alteration process, and this approach will be taken in the subsequent discussion. Analyses, previously published, of fresh rocks and their weathered counterparts will be used in the three examples which follow.

WEATHERING OF A MEDFORD DIABASE

The chemical weathering of several rocks, including a Medford diabase, was studied in detail by Goldich (1938, p. 17), who analyzed mineralogically and chemically the fresh rocks and some of their weathered counterparts during various stages of alteration. Goldich's chemical analyses, Nos. 9 and 10, of the fresh and weathered Medford diabase are reproduced in Table I, columns (a) and (b), respectively. His analyses have been recast in terms of the number of ions in combination with 160-oxygens (Barth's rock cell, 1948, p. 50), in columns (c) and (d), Table I.

It is noted that the number of ions of aluminum are practically the same (within analytical error) in the fresh and weathered materials, 17.82 and 17.39, respectively. Most probably aluminum remained static during weathering because Ca and Mg ions were abundantly present (column e) in the soluble products of weathering, and these divalent ions flocculated or immobilized any Al ions which otherwise might have been lost.

To determine what ions or constituents were added or lost during the weathering process, the amounts shown in column (d) are subtracted from those in column (c). The algebraic differences are shown in column (e), those preceded by a minus sign being lost during weathering, and the others added, or gained.

The reaction during weathering may be written in the same way a simple quick chemical reaction in the laboratory is described. The number of ions

TABLE I

	(a) ¹	(b) ²		(c) ³	(d) ⁴	(e) ⁵
SiO ₂	51.44	51.38	Si	49.59	48.02	—1.57
Al ₂ O ₃	15.67	15.92	Al	17.82	17.39	
Fe ₂ O ₃	2.25	10.92	Fe	8.33	9.65	1.32
FeO	8.37	2.60				
MgO	2.09	1.26	Mg	2.89	1.74	—1.15
CaO	6.31	3.52	Ca	6.48	3.48	—3.00
Na ₂ O	4.42	4.16	Na	8.21	7.52	— .69
K ₂ O	1.91	1.57	K	2.20	1.91	— .29
H ₂ O+	1.67	2.94	H	10.76	18.29	7.53
H ₂ O—	0.41	1.70				
TiO ₂	1.95	2.52	Ti	1.39	1.68	.29
P ₂ O ₅	0.97	1.03	P	.81	.79	— .02
MnO	0.18	0.22	Mn	.17	.18	.01
CO ₂	2.14	.07	C	2.84		—2.84
S	0.12	.01				
	99.90	99.82	O	160.00	160.00	160.00

¹ Analysis of fresh Medford diabase (Goldich, 1938, No. 9).

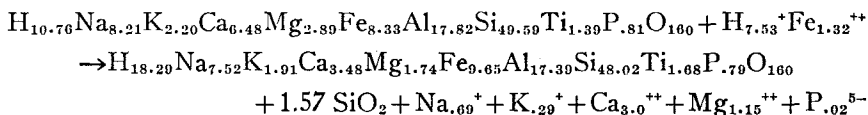
² Analysis of weathered Medford diabase (Goldich, 1938, No. 10).

³ Ions in 160-oxygen rock cell of (a).

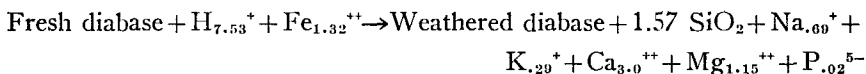
⁴ Ions in 160-oxygen rock cell of (b).

⁵ Loss and gain of ions from (c) to (d).

of the reactants and products are taken from columns (c), (d), and (e), and are written as shown below.



In even simpler form, the words "fresh diabase" and "weathered diabase" may be substituted for their lengthy formulas, as follows.

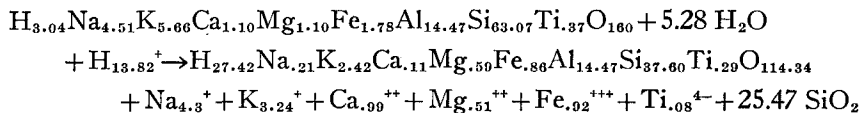


The equation describing the weathering of the Medford diabase is interesting for two reasons: no modification was necessary to hold Al essentially constant, and the weathering reaction calls for the addition of H ions to the fresh rock. This reaction supports numerous statements in the literature that H ions are important in the weathering of silicate rocks and minerals, recently discussed by Frederickson (1951, p. 221), Frederickson and Cox (1954, p. 738), Keller and Frederickson (1952, p. 594), and Keller (1955).

