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DIFFERENTIAL HELIUM RETENTTON IN ZIRCONS: IMPLICATIONS FOR NUCLEAR WASTE CORTAINMENT

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Abstract. A very sensitive helium leak detector was utilized to measure the helium liberated from groups of zircons extracted from six deep granite cores. The observed low differential loss of gaseous helium down to 2900 m (197°C) in these ancient Precambrian rocks is easily attributable to the greater diffusion of He at higher temperatures rather than losses due to corrosion of the zircons. This fact strongly suggests that deep granite burial should be a very safe corrosion—resistant containment procedure for long—term waste encapsulation.

Recent mass spectrometric studies (Gentry, et al. 1982) have revealed that lead has been retained in zircons extracted from deep (960 m to 11310 m) granite cores where the ambient temperature increases from 105°C to 313°C at the greatest depth. As a follow—up to those experiments we now report the results of differential helium retention in similar zircons extracted from the same granite core samples which were used in the lead analyses (Laney and Laughlin, 1981).

The procedure for separating the zircons from the six different granite cores (from depths of 960, 2170, 2900, 3502, 3930, and 11310 m) was the same as that used in the previous experiments. The high-density fractions, obtained by passing the crushed core samples through different methylene iodide separating funnels, were thoroughly washed with acetone before being placed on a standard microscope slide. A fine—tipped needle was used to pick out the individual zircons with the aid of a polarizing microscope. Groups of these separated zircons, usually about 10 in number, were then loaded onto the platinum filament of the thermal inlet probe of the mass spectrometer for differential helium analysis.

The helium measurements were performed on a Leybold—Reraeus model F helium leak detector that had a Chemical Data Systems Pyrolysis unit interfaced to the test port. The leak detector has a detection limit of less than 10^{-10} cm^3/sec when operating in the dynamic mode. (The instrument could have been operated in a near—static mode with increased sensitivity down to ~10^{-11} cm^3/sec of He, but our experiments did not necessitate this increased sensitivity.)

In our initial series of measurements our Spectrometer was calibrated against a 5 (±0.5) X 10^{-8} cm^3/sec standard He leak. A subsequent recalibration with a more precise 5 (±0.5) x 10^{-10} cm^3/sec standard He leak revealed the total helium liberated during these initial measurements was slightly underestimated. The general procedure was to measure helium evolution from a group of zircons at progressively higher temperatures of 400°C, 600°C, and 1000°C for 20 sec intervals. (Previous studies of helium diffusion (Magomedov, 1970) from zircons indicated 1000°C was sufficient to liberate the helium with an activation energy of 15 kcal/mol.) We did not include the small amount of He observed at 1100°C in the total He summation because of possible atmospheric contamination. Between six and eight groups of zircons were analyzed at each depth. Runs were repeated at a given temperature until background helium levels were observed. Data recordings and integration under the peaks were dome with a Nicolet 1170 signal averager.

The third column in Table 1 shows, as a function of depth, the total amount of He liberated per μg of zircon for zircon groups comprised of approximately equal—size (~50—75 μm) zircons. The fourth column in Table 1 shows the ratio of the amount of He actually measured in zircons from any particular depth to the estimated amount of He which should have accumulated in those same zircons assuming negligible diffusion loss. For the zircons taken from a surface outcrop we assumed this ratio was one because the specimens we used were small fragments from the interior of larger zircon crystals.

For the other zircons from the granite and gneiss cores, we made the assumption that the radiogenic Pb concentration in zircons from all depths was, on the average, the same as that measured (Zartman, 1979) at 2900 m, i.e., ~8o ppm with ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios of ten (Gentry, et al., 1982; Zartman, 1979). Since every U and Th derived atom of ^{206}Pb, ^{207}Pb, and ^{208}Pb represents 8, 7, and 6 α—decays respectively, this means there should be ~7.7 atoms of He generated for every Pb atom in these zircons.

