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ION-EXCHANGE CONSTANTS OF NATURAL GLASSES BY THE ELECTRODE METHOD[1]

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ABSTRACT

The ion exchange constants of twelve natural glasses were measured by an electrode method. All the glasses showed the selectivity sequence $2H^+ > 2K^+ > 2Na^+ > Ca^{++} \geq Mg^{++}$. The relation of the exchange behavior to composition is discussed in the light of recent theories and the experimental results. The geochemistry of glass weathering is in large part determined by its ion exchange behavior.

INTRODUCTION

An earlier paper (Truesdell, 1962) described the method of making membrane electrodes from natural glasses and the interpretation of electrode potential measurements to yield ion-exchange constants. In the earlier paper three natural glasses were studied; in the present paper seven natural glasses and five glasses synthesized to have the same composition as natural glasses were used. The simulated natural glasses were used because of lack of suitable natural samples. The analyses of the glasses studied are given in Table 1.

THERMODYNAMIC EQUATIONS

The appropriate basic electrode equations are (Garrels *et al.*, 1962):

$$E = C_A + \frac{RT}{2\mathfrak{F}} \ln \left(\frac{[A^+]^2}{\lambda_{A_2X_2}} + K_{AB} \frac{[B^+]^2}{\lambda_{B_2X_2}} \right),$$

$$E = C_A' + \frac{RT}{2\mathfrak{F}} \ln \left(\frac{[A^{++}]}{\lambda_{AX_2}} + K_{AB}' \frac{[B^+]^2}{\lambda_{B_2X_2}} \right),$$

and

$$E = C_A'' + \frac{RT}{2\mathfrak{F}} \ln \left(\frac{[A^{++}]}{\lambda_{AX_2}} + K_{AB}'' \frac{[B^{++}]}{\lambda_{BX_2}} \right).$$

The electrode equations have been derived using the ion-exchange equations:

$$A_2X_{2\,\text{glass}} + 2B_{aq}^+ = B_2X_{2\,\text{glass}} + 2A_{aq}^+,$$

$$AX_{2\,\text{glass}} + 2B_{aq}^+ = B_2X_{2\,\text{glass}} + A_{aq}^{++},$$

and

$$AX_{2\,\text{glass}} + B_{aq}^{++} = BX_{2\,\text{glass}} + A_{aq}^{++}.$$

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[1] Publication authorized by the Director, U. S. Geological Survey.

TABLE 1a. ANALYSES OF GLASSES STUDIED IN WEIGHT PER CENT[1]

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O	Sum
NG8	97.6	1.54	0.0	0.23	0.0	0.38	0.34	0.0	0.10	100.2
SG1	86.8	8.4	0.4	1.8	1.3	0.01	0.21	0.95	0.20	100.1
B2O	78.4	12.2	0.05	3.33	0.67	0.78	1.84	2.43	0.0	99.7
ST2	76.1	13.9	0.21	2.06	1.68	0.96	1.46	2.29	0.0	98.7
B76	74.9	14.8	0.13	4.68	0.43	0.66	1.50	1.84	0.0	98.9
NG5	76.0	12.1	0.52	0.78	0.6	0.70	3.4	5.15	0.27	99.5
NG2	76.4	12.7	0.56	0.58	0.4	0.30	4.1	4.57	0.67	100.3
B90	71.9	17.6	0.27	5.26	0.78	0.45	1.28	1.60	0.0	99.1
SG2	70.3	20.8	0.35	0.77	0.2	0.83	3.5	3.50	0.24	100.5
NG6	71.6	13.5	0.70	4.3	2.5	2.80	1.4	2.45	0.20	99.5
SG3	58.6	21.5	2.1	3.6	2.5	5.88	4.6	1.20	0.27	100.3
SG4	45.2	35.2	1.9	2.3	0.9	2.50	7.4	5.02	0.23	100.7

[1] Listed in order of decreasing mole per cent of silica.

