each other in succession onto one detector or they can all act simultaneously onto j detectors. The beams must all traverse the same region of the subject and so, because of this and drift considerations, a single detector is felt to be best even though some sort of memory or gating circuit is then required.

A piece of equipment already under construction in Sweden for a related operation was modified as a joint effort to test this new principle. The experimental arrangement and some results have been given (*1*). In this case the scheme was adapted to the detection of iodine (either the quantitative analysis of that normally present in human beings, or the sensitive mapping of a standard x-ray contrast medium). The two wedges were made of iodine and of plastic, the latter being similar to soft tissue. The monochromatic wavelengths were supplied alternately by a pair of rotating secondary emitters (fluorescent radiation). These wavelengths were chosen to fall just on opposite sides of the iodine k absorption edge for maximum sensitivity.

The position of the plastic wedge was automatically adjusted through suitable gating circuits to bring the longer wavelength always to a preset intensity value. The a-c component in the detector signal, as the two wavelengths alternated, was brought to zero by control of the iodine wedge position. This then brought the intensity of the shorter wavelength also to the preset value. The two wedges steadily hunted, at slightly different frequencies, in a small range about their proper positions, as hoped. Wedge position was used to control the frequency of a flashing light which blackened a film during the scanning process. Thus the iodine distribution was mapped.

Jacobson independently reported some observations with the unit (*2*) and noted that fat does not seem to act like water. Thus three wedges would be more suitable. He noted that 1 g of fat per square centimeter acted like 0.5 mg of iodine per square centimeter.

Nonuniform irradiation of the subject —for example, by applying most of the dose around the edges of the structure— can reduce the total dose to a subject in producing a given image quality; but constant-output intensity systems such as the present one tend to minimize dose (*3*). Another property of such systems is that they can be compensated against source-intensity fluctuations with an auxiliary detector and difference amplifier, rather than with a ratio detector.

From dose considerations this procedure is most practical in human beings for the relatively heavy elements because the lighter ones demand "soft" highly absorbed wavelengths, if use is to be made of absorption edges. Possibly heavier elements should be used in contrast media for this reason (at least for use in retrograde application). A similar system may have application in the ultraviolet, and the optical analog is sometimes a convenient guide to thought (*4*).

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References and Notes

1. For discussion of this see B. Jacobson and R. S. Mackay, *Advances in Biological and Medical Physics*, J. H. Lawrence and C. A. Tobias, Eds., (Academic Press, New York, 1958), vol. 6, pp. 201–261.
2. B. Jacobson, paper presented at the International Conference on Medical Electronics, Paris, 28 June 1958.
3. R. S. Mackay, *Brit. J. Radiol.* 31, 642 (1958).
4. This method was conceived while I was on leave from the University of California as a Guggenheim fellow.

31 July 1958

Geochemical Scavenging of Strontium

Abstract. Crandallite, an abundant mineral belonging to the alunite structure type, is a geochemical host for ordinary strontium in the soil profile and the deeper ground-water circulation. It may be useful in the scavenging or storage of the radioisotopes of strontium and certain other elements.

The chemical action by ground waters of the deeper meteoric circulation and of the zone of weathering on pre-existing rocks results in the formation of secondary minerals appropriate to the new environmental conditions. Certain of the minerals of the original rock that are resistant to chemical attack also may accumulate as residual deposits, and other material may be yielded in soluble form and ultimately removed in the surface drainage.

Elements present in trace amounts in the original rock, if not removed in solution, may be concentrated and redeposited locally by the ground waters either as specific compounds or in solid solution in variable amounts in certain other more abundant minerals. Adsorption and cation-exchange mechanisms also may be operative. The natural geochemical and crystallochemical behavior in the ground-water circulation of strontium and of other trace elements of interest in connection with radioactive wastes and fallout may be informative in relation to the artificial storage or scavenging of the radioisotopes of these elements in ways that involve geological environments and materials.

With regard to strontium, the hitherto known host minerals for this element are operative chiefly in the magmatic and sedimentary cycles. A few, such as members of the aragonite and barite structure types, are of consequence in the deeper ground-water circulation. None of these minerals normally form in, or are stable in, the soil profile, where they could act as hosts, and it has been generally believed that strontium released during weathering is retained in soluble form in the soil waters.