WEATHERING OF A GRANITE

A discussion of the weathering of silicate rocks may well include reference to the outstanding work of Harrison on weathering and laterization of silicate rocks in British Guiana. Harrison's (1933, p. 62) analysis of the average granite in a quarry at Kalacoon, B.G., is reproduced in Table II(a), and the analysis of the residual white sandy clay at the top of the quarry in II(b); ions in 160-oxygen rock cells of the rocks are tabulated in columns (c) and (d). The analysis of the weathered material, in column (d), is adjusted to hold Al constant (14.47) in column (e), and the gain or loss in ions during weathering is shown in column (f). Justification for holding Al constant arises, it is believed, from the presence of Ca and Mg ions (column f) in solution, but not complete removal of either, from the granite.

The equation below shows the weathering of the granite to sandy clay.



Noteworthy in the weathering of this granite is the requirement for a large number of H ions. As metal cations are removed, H ion replaces them. A large amount of silica is dissolved and removed, which should present no problem because Na and K ions are present in apparently sufficient abundance to stabilize the soluble silica.

TABLE II

	(a) ¹	(b) ²		(c) ³	(d) ⁴	(e) ⁵	(f) ⁶
SiO ₂	72.27	65.17	Si	63.07	52.61	37.60	-25.47
Al ₂ O ₃	14.01	21.30	Al	14.47	20.25	14.47	
Fe ₂ O ₃	1.95	1.38	Fe	1.78	1.21	.86	— .92
FeO	0.60	0.53					
MgO	0.84	0.70	Mg	1.10	0.82	.59	— .51
CaO	1.15	0.23	Ca	1.10	0.15	.11	— .99
Na ₂ O	2.70	0.19	Na	4.51	.29	.21	— 4.30
K ₂ O	5.03	3.27	K	5.66	3.39	2.42	— 3.24
H ₂ O+	0.52	7.13	H	3.04	38.37	27.42	24.38
MnO	0.27		Mn	.16			
TiO ₂	0.58	0.65	Ti	.37	.39	.29	— .08
P ₂ O ₅	0.04		P				
	99.92	100.55	O	160.00	160.00	114.34	-45.66

¹ Analysis of fresh granite from quarry in British Guiana (Harrison, 1933, p. 62).

² Analysis of white sandy clay at top of quarry of (a) (Harrison, 1933, p. 62).

³ Ions in 160-oxygen rock cell of (a).

⁴ Ions in 160-oxygen rock cell of (b).

⁵ Recalculated (d), holding Al constant to 14.47.

⁶ Loss or gain of ions from (c) to (e).

A TUFF AND BENTONITE FROM THE PUERCO VALLEY, ARIZONA

Weathering of a silicate rock may proceed without an excess of H ions being present, as is shown by a comparison of the analyses of fresh tuff and its daughter bentonite from the Chambers-Cheto bleaching clay deposit in Arizona. The bentonite mined from this deposit is widely known because of its extensive use in industrial processes. That it has originated from the alteration of a vitric tuff is well established because certain parts of the clay contain remnants of unaltered and partially altered tuff masses in the form of hills, "horses," and peripheral remnants. The gradual change from fresh tuff to "pure" montmorillonite can be traced in the field, and corroborated by microscopical examination and X-ray analysis.

The fresh tuff is composed of typical angular glass shards ranging in cross section from fine dust to about .25 mm., although the bulk of them range between about .06 and .25 mm. The index of refraction of the glass is 1.498, with very little variation. Almost no birefringent material is visible: it is a truly vitric tuff.

An X-ray powder diffractogram of the fresh tuff is shown in Figure 1a. This diffractogram shows no record of regular, interplanar spacings, as in a crystal, but is similar to diffractograms of artificially prepared glass (Warren and Loring, 1935), and diffractograms (Fig. 1d), of the perlite from Superior, Arizona. Keller and Pickett (1954, p. 96) inferred from infra-red and X-ray data that the structure of the glass in the Superior perlite was a random network of Si,Al-O₄ tetrahedra linked by hydrogen

