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Emanation of radon from rock minerals

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The mechanism of emanation of radon from terrestrial minerals and rocks is briefly discussed. Employing a technique which can locate nanometre-wide holes in materials, I have observed a network of very narrow (sub-micronic) openings/gaps within an individual mineral grain and between grains of different minerals. Radon enters this network by recoil-out from the solid walls, and is then subject to rapid transport by molecular diffusion in the air in the network.

Most of the natural minerals contain small amounts of uranium and thorium, and their decay products. Amongst these, ^{222}Rn, ^{220}Rn and ^{219}Rn arise from decay of ^{226}Ra (^{238}U series), ^{224}Ra (^{228}Th series) and ^{223}Ra (^{235}U series) respectively. Their half-lives are 3.8 d (^{222}Rn), 55 s (^{220}Rn) and 4 s (^{219}Rn). It has been known for long that somehow a sizable fraction of these three gaseous isotopes produced inside the terrestrial minerals is able to emerge out of the minerals into the pores from where it diffuses out into the atmosphere.

The inert gaseous isotopes of Rn have found numerous applications as tracers for investigating geophysical and geochemical phenomena. In some of these applications, a knowledge of the exact nature of the mechanism by which Rn atoms emerge out of crystalline minerals is important. Attempts have therefore been made to understand this mechanism which further happens to be relevant in choosing appropriate remedial measures for controlling levels of indoor Rn, a matter of general concern these days.

The basic mechanism was worked out by Zimens in the late thirties and the early forties. But certain aspects of the phenomenon still require unravelling and details remain to be worked out. A review article by Tanner[1] gives a comprehensive treatment of the subject. But there has been substantial progress since then. I wish to bring that out in this article. Here I have drawn heavily from the work of Rama and Moore[2–4].

Recoil-out

On decay, a nucleus of ^{226}Ra, ^{224}Ra or ^{223}Ra gives out an alpha particle and the residual nucleus of ^{222}Rn, ^{220}Rn or ^{219}Rn recoils with equal momentum in the opposite direction. The kinetic energy of the recoiling nucleus is in the 100 keV range, and differs slightly for the three isotopes; the respective ranges of the three recoiling isotopes in common rock minerals are about 60, 80 and 90 nm.

The recoiled Rn atoms loses its energy by atomic collisions inside the mineral, and then comes to rest within the mineral (Figure 1). There is no possibility of its coming out of the mineral since the diffusion coefficient of Rn in crystalline mineral is extremely small. However, there is a good chance for Rn atoms to be directly recoiled out of the mineral if they are generated in the skin of the mineral, i.e. within a depth equal to the recoil range from the surface (Figure 2). Considering the geometrical factors involved, one out of four such Rn atoms is expected to recoil out of the

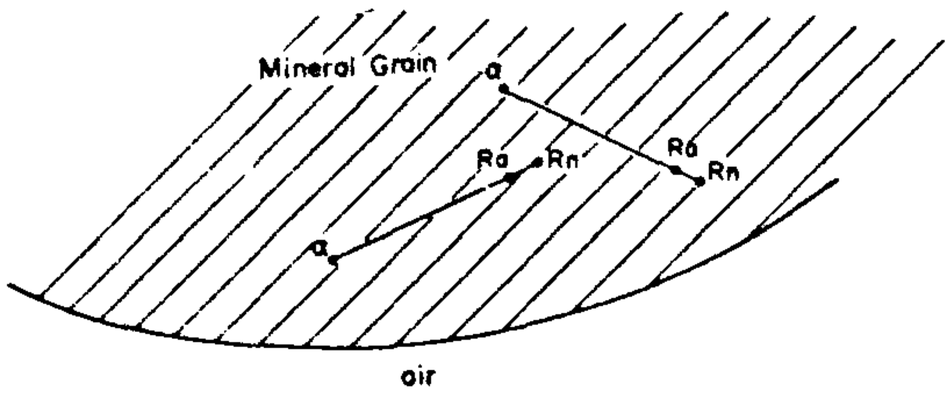

Figure 1. Rn generated inside a mineral grain is unable to emanate out.