NG8	Libyan Desert glass, Africa; analysis from P. A. Clayton, and L. J. Spencer, Mineral Mag., **23**, 501, 1934.
SG1	Synthetic Darwin glass; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro, U. S. Geol. Survey.
B20	Bediasite, (tektite), Lee County, Texas; analysis by M. K. Carron, and F. Cuttitta, U. S. Geol. Survey.
ST2	Synthetic tektite glass; analysis by M. K. Carron and F. Cuttitta.
B76	Bediasite, Lee County, Texas; analysis by M. K. Carron and F. Cuttitta.
NG5	Welded Walcott Tuff, American Falls quadrangle, Idaho; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro. Also contains MnO, 0.05 per cent and TiO_2, 0.21 per cent. Ion exchange constants for this glass and also for NG2 and NG6 have been published in Truesdell (1962).
NG2	Obsidian from Puerto de Abrigo, Jemez caldera, New Mexico; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro. Also contains MnO, 0.07 per cent and TiO_2, 0.10 per cent.
B90	Bediasite, Lee County, Texas; analysis by M. K. Carron and F. Cuttitta.
SG2	Synthetic tektite glass; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro.
NG6	Tektite, Marulas, P. I.; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro. Also contains MnO, 0.13 per cent and TiO_2, 0.81 per cent.
SG3	Synthetic fulgurite glass; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro.
SG4	Synthetic obsidian glass; analysis by H. J. Rose, Jr., F. J. Flanagan, and L. Shapiro.

The corresponding thermodynamic equilibrium expressions are:

$$K_{AB} = \frac{[A^+]^2[B_2X_2]}{[B^+]^2[A_2X_2]},$$

$$K_{AB}' = \frac{[A^{++}][B_2X_2]}{[B^+]^2[AX^2]},$$

TABLE 1b. ANALYSES OF GLASSES STUDIED IN MOLE PER CENT

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O
NG8	97.8	0.91	0.0	0.19	0.0	0.41	0.33	0.0	0.33
SG1	89.6	5.11	0.16	1.56	2.00	0.01	0.21	0.63	0.69
B20	83.8	7.68	0.02	2.98	1.07	0.89	1.91	1.65	0.0
ST2	82.3	8.86	0.08	1.86	2.72	1.11	1.53	1.58	0.0
B76	81.8	9.52	0.05	4.26	0.70	0.77	1.59	1.28	0.0
NG5	81.6	7.66	0.21	0.70	0.96	0.81	3.54	3.53	0.97
NG2	80.8	7.91	0.22	0.51	0.63	0.34	4.20	3.08	2.36
B90	79.3	11.4	0.11	4.84	1.29	0.53	1.37	1.13	0.0
SG2	77.3	13.5	0.15	0.71	0.33	0.98	3.73	2.46	0.88
NG6	76.4	8.47	0.28	3.83	3.96	3.19	1.44	1.60	0.71
SG3	64.4	13.8	0.87	3.31	3.93	6.92	4.90	0.84	0.99
SG4	53.9	24.8	0.85	2.29	1.60	3.20	8.56	3.82	0.92

and

$$K_{AB}'' = \frac{[A^{++}][BX_2]}{[B^{++}][AX_2]} .$$

In these sets of equations brackets denote activities, X^- represents a monovalent negative site, A and B represent two monovalent ions, one divalent and one monovalent ion, and two divalent ions; and R, T, and $\mathfrak{F}$ are the gas constant, absolute temperature, and the Faraday constant, respectively. Note that $K_{AB} > 1$ in the first and third equations (of each set) means that ion B^+ (or B^{++}) is preferred on the exchanger. Because only the activity of the monovalent ion is squared in the second equations its preference on the exchanger decreases with increasing dilution of the aqueous solution.