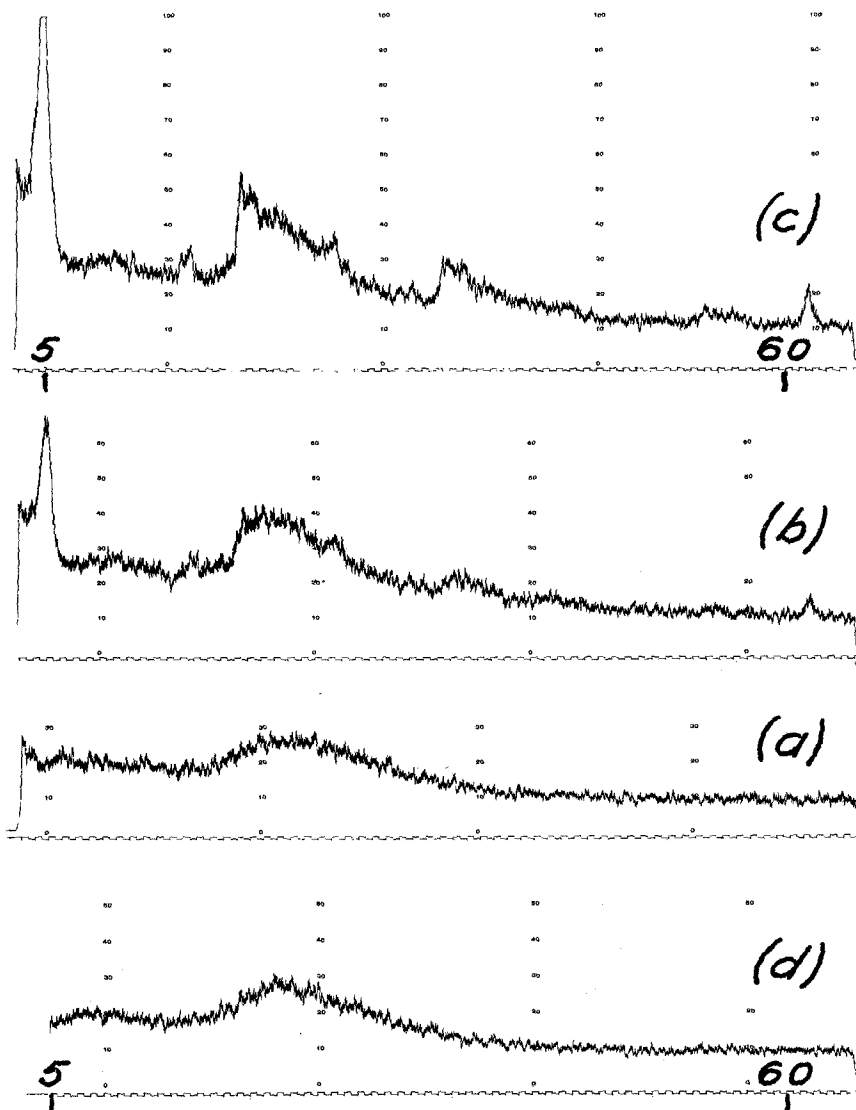


FIGURE 1 (a, b, c, d).—(a) X-ray diffractogram of fresh tuff, Cheto, Arizona. (b) X-ray diffractogram of partially altered tuff, Cheto, Arizona. (c) X-ray diffractogram of bentonite (montmorillonite), Cheto, Arizona, solvated in ethylene glycol. (d) X-ray diffractogram of perlite from Superior, Arizona (Keller and Pickett, 1954). North American Philips X-ray. Ni-filtered, $\text{Cu K}\alpha$ radiation. The high peaks at the left of the diffractograms of clay occur at $4.9^\circ 2\theta$.

and metallic cation bridges. It is believed that the structure of the glass in the Puerco Valley tuff is similar to that inferred for the Superior perlite and for artificially prepared glass.

A powder diffraction pattern of tuff partially altered to bentonite is shown in Figure 1*b*. It has been solvated in ethylene glycol which expands the basal spacing of the clay mineral to approximately 18 Å. Montmorillonite is developing through alteration of the glass. A powder diffractogram of the clay from the bentonite deposit surrounding the tuff remnant is shown in Figure 1*c*, which is a typical diffractogram of the Cheto-Chambers Camontmorillonite. A microscopical examination of the partially altered tuff shows the development of montmorillonite in the incompletely altered shards, which confirms the X-ray data.

The change in chemical composition during alteration of the tuff to bentonite is shown in chemical analyses published by Nutting (1943a, p. 183) of "the partly altered parent tuff and the bentonite formed locally in the same deposit." Nutting also computed the loss and gain of oxides referred to static Al_2O_3 during the alteration, but we will compute the changes in terms of ion transfer. The Puerco Valley deposit of Nutting is a part of that now called Cheto (Kiersch and Keller, 1955).

Nutting's analysis (done by Fairchild) of the "partly altered parent tuff" shows an $\text{H}_2\text{O}+$ content of 6.60 percent which is higher than that of the fresh tuff. Several ignitions of tuff, which was observed under the microscope to be fresh, yielded losses averaging 4.75 percent, with not more than .25 percent deviation. Accordingly, Nutting's analysis of the "partly altered parent tuff" was recalculated as moisture-free and containing $\text{H}_2\text{O}+$ in amount of 4.75 percent, which is shown in Table III(*a*). The analysis of bentonite from Nutting, recast also to moisture-free basis, is in column (*b*).