Recently, it has been established (*1*) that minerals of the alunite structure type also are specific geochemical hosts for strontium. Crandallite, $CaAl_3(PO_4)_2(OH)_5H_2O$, is of particular interest. In crandallite deposits of the deeper circulation, such as those of the Fairfield, Utah, type, where descending phosphatic solutions derived from marine phosphate-rock formations have reacted with argillaceous limestone, the crandallite is enriched in strontium. Crandallite develops analogously in the soil profile during the weathering of phosphatic limestone and marine phosphorites. The occurrence of crandallite in this way has been recognized only in recent years (*2*), and little is known of the extent of such occurrences over the world. The surficial crandallite deposits of one area in the Florida Gulf coastal region have been estimated at upwards of 800 million tons. The Senegal deposits are larger and have been mined for their phosphate content, but the resources are not known. Although the available data are very scant, the Senegal crandallite contains up to at least 0.50 percent SrO by weight, and it appears to be enriched in Sr over the phosphate rock from which it was derived.

The formation of crandallite by natural processes in the zone of weathering is restricted to areas of favorable bedrock and ground-water composition, and the mineral is not a constituent of soils in general. However, since it is stable under neutral and alkaline conditions, it probably would remain unchanged, without further control of the soil pH, if added to most soils. The availability of the mineral and its known ability to house strontium by both crystallization and cation-exchange mechanisms suggests that it possibly may be of interest as a scavenger in arable soils and as a vehicle for the storage of radioactive wastes. Knowledge of areas in which crandallite is a natural constituent of the soil profile would be pertinent to any general study of the distribution of strontium between the hydrosphere, the lithosphere, and vegetation.

In the alunite structure type (*3*), the monovalent and divalent ions are held in relatively open 12-coordinated positions that are very tolerant with regard to both the size and the valence of the contained ions. These ions include Sr, Pb, Ba, Ca, Cs, K, Na, NH_4, Ag, and Ce. Among them are several elements of interest with respect to radioactive wastes and fallout. The alunite type of structure is suited to the housing of relatively large cations, and it is primarily this factor that accounts for the observed preferential substitution of Sr for Ca in crandallite over coexisting Ca minerals, such as calcite and apatite, in which the cation coordination number is smaller.

Crandallite readily exchanges Ca for dissolved Sr. Since the 12-coordinated cation sites are not interconnected, as are the sites in cation-exchangers of the channeled zeolitic and layered phyllosilicate types, the exchange is limited to surface positions. For example, a freshly prepared gel of synthetic crandallite, a gel coarsened to microscopic crystals by hydrothermal treatment at 250°C, and crude Senegal crandallite rock crushed to pass 200 mesh were placed in 0.02M solutions of strontium nitrate. The amounts of solution and of solid phase were adjusted so that each contained the same number of Ca and Sr ions. In neutral and weakly alkaline solutions the percentages of exchange between Ca and Sr in the three preparations were roughly 31, 18, and 4 percent, respectively. Below *p*H 6.5 the amount of exchange decreases markedly. Natural crude Senegal crandallite rock was found to have an appreciable acidity-reducing capacity, presumably due to admixed basic aluminum phosphates and silicates. The reverse exchange, that of Ca for Sr in crystalline $SrAl_3(PO_4)_2(OH)_5H_2O$, was found to be quite small, in line with the relative solubilities and ionic adsorptive powers of Ca and Sr in general.

The mineral apatite, $Ca_5(PO_4)_3(OH)$, also takes up Sr in solid solution and has an appreciable adsorptive capacity for Sr in neutral solutions. The known reserves of natural phosphate rock (apatite) have been estimated at upwards of 40 billion tons suitable for conventional commercial applications. Apatite, however, is soluble in alkaline and carbonated ground waters and, unlike crandallite, is removed from the soil profile. Admixture of this mineral with crandallite as a top dressing might be useful both in controlling *p*H and in transiently affording ordinary Sr to the ground water. Natural phosphate rock contains roughly 0.01 to 0.20 per cent SrO by weight. The Sr and the Ca afforded by dissolution may act as a diluent for Sr^{90} available to plant life either directly from the ground water or by biochemical decomposition of the scavenger mineral.