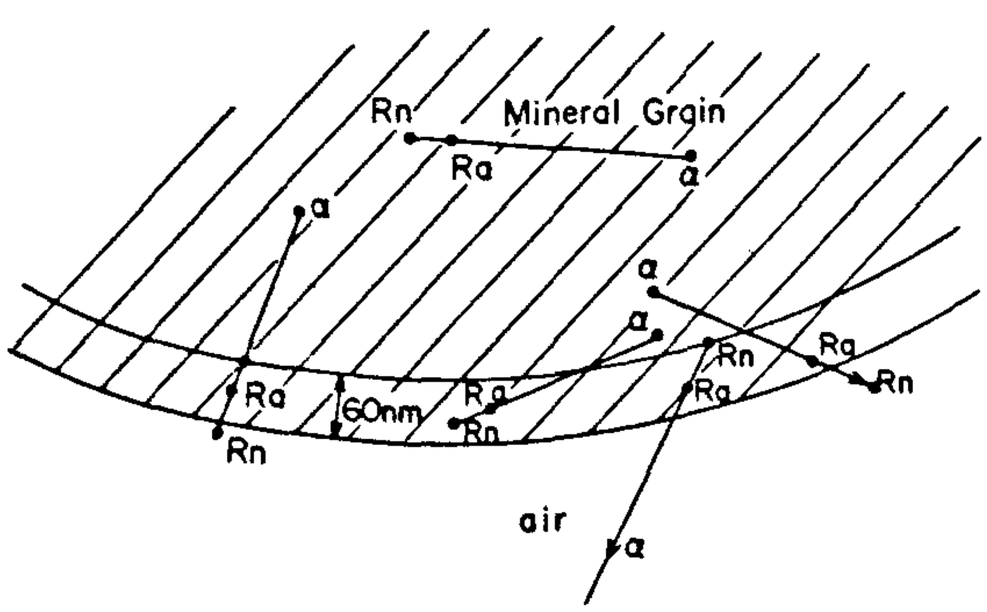

Figure 2. Some of the Rn generated in the skin of a mineral grain recoils out into air.

skin, while those generated deeper than the recoil range cannot come out at all. Thus only a small fraction, depending upon the size of the mineral grain, of the Rn atoms generated inside the grain can recoil out. If we assume that the Ra atoms are distributed uniformly within the grain, the fraction of Rn atoms recoiling out of the grain should be about 0.0005% for 1-cm-size grain, 0.005% for 1 mm size, 0.05% for 100 μm, 0.5% for 10 μm, and 5% for 1-μm-size grain. This fraction, also termed emanation coefficient, increases sharply for submicronic grains. This is the expectation for the single grain lying in air. But if the grain is surrounded by other grains (as in soil or in rocks), some of the recoiled Rn atoms may get embedded in the neighbouring grain (Figure 3). The recoil range in air is long ($\sim$ 150 μm). If the air gap between the grains is much less than 150 μm (let us say, $\sim 1\,\mu$m), then there is essentially no stopping by air in the gap, and most of the recoiled Rn atoms should be reimplanted in the opposite grain. Thus the emanation coefficients should be far less than those indicated above. When the pores are however filled with water, all of the recoiled Rn should stop in water (recoil range in water 100–200 nm), and the emanation coefficients should shoot up to the values indicated above. Actual observations however show that the emanation coefficients are rather large; further, the enhancement due to introduction of water in the pores is rather small ($\sim$ a factor 2). To explain these observations, a hypothesis is invoked