Although in the derivation of these equations no assumptions are made concerning the activities of the adsorbed ions, or their activity coefficients, it is generally observed that in inorganic ion-exchange reactions the adsorbed ions form symmetrical regular solutions (Garrels *et al.*, 1962; Garrels and Christ, 1965), and the rational activity coefficients for the adsorbed ions, *e.g.*, λ_{AX_2} and λ_{BX_2}, are related to the mole fractions of the adsorbed ions (N_{AX_2} and N_{BX_2}) by the simultaneous equations:

$$\lambda_{AX_2} = \exp\left(\frac{W_{AB}}{RT} N^2_{BX_2}\right)$$

$$\lambda_{BX_2} = \exp\left(\frac{W_{AB}}{RT} N^2_{AX_2}\right).$$

Although the electrode ion-exchange constant, K_{AB}, alone may be determined, the complete description (at a given temperature) of each exchange requires the determination of two constants: K_{AB}, and the regular solution constant, W_{AB}. The constants C_A, C_A', etc., are eliminated by a calibration procedure.

EXPERIMENTAL METHOD

The glass to be studied is ground to a thin membrane and cemented to an ordinary glass tube; the tube is filled with 0.01 M HCl and a AgCl-coated silver wire is inserted. The completed membrane electrode is immersed, together with a reference electrode having a saturated KCl liquid junction, in a salt solution with a known activity of one of the exchangeable cations. Increments of the second salt are added and the equilibrium potential of the membrane electrode (as measured with a high impedance vibrating-capacitor electrometer) and the activity of each cation are recorded after each addition. In most of the experiments, glass electrodes specifically sensitive to H^+, Na^+, or K^+ and insensitive to alkaline earth cations and anions are used to measure activities of these ions.

In each case the electrode is calibrated with one or more standard solutions of known activity of a given monovalent ion. The activity of the ion in the test solution is then calculated from the equation

$$\log a_x = \log a_s + \frac{E_x - E_s}{2.303\ RT/\mathfrak{F}}$$

where E_x is the potential of the glass electrode relative to a calomel electrode in the test solution, and E_s its potential relative to a calomel electrode in the standard solution, a_x is the ion activity in the test solution and a_s is the ion activity in the standard solution.

A pH electrode was used for the H^+-K^+ and H^+-Na^+ exchanges, a Na^+-specific electrode for NA^+-K^+ exchanges and a K^+-Na^+ electrode for the K^+-Ca^{++} and Na^+-Ca^{++} exchanges. Except in the H^+-K^+ and H^+-Na^+ exchanges, 0.01 mg of $Ca(OH)_2$ was added to 200 ml solution ($= 1 \times 10^{-7}$ M Ca^{++}) to raise the pH above 7.

For each exchange, the potential of the test electrode is plotted against the log of the activity of the cation added. The resulting points are fitted by one of a family of curves calculated for various values of the regular solution constant, W_{AB} shown in Fig. 1. The electrode curve for the K^+-Ca^{++} exchange on a tektite from the Philippines (NG6), shown in Fig. 2 illustrates the procedure.

In Fig. 2 the first point recorded was the potential of the electrode in 200 ml of a 0.0001 M KCl sooution without any $CaCl_2$ added. In this solution $[K^+] = 9.63 \times 10^{-4}$, and $\log [K^+] = -3.016$. The activity of Ca^{++} is initially about 10^{-7} from the $Ca(OH)_2$ added to suppress H^+ ion. Two successive 1.0 milliliter additions each of 0.001 M, 0.01 M and three of 0.1 M $CaCl_2$ were made, and after each addition the equilibrium potential of the

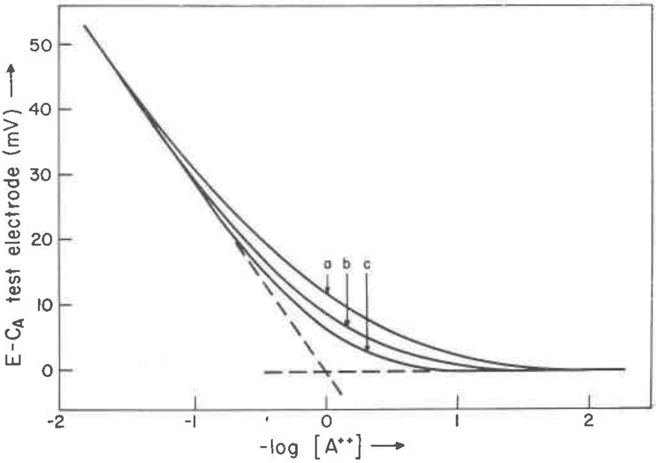

FIG. 1. Effect of changing the regular solution constant W_{AB} on the electrode curve. The electrical potential is plotted for various values of $\log[A^{++}]$ and W_{AB} when the product $K_{AB}[B^{++}]$ (or $K_{AB}[B^{+}]^2$) = 1. If A is a monovalent ion the electrical potential change will be twice as great for each value of $-\log[A^{+}]$.

