

SOME ASPECTS OF HELIUM LEAKAGE FROM ROCKS AND MINERALS

BY V. S. VENKATASUBRAMANIAN

(Department of Physics, Indian Institute of Science, Bangalore-3)

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ABSTRACT

The arguments dealing with the impossibility of helium leakage from perfect crystals of rock-forming minerals, are summarized. The distribution of uranium mineral grains is considered and leakage through the grain boundaries examined. A relationship is derived between grain size and the retentivity. The case of zircon is considered in relation to other data.

I. INTRODUCTION

Very considerable work has been done on the alpha-helium method of determination of geologic time, in which the "helium ratios" are computed from the measured helium content and alpha activity for each specimen.¹ It is found that the helium ratios are, in most cases, less than the absolute ages, computed by other methods, e.g., the lead method. While earlier measurements are due to Holmes and Paneth, the later measurements covering all aspects of the alpha-helium method are due to the M.I.T. workers, Evans and Goodman, later Keevil, Larsen, Hurley and others. An excellent summary is provided by Hurley.²

The general results on helium ratios are:—

- (1) Granitic rocks yield consistently low helium ratios.
- (2) Helium ratios of separated mineral constituents from a rock sample are different and maintain roughly the same difference for various specimens.
- (3) On this basis, one can specify certain "retentivity factors",—these being very low for acid felsitic and glassy rocks (< 0.1) low for feldspars and quartz (0.25–0.3) and higher for ferromagnesian (0.6–0.7).
- (4) The highest retentivity (approaching unity) is exhibited by fresh magnetites.

Many of these conclusions have been corroborated by determinations of helium ratios on Archæan specimens of the Peninsula, carried out in this laboratory.³ The conclusion is thus suggested that helium loss occurs in rocks and minerals by diffusion.

2. THEORETICAL CONSIDERATIONS

This conclusion however, is in complete contradiction to theoretical computations regarding the diffusion in rocks and minerals, taking into account the very considerable advances in our knowledge concerning the atomic structure of rocks and minerals and interatomic forces. A very brief outline of these calculations and their significance is given below, based on a long discussion given by Keevil.⁴

(1) First of all, the "Size" of the helium atom in the environments pertaining to the crystal structures of ordinary rock-forming minerals can be determined by plotting potential energy curves for the appropriate systems—using He-O, He-K, He-Si, etc., and finding the distance at which a marked rise in the P.E. curve takes place. Using as the main attractive terms, the Van Der Waals contribution and partial ionic interaction and a repulsive potential term, Keevil has found that the critical radius (~ 0.95 Å) is practically the same for all systems, and is thus much greater than the radii of the commonly found anions in rock structures.

(2) Now, atoms in the interstitial positions will be able to move from one interstitial to another, the probability for a jump per unit time being $(\nu_0 e^{-E/RT})$, where ν_0 = vibration frequency of the interstitial atom; E = activation energy in cal./mole required for a jump. From this, it follows that the R.M.S. displacement/in time t

$$\overline{d^2} = \delta^2 \nu_0 e^{-E/RT}$$

while the diffusion coefficient

$$D = \frac{\delta^2}{6} \nu_0 e^{-E/RT}$$

(3) Following Keevil, we can now compute for various values of the interatomic distance R (distance between the centre of the O atom and any impurity atom as He), the activation energy, for any temperature and the average distance of diffusion for a certain time $t = 10^9$ years $\approx 10^{16}$ secs. Once this is done, the remarkable fact emerges that this interatomic distance is very critical (1.85–1.90) A.U. with O atoms constituting the predominant structural unit, this corresponds to a hole of diameter—(1.0–1.1) A.U. and an activation energy— 10^4 – 4×10^4 cal. mole.

Now, the main point is that this is larger than any spacing in the perfect crystal structures of all common rock minerals, as illustrated by Keevil using models of feldspars, pyroxenes, micas, zircon, etc. Thus practically no diffusion can be expected from perfect crystals, for temperatures $\sim 600^\circ$ C.