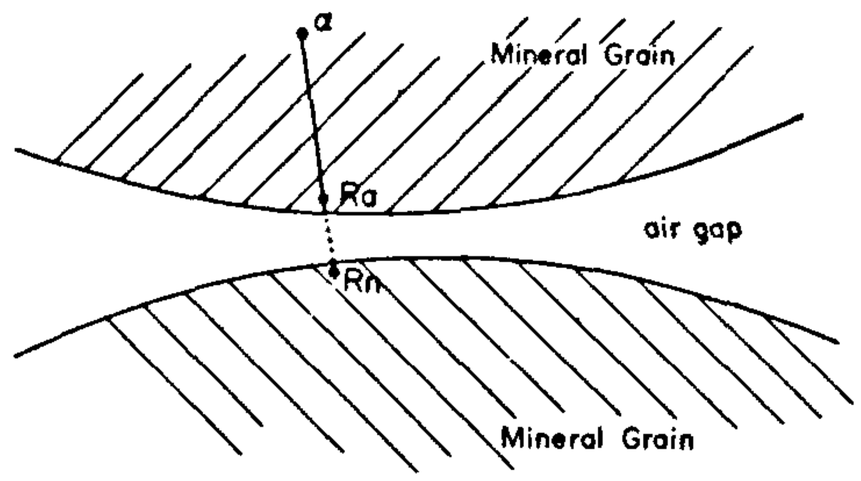

Figure 3. Rn recoiled out of the skin of a mineral grain gets embedded in the skin of a neighbouring grain.

which says that the implantation efficiency in the opposite surface must be poor, i.e. Rn atom somehow gets out of the skin of the neighbouring grain and comes back into the pore.

Reimplantation discounted

It is known that the recoiled Rn atom deposits its kinetic energy very fast. It is further hypothesized that it is able to melt (perhaps even vapourize) the material, about 1-nm-thick, along its track, and is able to diffuse out of the pit, back into the pore, before the material solidifies (Figure 4). This appears to be a reasonable hypothesis, but needs to be experimentally verified and details worked out. We have some experimental data which further provide indirect evidence that in granitic material only about 50% of the recoiled ^{220}Rn atoms get implanted in the opposite surface and the other 50% are able to diffuse back into the gaps. We leach ^{224}Ra selectively out of a rock sample. This causes reduction in ^{220}Rn emanation from the rock. But this reduction is only half as much as the emanation given by ^{224}Ra in the leach. These experiments provide good indirect evidence that the reimplantation of ^{220}Rn in the rock is about 50%; neither very efficient nor very poor. It may differ with recoil energy, also with the nature of projectile and the mineral. It should be possible to verify the hypothesis with direct experiments

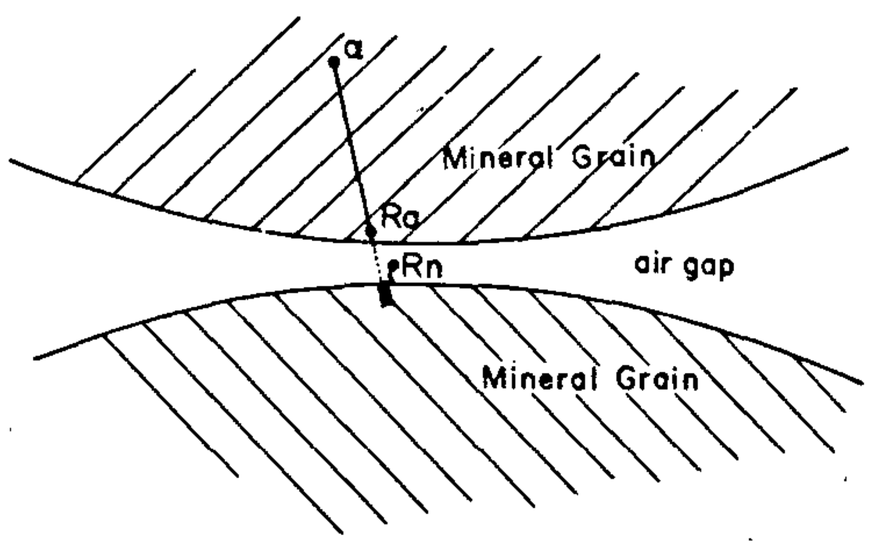

Figure 4. Rn implanted into the opposite wall is able to diffuse back into the gap.

and work out the details. We have in fact carried out some of these experiments recently. They show that the implantation efficiency of ^{220}Rn atoms (in energy range 20–100 keV) in Cu, Al and mica is 50±15%, thus confirming the results of earlier indirect experiments. We can therefore expect that a large fraction of Rn recoiling out of any mineral surface will come back into an adjoining gap (if there exists one), it does not matter if the gap happens to be narrow.