a. $\frac{W_{AB}}{RT} = -1$, $W_{AB} = -0.6$ (25° C.),

b. $\frac{W_{AB}}{RT} = 0$ $W_{AB} = 0$ (25° C.),

c. $\frac{W_{AB}}{RT} = \frac{1}{2}$, $W_{AB} = +0.3$ (25° C.).

test electrode was recorded. The two straight lines (a, b) on the graph of Fig. 2 represent the potential the electrode would assume if the solution contained only Ca^{++} (a), or only 0.001 M K^{+} (b). The intersection of these lines is the activity of Ca^{++} alone that would produce the same potential as 0.001 M K^{+}. When $[K^{+}]=0$, and therefore $N_{K_2X_2}=0$ and $\lambda_{CaX_2}=1$ the electrode equation

$$E = C_{Ca} + \frac{2.303\,RT}{2\mathfrak{F}} \log\left(\frac{[Ca^{++}]}{\lambda_{CaX_2}} + K_{CaK}\frac{[K^{+}]^2}{\lambda_{K_2X_2}}\right)$$

reduces to

$$E_1 = C_{Ca} + \frac{2.303\,RT}{2\mathfrak{F}} \log\,[Ca^{++}].$$

When $[Ca^{++}]=0$ and therefore $N_{CaX_2}=0$ and $\lambda_{K_2X_2}=1$,

$$E_2 = C_{Ca} + \frac{2.303\,RT}{2\mathfrak{F}} \log K_{CaK}[K^{+}]^2.$$

When $E_1 = E_2$:

$$\log [Ca^{++}] = \log K_{CaK}[K^+]^2$$
$$\log [Ca^{++}] = \log K_{CaK} + 2 \log [K^+]$$

In Fig. 2, $\log [K^+] = -3.016$, and at the intersection $\log [Ca^{++}] = -4.40$. Therefore, $\log K_{CaK} = 6.032 - 4.40 = 1.632$, and finally $K_{CaK} = 42.8$.

The experimental results for all of the glasses studied agree, within experimental error, with the values calculated from the appropriate electrode equations, which in turn are based on the assumption that the absorbed ions form a symmetrical regular solution. The constants W_{AB} and K_{AB} for each exchange are given in Table 2. Other exchange constants may be derived from these by applying the rule, $K_{AB}K_{BC} = K_{AC}$. In order to preserve this relationship in mixed valence exchanges the monovalent-monovalent constants are given for $A_2X_2 + 2B^+ = B_2X_2 + 2A^+$ rather than for $AX + B^+ = BX + A^+$ reactions. To convert to the constants for the latter exchanges, the square roots of the constants in Table 2a must be taken.

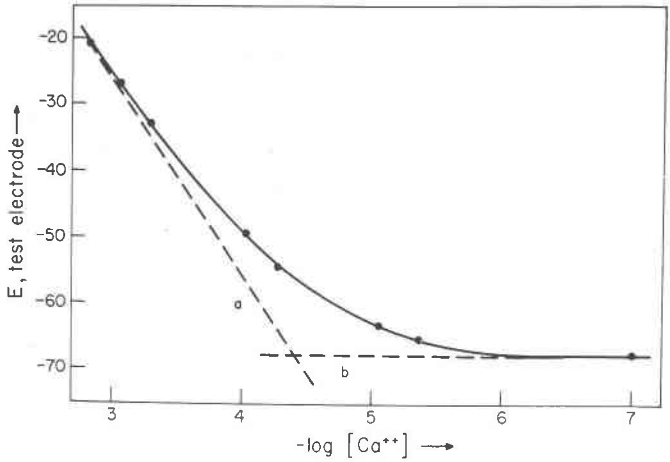

FIG. 2. Electrode potential curve of a tektite, NG6, for additions of Ca^{++} to a solution containing 10^{-3} M KCl ($\log [K^+] = -3.016$). The points are experimental values. The curve is represented by