Knowledge of the zircon mass and the appropriate compensation factor (to account for differences in initial He loss via near—surface α-emission) enabled us to calculate the theoretical amount of He which could have accumulated assuming negligible diffusion loss. This compensating factor is necessary because the larger (150—250 μm) zircons lost a smaller proportion of the total He generated within the crystal via near—surface α—emission than did the smaller (40—50 μm) zircons. For the smaller zircons we estimate as many as 30—

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TABLE 1: The values listed below show first, as a function of depth and temperature, the amount of helium liberated from various groups of zircons in units of 10^{-8} cc per μg and second, the ratio of the amount of helium liberated to the theoretical amount which would have been retained assuming no diffusion loss. The near equality of the He concentrations in the surface and 960 m depth zircons is not particularly meaningful because the surface zircons were from an entirely different geological unit and doubtless have different U—Th—Pb concentrations than the zircons from the core samples.

Sample Depth (m)	Sample Temp. (°C)	He (10^{-8} cc/μg)	He (measured) He (theoret.)
Surface	20	8.2	1
960	105	8.6	0.58
2170	151	3.6	0.27
2900	197	2.8	0.17
3502	239	7.6×10^{-2}	1.2×10^{-2}
3930	277	$\sim 2 \times 10^{-2}$	$\sim 10^{-3}$
11310	313	$\sim 2 \times 10^{-2}$	$\sim 10^{-3}$

40% of the α—particles (He) emitted within the crystal could have escaped initially whereas for the larger zircons we studied only 5—10% of the total He would have been lost via this mechanism. The ratio of the measured to the theoretical amount of He is shown in the last column of Table 1. The uncertainties in our estimates of the zircon masses and compensation factors probably mean these last values are good only to ±30%.

In spite of these uncertainties, it is quite evident from Table 1 that the zircons from 960 m seem to have retained considerable amounts of He, and perhaps more significantly, differential He loss with increasing depth (and temperature) has occurred rather slowly down to 2900 m (197°C) before a precipitous drop is observed at 239°C (3502 m). In fact, at present we are not certain whether the minute amounts of He recorded from the deepest zircons (3930 and 4310 m) are actually residual He in the zircons or derived from some other source. That is, in the two deepest zircon groups (3930 and 4310 m), we observed only short bursts of He (~1—2 sec) in contrast to the prolonged 20 sec or more evolution of He which was typical of He liberation from zircon groups down to and including 3502 m. In fact, it was this prolonged He liberation profile seen in two 150—250 μm size zircon groups from 3502 m which convinces us that some residual He is still trapped in the zircons down to that depth (239°C).

Now it was recently noted that the high retention of Pb in even the deepest granite cores had favorable implications for nuclear waste containment in deep (1000 to 3000 m) granite holes (Gentry, et al., 1982). The rationale for these implications is straightforward: If zircons, which have been exposed to the same type of elevated temperature environment anticipated in deep granite burial, show no detectable Pb loss either from higher temperatures or from aqueous solution corrosion effects, then nuclear wastes buried in that same granite should, if anything, experience even greater retention because of the comparative immobility of waste—type elements as compared to Pb.

The present results are important in that they provide clear evidence that the dominant factor in slow He loss down to 2900 m is attributable to greater diffusion loss at higher temperatures rather than any corrosion induced losses from the zircons. This is not at all surprising because microscopic examination shows first that zircons from all depths exhibit well—defined prismatic faces without any evidence of external corrosion, and secondly that the delicate internal inclusions within the zircons do not show any evidence of alteration from aqueous intrusion via any microstructural defects. Indeed, the relatively slow liberation of He over several 20 sec intervals observed in zircons from the surface all the way down to 2900 m is strong evidence that these zircons are virtually free of any microfractures which would have permitted a more rapid He escape. In fact, considering the Precambrian age of the granite cores (Zartman, 1979), our results show an almost phenomenal amount of He has been retained at higher temperatures, and the reason for this certainly needs further investigation for it may well turn out to have a critical bearing on the waste storage problem.

Thus the additional evidences reported herein considerably reinforce the view that deep-granite storage should be a very safe corrosion—resistant waste containment procedure. The certainty of these results stands in clear contrast with the uncertainties about how well alternative storage sites (e.g., salt domes) could withstand corrosion and/or dissolution from intruding aqueous solutions.

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