Considerable progress is made towards the solution of this impasse when account is taken of two factors that emerged from the systematic studies of Hurley and his collaborators. The first is radiation damage, whose effect, it is well known, lies in the creation of vacancies and interstitials and the general disordering of the

crystal structure. This breakdown of the crystal lattice with consequent loss in anisotropy and crystalline X-ray pattern has long been known as the metamict state. It was observed by Hurley that helium ratios for Zircons of the same age, decreased progressively with increasing activity and radiation dosage. In fact, the earlier discovery and much more well-known fact of the diffusion of helium through glasses has been explained as the result of the disordered structure that leads to a continuous distribution of channels. Diffusion experiments in this case have shown that the activation energy in this case is reduced to ~ 5500 cal./mole.

Secondly, it might be expected that the effect of imperfections, surfaces of fracture be important. This grain-boundary effect may be expected to predominate in composite rocks, whose minerals like quartz contain the radioactive elements not as part of the crystal structure (diadochical substitution as $ZrSiO_4$) but as inclusions of mineral grains (Zircon, Sphene, etc.). Even here the helium driven into the crystalline structure remains as an interstitial solid solution, but where it is driven into the grain boundaries, and this is especially so in the vicinity of these minute inclusions susceptible to radiation damage, there is a high probability of its escape. In fact, a calculation of the interaction energy of a helium atom in a channel bounded by O atoms shows that it can freely escape for a channel width greater than 4 A.U. It should be mentioned that definite proof that radioactivity of ordinary rocks and minerals is mainly concentrated on the surfaces of fractures was obtained by Hurley in his acid leaching experiments. This showed the considerable decrease in α -activity in quartz and feldspar on leaching in HCl. Our experiments have also confirmed this fact, in quartz-magnetite, the activity drops to 25%.

3. DEPENDENCE OF DIFFUSION ON GRAIN SIZE

It thus becomes of interest to consider the possibility of this type of diffusion through grain boundaries. In fact, Gentner⁵ has already pointed out diffusion of argon from K-minerals, in the course of age determinations by the $A^{40}K^{40}$ method, the retentivity decreasing with decrease of grain size. We shall now derive a semi-quantitative relationship between grain size and diffusion. For this purpose, we consider a cube of side a , containing thus $(a^3 P_0)$ radioactive nuclei, the rate of production of the end product Q being $\lambda a^3 P_0 e^{-\lambda t}$. Regarding diffusion as the result of interstitial jumps, followed by a period of quiescence in the new position, we can define an average "wandering velocity", $\omega = \delta/\tau$, where $\delta =$ average distance between the interstitial positions, and $\tau = \tau_0 e^{12/RT}$ is the period of sedentary stay. The rate of escape of atoms per unit area of any face of the cube is then the Kinetic theory expression $\delta a^2 Q / \omega$; hence we have the relation,

$$\frac{dQ}{dt} + lQ = \lambda P_0 e^{-\lambda t}$$

where

$$l = (\omega/a),$$

We are interested in the case where $l > \lambda$.

In this case the solutions are, [for the case, $Q = 0$ at $t = 0$]

$$Q = \frac{\lambda}{l - \lambda} \cdot P_0 e^{-\lambda t} [1 - e^{-(l-\lambda)t}]$$

and the retentivity

$$R = \frac{\lambda}{l - \lambda} \cdot \frac{[1 - e^{-(l-\lambda)t}]}{[e^{\lambda t} - 1]}$$

and for the case,

$$\lambda t \ll 1,$$

R falls to 63% for $lt = 1$,

In the case $l \gg \lambda$, $R = 1/lt$

This is roughly in accordance with Gentner's data.

4. DISCUSSION

Now, calculating backwards, from this equation we find that for grain dimensions $0.01-100 \mu$, diffusion becomes appreciable for $U = 2 \times 10^4 - 4 \times 10^4$ cal./mole and $r = 1.85-1.95$ A.U. Since as Keevil has shown, the largest spacing in the Zr structure is such that $[Zr-O] = 1.6 \text{ \AA}$, the average relative displacements should amount to about 0.25 \AA . Actually, the systematic measurements of Holland and Gottfried⁶ have shown a variation in the a and c spacing— $5.98-6.09$; $6.60-6.71$ A.U. for dosages $\sim 0.5 \times 10^{16}$ a/mg. Further, from the decrease in specific gravity of zircon (completely metamict) it is known that the drop is = 16%. Taking this to mean that the structure is saturated with displacements, this would mean that the volume of the "displaced atom-vacancy" pair is on the average 16% greater than the volume originally, before damage. This is in fact greater than the lattice expansion that would take place if we assume that two holes open up to a size 1.85 A.U., so that diffusion can be expected to take place freely in such a structure.

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