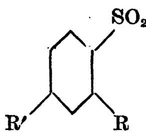
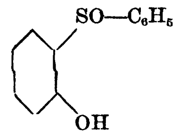
$VIII_1$ and $VIII_2$, and of compound IX cryoscopically in naphthalene.[5] These data, shown in Table 1, illustrate the striking difference between the isomers, and the very considerable extent of group interaction. It is hardly to be doubted that molecular weight determinations on other similar pairs would afford comparable results. The monomeric nature of *o*-hydroxydiphenyl sulfoxide is also demonstrated.

As a means of detecting chelation or association in the remaining compounds listed in Table 2 we have used the convenient and reliable method of wet melting point depression.[6] These materials were synthesized partly as intermediates and also to provide the basis for the further study of related compounds.

TABLE 2

	Compound	Melting point in °C Dry	Melting point in °C Wet	Depression in °C
	VIII			
1.	R=OH, R′=H	96–98	83.5	12.5
2.	R=H, R′=OH	135–136.2	84	51
3.	R=OH, R′=OCH_3	114–115.4	103.5	10.5
4.	R=OCH_3, R′=OH	167–170	116	51
5.	R=H, R′=OCH_3	90–90.6	80	10
6.	R=OCH_3, R′=H	141–142	125	16
7.	R=R′=OCH_3	119–119.5	103	16
8.	R=NH_2, R′=H	118–120.5	107	11
9.	R=H, R′=NH_2	166–172	133.5	32.5
10.	R=NH_2, R′=OCH_3	126–127.5	113	13
11.	R=OCH_3, R′=NH_2	130–131	102	28
	IX	162–164	159	3


(VIII)


(IX)

It is apparent from the data in Table 2 that both the hydroxyl group and the amino group are capable of significant interaction with the sulfone group. When the interacting groups are *para*, the result of interaction is association of molecules, whereas when they are *ortho*, the result is the establishment of a chelated structure which would be expected to be essentially monomeric. Hence, when the *para* isomer is melted in the presence of moisture, the polar water molecules become bonded with the sulfone group, displacing the phenolic hydroxyls (or amino groups) and thereby breaking up the associated complex. In the case of the *ortho* isomer, it appears that water molecules are bound but, due to the absence of polymeric units, the effect is relatively minor. This interpretation seems to be indicated because of the behavior of the methoxy sulfones, which also suffer melting point depressions when wet. Since *p*-hydroxydiphenyl sulfoxide was not available for study, no comparison with the *ortho* isomer can be made, but the very small depression of this isomer indicates strong chelation.

A more complete account of the experimental details of this work will be published elsewhere.

References

1. Baker, Wilson. *J. chem. Soc.*, 1934, 1684.
2. Chaplin, H. O. and Hunter, L. *J. chem. Soc.*, 1938, 375.
3. Hilbert, G. E., *et al. J. Amer. chem. Soc.*, 1936, **58**, 548.
4. Toussaint, J. *Bull. Soc. chim. Belg.*, 1945, **54**, 319.

---

[5] Details of the apparatus and method employed will be discussed fully in a forthcoming paper by one of us (I. M. H.).

[6] The use of the comparison of wet and dry melting points to distinguish between chelation and association has been well established by the work of Baker (*1*) and Hunter (*2*).

Abundance of N^{15} in the Nitrogen Occluded in Radioactive Minerals

William C. White and Herman Yagoda[1]

Laboratory of Physical Biology, Experimental Biology and Medicine Institute, National Institutes of Health, Bethesda, Maryland

The presence of elementary nitrogen in the gases occluded by uranium minerals was established by Hillebrand's (*3*) analyses of uraninites and pitchblendes from diverse localities. This discovery was overshadowed by the detection of helium in these minerals by Ramsay (*5*). Subsequent investigation of pitchblende from Katanga, Belgian Congo, and of a uraninite crystal from Keystone, South Dakota, by Davis and Kennedy (*1*) revealed the presence of nitrogen as well as helium. Analyses of the occluded gases showed the presence of 0.159% helium by weight and 0.075% nitrogen in the pitchblende, and about 0.03% of each in the uraninite.

In an investigation of the occluded gases in radioactive minerals by means of the mass spectrometer, we have detected nitrogen and helium in the fraction isolated by ignition of the samples and remaining uncondensed in a liquid air trap. The isotopic ratio of N^{15} to N^{14} in these samples was invariably higher than in samples of atmospheric air or in nitrogen isolated from nitrogenous compounds.

The gases were isolated by heating the freshly ground minerals to a bright red heat for several hours in a quartz tube sealed through a graded seal to the gas inlet system of the mass spectrometer. To eliminate interference with the nitrogen peaks at masses 28 and 29 by the carbon monoxide peaks at the same masses, the liberated gases were passed through a U-tube containing I_2O_5 maintained at 145° C to oxidize any carbon monoxide that might be present. Water, carbon dioxide, and oxides of sulfur, liberated by the thermal decomposition of the mineral and its associated gangue, were separated by means of two liquid air traps. The gases not condensed in the liquid air traps were analyzed from mass 12 through mass 44 in all of the samples and from mass 4 to mass 90 in many of them. The mass spectra showed a high percentage of helium, a trace of methane, and from 5% to 10% nitrogen by volume. No attempt was

---

[1] We wish to express our appreciation to W. F. Foshag and E. P. Henderson of the U. S. National Museum for providing us with certain of the specimens used in this work.