$$E = C'_{Ca} + \frac{2.303\ RT}{2\mathfrak{F}} \log \left(\frac{[Ca^{++}]}{\exp(-0.9N^2_{K_2X_2})} + 42.8 \frac{[K^+]^2}{\exp(-0.9N^2_{CaX_2})} \right).$$

DISCUSSION

The relation between composition and ion-exchange behavior of these multicomponent natural glasses is complex. However, Eisenman (1962)

Table 2a. Exchange Constants for Some Glasses at 25° C.

	K_{NaH}	K_{KH}	K_{NaK}	K_{CaNa}	K_{CaK}	K_{MgCa}
NG8	170	33	5.0	100	480	1.6
SG1	400	35	11	100	1200	4.0
B20	360	21	16	250	1400	2.6
ST2	350	48	7.3	150	1100	n.d.
B76	400	22	13	130	1800	2.8
NG5[1]	12	2.0	5.8	20	120	1.0
NG2[1]	10	1.7	6.3	24	87	1.0
B90	120	24	4.8	150	710	1.4
SG2	990	140	6.8	250	1500	3.6
NH6[1]	9	2.2	4.0	11	43	1.3
SG3	1200	140	9.0	100	910	2.2
SG4	360	62	5.8	120	580	1.9

n.d. means not determined.

[1] Constants for NG2, NG5, and NG6 which have been previously published (Truesdell, 1962) are repeated here to facilitate comparisons.

has published a theory of ion-exchange selectivity for monovalent ions which has been extended to divalent ions by Truesdell (1963). These theories provide a basis for the discussion of the results obtained on these glasses.

Eisenman has shown that the selectivity order or displacement sequence among monovalent ions depends on a single parameter, the "anionic field strength," or electronegativity of the exchange sites, which in turn, for simple alkali aluminosilicate glasses, depends on the alkali/

Table 2b. Regular Solution Constants in Kcal Mole^{-1} for Some Glasses at 25° C.

	W_{NaH}	W_{KH}	W_{NaK}	W_{CaNa}	W_{CaK}	W_{MgCa}
NG8	0.0	+0.3	+0.3	+0.1	0.0	+0.2
SG1	+0.2	−1.2	+0.2	+0.3	+0.3	n.d.
B20	+0.3	−0.3	+0.2	+0.3	+0.5	n.d.
ST2	+0.3	n.d.	+0.3	n.d.	+0.3	n.d.
B76	+0.3	−0.6	+0.1	+0.1	0.0	+0.3
NG5	−0.5	+0.4	n.d.	n.d.	−0.5	0.0
NG2	−0.2	−0.6	−0.2	−0.2	+0.2	n.d.
B90	−0.4	−0.6	n.d.	+0.3	−0.1	+0.5
SG2	+0.4	n.d.	−0.6	+0.3	+0.3	+0.3
NG6	−0.4	0.0	n.d.	−0.4	−0.5	0.0
SG3	+0.5	−1.0	+0.4	+0.2	+0.2	+0.4
SG4	−0.9	−1.8	+0.3	+0.3	+0.1	n.d.

n.d. means not determined.

aluminum ratio. Although no such simple relation to composition exists for natural glasses, it follows from Eisenman's theory that the mono-monovalent and di-divalent exchange constants should each be functions of the anionic field strength and therefore be inter-related. That the exchange constants are inter-related can be seen in Figs. 3, 4 and 5.

The generally positive correlation between K_{MgCa} and K_{NaH} and K_{KH} suggests that H^+ enters the glass as the hydronium ion, H_3O^+, comparable in size to Na^+, and K^+. This is supported by the finding that hygroscopicity and pH selectivity are directly related (Hubbard, 1946).