Emanation from rocks

Rocks are assemblages of minerals lying in close contact with each other. The mineral grains can differ greatly in size in various rocks, but it is convenient to choose rocks with millimetre-size mineral grains. We have found that the emanation coefficients for Rn in centimetre-size pieces of such a rock often lie in the range of 1 to 20%, i.e. far in excess of the value calculated for this size. The observed high emanation coefficient would indicate that the minerals in the rock are made of micron-size particles, with gaps in between, i.e. with very large open area inside. Since the open volume inside a rock is very small, the gap width must be very small (a few nm). However, this deduction rests on the assumption that Ra is distributed uniformly in each individual grain. An alternative explanation for the observed large emanation coefficients is also possible. It invokes two hypotheses: existence of high concentration of Ra on grain boundaries and existence of gaps at the grain boundaries. Accordingly, Ra-rich surfaces at the grain boundaries may yield enough Rn in the intergranular gaps from where it diffuses out to the surface of 1 cm or even 100-cm-size rock boulder. This explanation however does not appear to be valid in the case of several samples of granite we studied. Alpha radiographs of these granites do not show presence of excessive amount of Ra on grain boundaries, nor does an optical microscope reveal gaps along the boundaries. On the other hand, direct and reliable evidence for the existence of large open areas inside the rocks was also not forthcoming. The problem, therefore, appeared to be an intriguing one.

Recent investigations

In the case of rocks, we may get into the complication of possible existence of optically invisible narrow gaps along grain boundaries and the existence of submicronic U–Th-rich accessory minerals in these gaps. We can avoid these complications if we study large size single crystals of pure minerals. A single crystal of a pure mineral has no internal mineral boundaries and is expected to be essentially free from U–Th enrichment at its surface. But a large crystal of a pure mineral (like quartz or feldspar) tends to be free from U–Th impurities also, and emanation of Rn from such a crystal is difficult to measure. The choice therefore falls on single crystals of minerals which incorporate U–Th as part of their structures or as substitution elements. Our observations on mm-to-cm-size crystals of apatite, uraninite and monazite yielded large emanation coefficient similar to those for rocks. But zircon crystals yielded very low values. It thus appears that at least apatite, monazite and uraninite may often exhibit micro-crystallinity and associated network of internal gaps which necessarily have to be very narrow (nm wide), since the porosity of these crystals is extremely low. But these are rather special materials. The important thing is to find out what causes large emanation coefficients for Rn in common rocks.

Our experiments with large blocks of granite show unambiguously that Rn generated at depths of decimetres inside the rock is able to emerge at the surface. This is possible only if there exists a network of some kind of openings/gaps all through the volume of the rock. This however is again only a deduction. The nature and abundance of deduced openings remain a matter of conjecture. In order to unravel this, we took recourse to a different strategy. We argued that since Rn can come out of the openings, it should also be able to go in, from an external source. We may therefore be able to map the openings if we place a strong external source of Rn on the one side of a thin slice of a rock and monitor the exit points of Rn on the other side with a suitable sensor. The actual experiment however required some innovation. If nanometre-wide openings are to be mapped by this method, the external source of Rn should have high specific activity ($\sim 10^{10}$ dpm cm^{-3}). Further, if the openings are to be mapped precisely, the spatial resolution of the detection of Rn at the exit should be good (a few μm). This implies that Rn should be confined and detected within a few microns from its exit. These requirements were met by choosing short-lived ^{220}Rn as the external source which was placed on one side of the slice. For the detection of ^{220}Rn on the other side, an alpha-sensitive cellulose nitrate sheet was stuck flush on the slice with a few drops of ethyl acetate solvent; this effectively confined ^{220}Rn close to its exit till it decayed.