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20 August 1958

Rate of Swelling of Collagen

Abstract. The osmotic pressure gradient across the collagen solid matrix-solution interface forces the solid to imbibe fluid and thereby increases its volume. Concurrently, the decrease in entropy of the solid matrix produces a force which tends to resist any further increase in volume. The instantaneous velocity at which the swelling takes place is related to the difference between the osmotic and entropic forces. Finally, an explicit relationship is obtained between volume and time.

Swelling is an important property of polymers and is an outstanding characteristic of collagen. The two types which can be distinguished are (i) osmotic and (ii) lyotropic (bond scission). In type i the matrix imbibes fluid due to an osmotic pressure gradient across its solid-solvent interface; the restraining pressure of the matrix finally equals the osmotic pressure so that an equilibrium is attained. Certain fluids react with the matrix so as to loosen bonds (type ii); the swelling then proceeds to a greater extent because the restraining pressure of the matrix is reduced.

In a polyelectrolyte such as collagen, the equilibrium swelling volume depends upon the *p*H of the solvent (*1*). A minimum of swelling occurs near the isoelectric point, whereas pronounced swelling develops in the acid and alkaline *p*H regions. Acetic acid, particularly, is effective in both the solubilization and swelling of collagen.

Studies of types i and ii have been done particularly from measurements based on equilibrium swelling. Little attention has been given to the rate of the swelling process. The purpose of this report is to describe a rate mechanism of the swelling process which embodies both osmotic and lyotropic attributes of the system, collagen–acetic acid–water.

The isoelectric point of limed hide powder collagen is about *p*H 5.5. When this is placed in water, hydrogen ions leave the matrix to a certain extent and dissolve in the interstitial water phase. The matrix becomes an anion and its counter-ion is trapped inside. When it is placed in dilute acetic acid at *p*H 2 to 3, hydrogen ions are forced on to the matrix which thereby becomes a cation; its counter-ion again is trapped inside. This description of type i may be formulated to give the pressure inside the matrix which produces swelling—that is,

$$\pi = nRT/V = A/V,$$

where π is the osmotic pressure of the interstitial fluid phase of volume V for n moles of ions at a temperature T. Since the gas constant (R), n, and T are independent of the volume they may be combined to form A. The increased volume of the matrix forces random chains of collagen to become more uniformly aligned, with a subsequent decrease in their entropy. This reduction in entropy causes an increase in the matrix pressure which resists further volume increases. The retarding pressure of the matrix may be considered to be linearly related to its volume—that is, $P = \alpha V$, where α is a constant characteristic of the matrix restraining ability. The rate of change of volume with time can now be stated as being proportional to the difference in osmotic pressure π and the restraining pressure P in Eq. 1.

$$dV/dt = k(\pi - P) = k(A/V - \alpha V) \quad (1)$$

At swelling equilibrium Eq. 1 equals zero. Thus, Eq. 2 shows the dependence

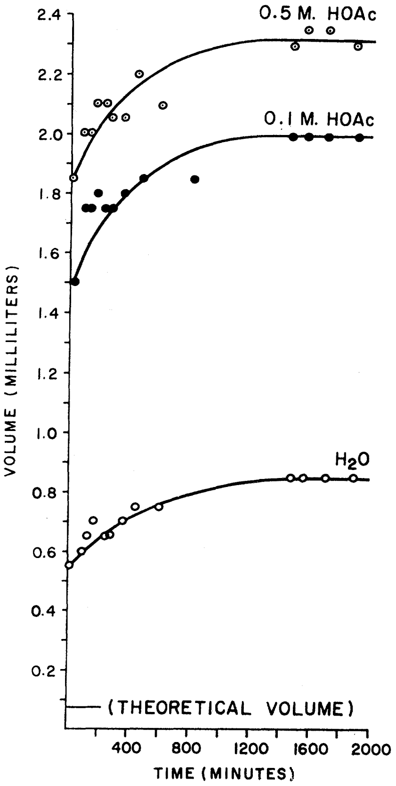

Fig. 1. Volume of 100 mg of hide powder collagen as a function of time in water and in 0.1 and 0.5*M* acetic acid at temperature 23° to 25°C.