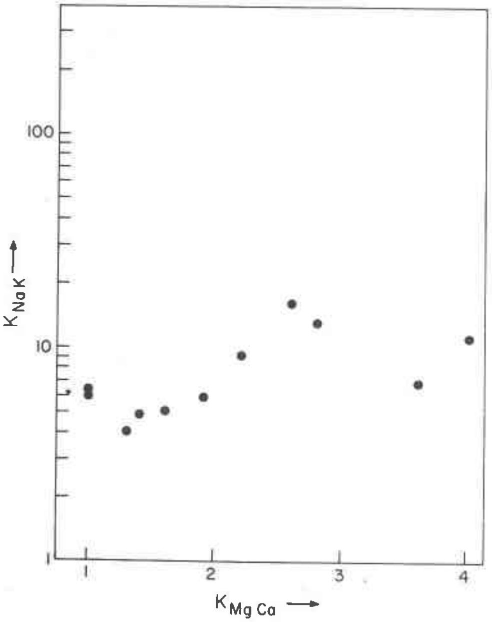

FIG. 3. Plot of K_{MgCa} against K_{NaK} for some natural glasses.

The addition of very small quantities of alkaline-earth oxides to an alkali-aluminosilicate glass considerably increases the selectivity for divalent ions relative to monovalent ions. The Libyan Desert glass (NG8) with 0.4 wt per cent CaO, has appreciable divalent ion selectivity, $K_{CaNa} = 10^2$, whereas the equivalent sodium aluminosilicate glass has negligible selectivity for divalent ions, $K_{CaNa} > 10^5$. It seems probable that the introduction of divalent ions into the glass framework produces a spacing of the exchange sites favorable for divalent selectivity. The theoretical justification and ramifications of this idea are being developed and will be published elsewhere.

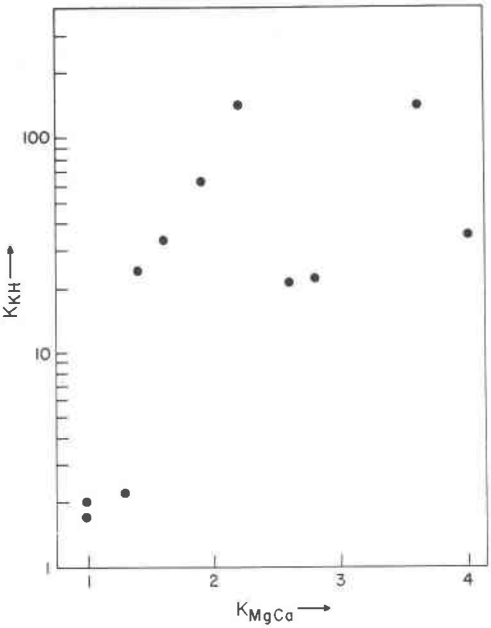

FIG. 4. Plot of K_{MgCa} against K_{NaH} for some natural glasses.

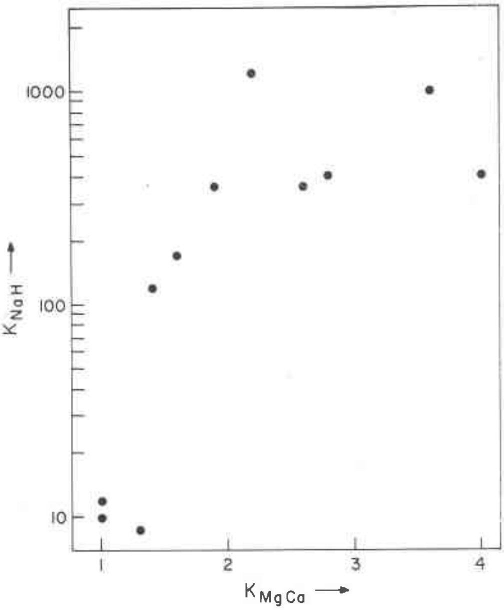

FIG. 5. Plot of K_{MgCa} against K_{KH} for some natural glasses.