TABLE 1

N^{15} CONTENT IN GASES OCCLUDED BY URANIUM MINERALS

Specimen	Locality	Composition		Geological age in years	N^{15} abundance atom%
		U_3O_8%	ThO_2%		
Pitchblende	Woods' Mine,* Central City, Colorado	76.7	0.018	57×10^6†	0.532 ± 0.005
Uraninite crystal	Spruce Pine,§ North Carolina	~ 91	~ 3	251×10^6‡	0.546 ± 0.009
Samarskite	Spruce Pine,‖ North Carolina	11.3	0.8	~ 250×10^6	0.549 ± 0.015
Pitchblende	Katanga, Belgian Congo	78.8‖	.....	625×10^6¶	0.575 ± 0.003
Pitchblende	Shinkolobwe, Katanga, Belgian Congo	~ 89	.....	625×10^6**	0.574 ± 0.011
Uraninite	Wilberforce, Canada	72.5	10.6	1050×10^6¶	0.614 ± 0.012
Pitchblende	Great Bear Lake, Canada	63.6††	.....	1251×10^6¶	0.586 ± 0.005

* U. S. Nat. Mus. 83629, analysis by H. Yagoda.

† Nier, A. O., Thompson, R. W., and Murphy, B. F. *Phys. Rev.*, 1941, **60**, 112.

‡ Holmes, A. *Radioactivity and Geological Time,* Bull. No. 80, Nat. Res. Council, Wash., D. C., 1931, p. 342.

§ Approximate analyses cited by Holmes‡ for specimens from the same locality.

‖ Analysis by H. Yagoda.

¶ Nier, A. O. *Phys. Rev.*, 1939, **55**, 159.

** U. S. Nat. Mus. 8403, a high grade specimen with U_3O_8 content of approximately 89% and probably of the same age as the other Katanga mineral.

†† A specimen from vein 2; analysis by H. Yagoda.

made to obtain accurate quantitative measurements on these gases. A small peak at mass 30 was observed in most of the minerals analyzed, and it may be attributed to $N^{14}O^{16}$ formation. There was no evidence of argon in any of the samples within the sensitivity of the instrument (approximately 0.03% A^{40}).

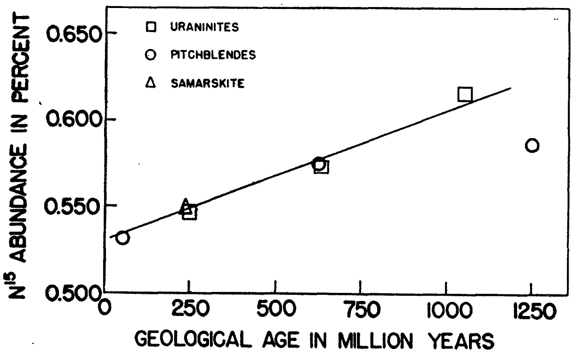


FIG. 1. N^{15} abundance of uranium minerals plotted against their probable geological age.

As shown in Table 1 the percent abundance of N^{15} in the nitrogen from old uranium minerals is abnormally high, measuring from 0.532% to 0.586%, as compared with the normal abundance of 0.376% (*6*). Determinations with our mass spectrometer[2] gave a value of 0.371 ± 0.002 for atmospheric nitrogen and 0.374 ± 0.001 atom % N^{15} in nitrogen isolated by the thermal decomposition of ammonium dichromate. In an effort to obtain a measurement on occluded nitrogen from a nonradioactive, but old, source, a sample of scheelite was ignited, but the quantity of gas liberated was too small for analysis. A sample of monazite sand from India, containing about 10% thorium and only traces of uranium, furnished a small quantity of nitrogen with an abundance of 0.600 ± 0.006 atom % N^{15}.

The association of nitrogen with helium in radioactive minerals has been attributed either to mechanical occlusion or internal accumulation by the hypothetical decay of U^{238} into nitrogen nuclei (*2*). Lind (*4*) has proposed that the nitrogen gas is formed in the mineral by the radiochemical decomposition of some nitrogen compound, possibly uranium nitride, by the action of alpha particles. Our observation of an abnormal N^{15} abundance, roughly proportional to the geological age of the specimen (Fig. 1), suggests that the nitrogen may have been present as a constituent of the mineral at the time of its formation and that the N^{15} content was augmented by the more rapid diffusion of the N^{14} isotope. However, with our present knowledge, none of these hypotheses adequately explains this phenomenon.

---

[2] Westinghouse Type LV mass Spectrometer with a Nier type capillary leak.

References

1. DAVIS, C. W. *Amer. J. Sci.*, 1926, **11**, 201.
2. FOOTE, P. D. *Nature*, Lond., 1924, **114**, 789.
3. HILLEBRAND, W. F. *Bull. U. S. Geol. Survey No.* 78, 1891, p. 43.
4. LIND, S. C. *Proc. nat. Acad. Sci.*, 1925, **11**, 772.
5. RAMSAY, SIR WILLIAM. *Proc. roy. Soc.*, 1895, **58**, 65 and 81.
6. VAUGHN, A. L., WILLIAMS, J. H., and TATE, J. T. *Phys. Rev.*, 1934, **46**, 327.