After some experimentation, the following procedure was adopted:

A 250-μm-thick cellulose nitrate sheet is first stuck on one side of the rock slice (1–2 mm thick and a few cm across). The ^{220}Rn external source is then placed on the other side. After an exposure of ~4500 min, the source is removed and put in its container far away. The cellulose nitrate sheet is now stripped from the slice and etched to reveal alpha tracks from decay of ^{220}Rn and its progeny (Figure 5). Several experiments were carried out on Indian and American granites. These

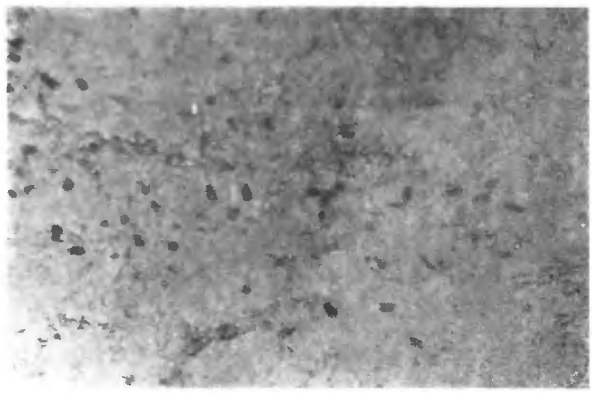

Figure 5. Tracks of alpha particles in cellulose nitrate sheet. Field: 600 μm × 400 μm. Short exposure.

granites had large grains (several mm across) of individual minerals, and the same mineral grain could often be seen on both sides of the slice. Thus, any openings in individual mineral grains or at grain boundaries could be conveniently located. The results of a few of the experiments carried out by employing the above method of radonographing the openings are shown in Figure 6.

From Figure 6 we see that the track distribution is very non-uniform spatially. The tracks tend to exist in narrow bands (50–500 μm wide) of approximately uniform track density ($\sim 10^6$ cm^{-2}). Since the presence of a track signifies the existence of an opening/gap very close to it, the band of tracks is a kind of replica of a zone of openings/gaps through which ^{220}Rn can diffuse. These openings however are not visible under an optical microscope. Most of the area of the zone is occupied by solid mineral. On the other hand, the number of tracks per unit length present in a zone ($\sim 10^4$ cm^{-1}) places a limit of $\sim$ 100 nm (with an estimated uncertainty of a factor of 5) on the total width of the openings in the zone. Further, the estimated resolution (~ 10 μm) of the method places a constraint that there may be several openings within a single zone. In other words, the mineral in this zone may exist as a mass of micron-size crystals with