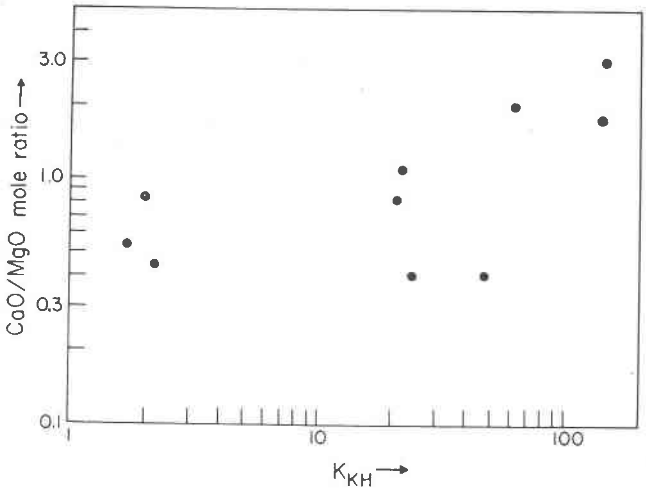

FIG. 6. Plot of K_{KH} against CaO/MgO mole ratio for some natural glasses.

The nature as well as the amount of the alkaline earth oxide in a glass has a considerable effect on its exchange behavior. MgO increases the selectivity for H^+ relative to K^+ (Fig. 6) and for Mg^{++} relative to Ca^{++} (Fig. 7).

The experimentally determined ion-exchange constants of natural glasses indicate qualitatively what chemical changes may be expected from the interaction of an obsidian or vitric tuff with surface and ground

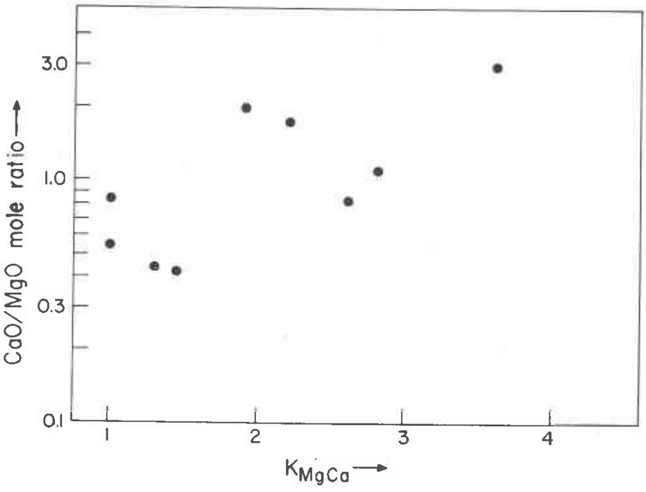

FIG. 7. Plot of K_{MgCa} against CaO/MgO mole ratio for some natural glasses.

water. An exact calculation of these changes would require a knowledge of the temperature, the microcomposition of the glass and of the water at their interface as well as the constants K_{AB} and W_{AB}, and their temperature dependence. Qualitatively, however, the preference of the glasses studied for H^+, K^+, and in dilute solutions Ca^{++} relative to Na^+, would result in the glass losing Na^+ and gaining H^+, K^+ and Ca^{++} during the interaction with average natural waters. If the quantity of water is limited relative to that of the glass, the water will become soft and sodium-rich. Such water is found in those parts of the arid southwest in which vitric tuff makes up a considerable part of the subsurface formations. This type of water was considered by Hostetler and Garrels (1962) to have been the main ore-forming fluid in the Colorado Plateau type uranium deposits.

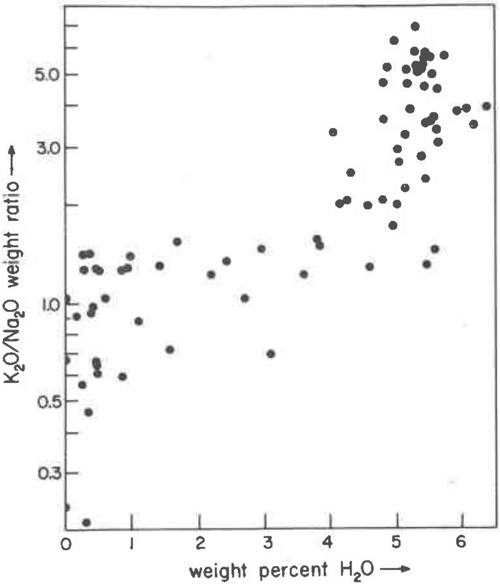

FIG. 8. The relation between weight per cent H_2O and K_2O/Na_2O weight ratio for natural glasses.

