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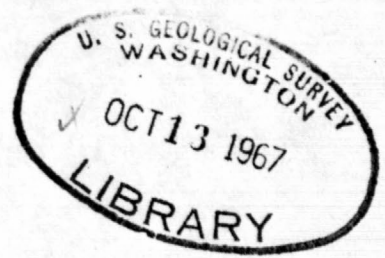
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

BIBLIOGRAPHY OF ION EXCHANGE SELECTIVITY

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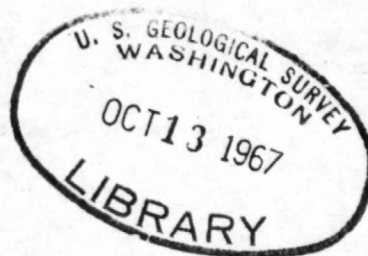
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1. Reconnaissance geologic map of the Yadkin Valley region, North Carolina, by G. H. Espenshade. 2 sheets. Scale 1:200,000. Room 11, Post Office Bldg., Knoxville, Tenn. 37902; Office of the State Geologist, Division of Mineral Resources, Dept. of Conservation and Development, Raleigh, N.C. 27602.
2. Principal facts for gravity stations in the Yuma, Arizona, and Blythe, California, areas, by Donald L. Peterson, Arthur Conradi, and Adel A. R. Zohdy. 34 data pages. 15426 Federal Bldg., Denver, Colo. 80202; 8102 Federal Office Bldg., Salt Lake City, Utah 84111; 504 Custom House, San Francisco, Calif. 94111; 7638 Federal Bldg., Los Angeles, Calif. 90012; Arizona Bureau of Mines, University of Arizona, Tucson, Ariz. 85721.
3. Availability of palynological material from Naval Petroleum Reserve No. 4, I: Simpson Test Well No. 1 and Simpson Core Tests Nos. 13 and 14, by Richard A. Scott. 2 p.
4. Bibliography of ion exchange selectivity, by A. H. Truesdell, Dorothy Carroll, and Marian Schnepfe. 90 p.
5. Seismic measurements of explosions in the Tatum Salt Dome, Mississippi, by R. D. Borchardt, J. H. Healy, W. H. Jackson, and D. R. Warren. 11 p., incl. 2 tables; 53 p. of text figures.
6. Preliminary notes on sulfur and associated diamonds in the Santo Inacio area of northwestern Brazil, by J. B. Pomerene, Wanderlei Mansanares, Juarez Fonseca, and Urias Rodrigues. 6 p., 1 fig.

Departamento Mineral Produção Nacional, Rio de Janeiro, Brazil.



BIBLIOGRAPHY OF ION EXCHANGE SELECTIVITY

By

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Menlo Park, California and Washington, D. C.

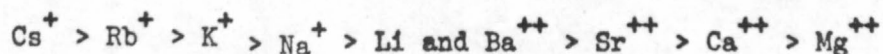
In recent years ion exchange has come to be appreciated as the most accessible of the many phenomena exhibiting selective differentiation between ions. Ion selectivity is known to occur in shallow and deep-seated geologic processes. Feldspars crystallizing from a magma undergo alkali ion exchange with the parent magma as the temperature decreases and the selectivity changes. Hydrothermal solutions exchange ions with the rocks they contact and a solution's composition at any point may reflect more its travel path than its original composition. Clay minerals and zeolites produced by weathering processes have exchange sites occupied by the available cations. Transport by erosional processes can carry these minerals into different environments where cations are released. Ion exchange of H^+ for Na^+ during weathering natural glasses seems to be a major source of saline ground waters and possibly of mineralizing solutions. The role of natural ion exchanging membranes in modifying the composition pressure and salinity of ground waters has been increasingly recognized. Thus ion exchange has a pervasive influence on geologic processes.

Ion exchange is also known to play a part in the life processes of animals and plants. The seat of this selectivity in life processes is the unit membrane which separates the internal milieu of the cell from the external solutions. In a resting state the intracellular fluid is rich in

potassium ions and has very few sodium ions. These conditions are reversed in the fluid outside the cell. The cell membrane must thus selectively pass potassium into, and sodium out of, the cell. The transmittal of nerve impulses is effected by changing the selectivity of the cell membrane and allowing the flow of potassium and sodium ions to be reversed.

Selective differentiation between sodium and potassium ions also occurs in ion exchanges. If ultramarine and chabazite are both immersed in a solution containing equal quantities of Na^+ and K^+ ions the ultramarine will absorb more Na^+ than K^+ ions, and the chabazite will absorb more K^+ than Na^+ . This analogy between ion exchangers and cell membranes led Eisenman (1961a) to formulate his theories on the atomic basis of ion specificity. These theories have stimulated research on ion exchange and ion-exchange membrane electrodes.

The older studies of selectivity were limited to sulfonate resin ion exchangers and synthetic aluminosilicate gels for which a single selectivity order obtains



(Walton, 1949). This "lyotropic" sequence was explained by assuming that the ions remained hydrated in the exchanger and that the negative sites of the exchanger exerted an attraction on the ions inversely with their hydrated ionic radius. In developing this theory, experimental results showing that certain ion exchangers gave sequences differing from or even reversed to the "lyotropic" series (e.g., ultramarine, Barrer and Raitt, 1954) were ignored. These experiments cast doubt on the ion exchange theories which concentrated on the properties of the ions alone and neglected differences

in the structure of the exchangers. In 1961, Eisenman (1961a) published a simple theory of ion exchange selectivity which has explained the "anomalous" exchange sequences observed by others as well as a large amount of new data on the ion exchange behavior of Na aluminosilicate glasses (Eisenman, Rudin, and Casby, 1957).

Eisenman's theory considers ion exchange as a competition for cations between the negatively charged sites on the exchanger and the water dipoles in the aqueous solution. Since the properties of the cations and the aqueous solution are the same for exchange on different exchangers, the variation in selectivity must depend solely on the properties of the exchanger.

Eisenman considered only coulombic interactions between the cations and the exchange sites and he introduced the idea of an effective anionic radius to represent differences of electronegativity of the sites. The effective anionic radius (r^-) is the radius of a hypothetical spherical ion with a charge of minus one, having the same electronegativity as the exchange site. When combined with experimental cation hydration energies, this abstraction allowed the calculation of ion exchange energies (Fig. 1). By varying r^- , a series of eleven exchange orders were generated for the five alkali cations (instead of $5! = 125$). At large values of r^- the differences of ΔU_{diss} (Fig. 1) are smaller than the differences of ΔU_{hyd} and the lyotropic series is obtained. At small values of r^- the energy differences of ΔU_{diss} dominate the differences in ΔU_{hyd} and the reversed sequence occurs. At intermediate values of r^- intermediate sequences are generated.

The selectivity of ion-exchange materials is also of great current interest in the search for less expensive methods of desalting water, and in the need for purification of fissionable materials for power reactors. The need in reactor technology for ion exchangers which will withstand high temperatures and high radioactive flux densities has led to discoveries of highly selective inorganic ion-exchange materials. The need for the disposal of radioactive waste products has produced studies of the selectivity for cesium and strontium of natural soils and rocks.

The selective adsorption and accumulation of cations by biological materials and by synthetic and natural ion exchangers is considered by the compilers of this bibliography to be among the most important processes that have shaped man's nature and environment. This bibliography attempts to emphasize selectivity and the mechanisms by which it originates; it lists all the pertinent papers published in this field up to and including 1960; some of the most important later publications are also given.

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