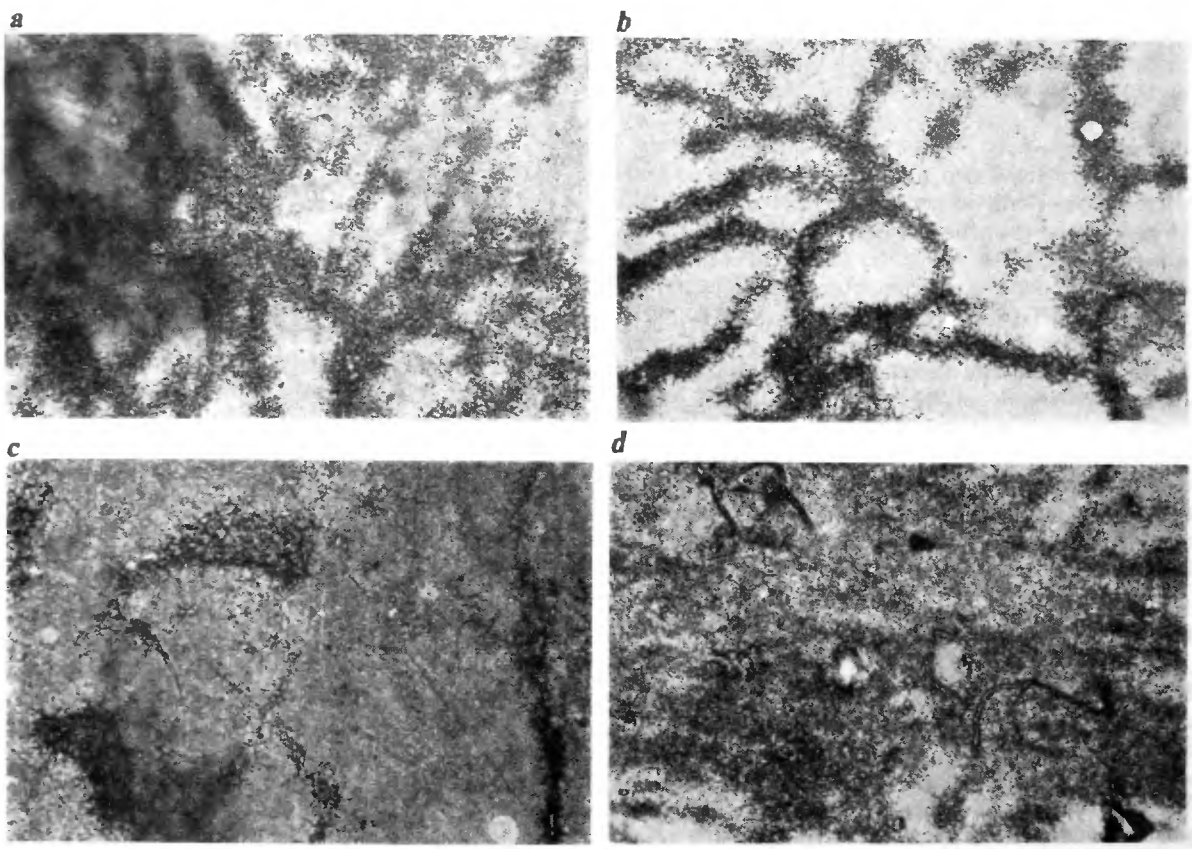

Figure 6. Radonograms of the holes in grains of various minerals. Field: 3 mm × 2 mm. Exposures: 4000–4500 min. *a*, Quartz (Monticello); *b*, plagioclase (Liberty Hill); *c*, plagioclase (Liberty Hill). Tracks can be seen to occur in patches also; *d*, amphiboles (mainly hornblends, Monticello).

submicronic gaps in between. These zones of submicronic porosity were seen to form a network which connects to the grain boundary network.

The observations in case of amphiboles (Figure 6,*d*) are quite different. Here, the entire grain appeared to be uniformly leaky with a few blank spots.

Radonograms of the holes in fresh samples of granites studied so for have revealed large areas completely free of tracks, and therefore free of porosity (Figure 6). In feldspars and quartz only 10–20% of the area exhibited porosity (submicronic), while in amphiboles almost entire area was leaky. Of the samples we have measured, only the amphiboles have abundant porosity and large internal area. Indeed, hornblends separated from a sample of a metamorphosed granite (Matkadguda, near Hyderabad, India) and the micas separated from Liberty Hill granite were found to have Rn emanation rates (per g), an order of magnitude greater than that of a bulk sample of granite, mainly as a result of their open structure, not because of any excess of Ra in them. In these samples, emanation from amphiboles alone could account for a large fraction of the observed bulk emanation provided Rn could move from the amphiboles through the surrounding minerals. Since we have observed that a connected network of zones of porosity exists in the common minerals in the rocks we have studied, Rn emanated from any material can be transported out via this network.

The zones of porosity observed in the samples are, however, circuitous and therefore not as effective for transport of Rn as is unrestricted air. The network reduces the effective diffusion length, $\sqrt{D/\lambda}$ of ^{220}Rn and ^{222}Rn to $\sim$3 mm and 30 cm respectively in granite, while the corresponding values in air are 3 cm and 3 m.

It appears that the existence of a network of submicronic openings in rocks is a general phenomenon. This may be partly responsible for some oddities observed in their behaviour,

Conclusion

(i) Zones of submicronic porosity run both along the grain boundaries and across the grains. The network of these zones on an individual mineral grain implies the existence of grains within a grain.

(ii) Depending upon the mineral and rock type, variable fractions of grain volume (10–80%) may exhibit submicronic porosity.

(iii) In the samples we have studied, the bulk of emanation of Rn appears to originate from amphiboles despite their low abundance. Outward transport of Rn can take place by diffusion in the surrounding network of zones of porosity found to exist in common minerals. Similar processes may control the exchange of other progeny.

(iv) Radonography as described here can be used to delineate the regions of submicronic porosity in any solid. The method is extremely sensitive, convenient and robust.

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