The effect on the glass of continued passage of ground water, would be a loss of Na^+ and a gain of K^+ and H_2O. Part of the H_2O would exist as H^+ on exchange sites and part as water of hydration. In Fig. 8, the weight per cent H_2O and the K_2O/Na_2O weight ratio of a large number of fresh-appearing glasses are plotted. These were taken from analyses published by Boyd (1961), Clarke (1920), Hay (1959), Morey (1938), Washington (1917), and Swineford *et al.* (1955). There is a strong positive correlation between increasing hydration and increasing K_2O/Na_2O ratios. This is because potassium is preferred over sodium on the glass (K_{NaK} is >1 for all glasses studied) and potassium is preferentially taken up and sodium released at the same time that the glass is absorbing water and hydrogen ions.

If the glass reacts with rain water, snow-melt water, or ground water containing little dissolved material, the Na^+ may be preferentially leached to produce the same effect. This process has been described by Noble (1965). In either case, the preference of the glass for K^+ controls the reaction. The finer the state of division, the wetter the climate, and the older the glass, the more likely it is to have a high K_2O/Na_2O ratio and a high per cent H_2O. A plot of Na_2O per cent against K_2O per cent for the glasses of Fig. 8 suggests that the average stoichiometry of the exchange is $2K^+$ plus $1H^+$ (or $\frac{1}{2}$ Ca^{++}) for $3Na^+$.

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REFERENCES

BOYD, F. R. (1961) Welded tuffs and flows in the rhyolite plateau of Yellowstone Park, Wyoming. *Geol. Soc. Am. Bull.* **72,** 387–486.

CLARKE, F. W. (1920) The data of geochemistry, 4th ed. *U. S. Geol. Survey Bull.* **695,**

EISENMAN, GEORGE (1962) Cation selective glass electrodes and their mode of operation. *Biophys. Jour.* **2,** 259–323.

GARRELS, R. M. AND C. L. CHRIST, (1965). *Minerals, Solutions and Equilibria.* Harper, New York.

GARRELS, R. M., M. SATO, M. E. THOMPSON AND A. H. TRUESDELL (1962) Glass electrodes sensitive to divalent cations. *Science* **135,** 1045–1048.

HAY, R. L. (1959) Origin and weathering of late Pleistocene ash deposits on St. Vincent, B.W.I. *Jour. Geol.* **67,** 65–87.

HOSTETLER, P. B. AND R. M. GARRELS (1962) Transportation and precipitation of uranium and vanadium at low temperatures with special reference to sandstone-type uranium deposits. *Econ. Geol.* **57,** 137–167.

HUBBARD, DONALD (1946) Electrode function (pH response) of potash-silica glasses. *Natl. Bur. Stand. Jour. Res.* **37,** 223–228.

MOREY, G. W. (1938) *The Properties of Glass.* ACS Monograph Series, Reinhold, New York.

NOBLE, D. C. (1965) Ground water leaching of sodium from quickly cooled volcanic rocks. (abs.). *Am. Mineral.* **50,** 289.

SWINEFORD, ADA, J. C. FRYE AND A. B. LEONARD (1955) Petrography of the late Tertiary volcanic ash falls in the central Great Plains. *Jour. Sed. Petrology* **25,** 243–261.

TRUESDELL, A. H. (1962) Study of natural glasses through their behavior as membrane electrodes. *Nature* **194,** 77–79.

——— (1964) A theory of divalent-cation exchange selectivity (abs.). *Geol. Soc. Am. Spec. Paper* **76,** 170.

WASHINGTON, H. S. (1917) Chemical analyses of igneous rocks published from 1884 to 1913. *U. S. Geol. Survey Prof. Paper* **99.**

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