TABLE III

	(a) ¹	(b) ²		(c) ³	(d) ⁴	(e) ⁵
SiO_2	69.87	60.13	Si	58.13	37.87	-20.26
Al_2O_3	13.94	18.45	Al	13.68	13.68	
Fe_2O_3	2.77	3.98	Fe	1.70	1.89	0.19
MgO	2.20	5.32	Mg	2.75	5.03	2.28
CaO	1.83	2.42	Ca	1.65	1.63	-0.02
Na_2O	1.25	0.27	Na	2.00	.30	-1.70
K_2O	3.50	0.18	K	3.70	.15	-3.55
$\text{H}_2\text{O}-$						
$\text{H}_2\text{O}+$	4.75	8.40	H	26.37	35.30	8.93
TiO_2	.34	0.48	Ti	.20	.22	0.02
			O	160	124.08	-35.92

¹ Tuff, Puerco Valley, with assumed $\text{H}_2\text{O}+$ content 4.75 percent.

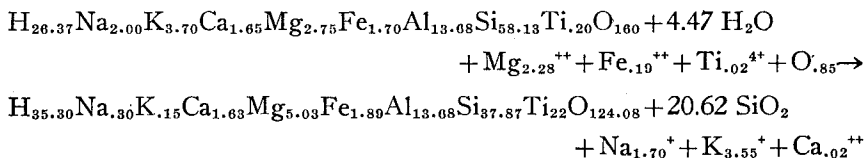
² Bentonite, Puerco Valley, free of $\text{H}_2\text{O}-$.

³ Ions in 160-oxygen cell of tuff in (*a*).

⁴ Ions in 160-oxygen cell of bentonite adjusted to 13.68 ions of Al.

⁵ Loss or gain in cations during alteration when Al is constant.

These analyses were converted to ratios of ions present with 160-oxygens and Al held constant in the bentonite to that of the fresh tuff, tabulated in columns (c) and (d). Losses and gains are shown in column (e), as before. The equation describing the alteration follows.



Substances added in significant quantity were H₂O and Mg ions. H ions, other than those in the water and in the solids, do not appear in the reaction. This is in keeping with the idea that bentonites are not formed in an environment of strong leaching by acid solutions (Ross, 1943, p. 225). Instead, the geologic evidence usually suggests their formation by hydrolysis in a more or less enclosed basin, as in a lake. Presumably the reaction was not acid in character.

The source of the Mg ions in this reaction is not known, but it was probably the water present in the old Cheto basin, or the rocks from which upon weathering soluble Mg was carried into the environment of the hydrolyzing Cheto volcanic dust. It should be recognized that the analysis of the bentonite represents the summation of reactions of weathering and possibly some of diagenesis which can not be separated.

INFERENCES

Three samples of rock weathering constitute a very short base line upon which to extrapolate inferences about ion transfer during weathering, but a few speculations about the process may stimulate additional effort in this direction. More pairs of good analyses of fresh rocks and their weathered counterparts, where reasonable certainty exists that the two are genetically related, are needed to define more accurately the weathering process. Not all environments of weathering are illustrated by the three samples treated in this paper, and it is not meant that all weathering proceeds to the same products as herein described.

It seems logical, however, to infer that the weathering of silicate rocks begins commonly with hydrolysis and hydration. H ions may be added from the water (Frederickson and Cox, 1954, p. 738), organic sources (Keller and Frederickson, 1953, p. 594), carbonic acids, and other natural, strong, so-called mineral acids. Silica and ions of the alkali metals apparently precede in susceptibility the removal by solution of alkaline earth metallic ions. The latter are displaced by H ions if acidity is high enough.

Weathering of silicates is fundamentally hydrolysis on a large scale, augmented by numerous side reactions. The net result is to concentrate the H ions from the hydrolysis into the clay minerals, which remain temporarily on the land, and to concentrate the OH ions in the ocean (the pH is above 7, as is well known).

In an environment of relatively stagnant water like that in a lake basin — that is, where fresh rain water does not renew the leaching solutions — the hydrolysis may occur on the alkaline side. Metallic ions may be added to the weathered product here to form bentonite, also possibly analcime (?) (Keller, 1952, p. 81). Bentonite clays found under a wide variety of geologic conditions suggest that much is yet to be learned and published about the alteration of vitric and crystal tuffs under subaerial, oxidizing, subaqueous, reducing, acid, and alkaline environments.

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