Table 1. Reflectivities (R), specific extinction coefficients (K), and the optical constants, refractive index (n), and absorption index (k), of Bruceton vitrain.

λ (A)	K	k	R (%)	n
7750	0.8	0.006	7.66	1.766
7000	1.2	0.011	7.69	1.767
6000	2.5	0.020	7.75	1.771
5461	3.7	0.026	7.88	1.779
5000	5.4	0.035	7.93	1.781
4000	10.0	0.052	8.11	1.788
3500	14.5	0.066	8.02	1.778
3000	20.0	0.079	7.17	1.715
2750	23.0	0.088	6.49	1.664
2500	24.0	0.086	6.04	1.633
2200	28.0	0.093	5.37	1.583
2150	29.0	0.093	5.13	1.563

region was reported along with calculated absorption indices, k (*2*); the value for k at 5461 A was found to be appreciably smaller than published values obtained from reflectivity measurements (*3, 4*). From the reflectivity spectrum (Fig. 1), refractive indices, n, over the entire spectral region have been calculated (Table 1) by Fresnel's equation

$$R = \frac{(n-1)^2 + n^2k^2}{(n+1)^2 + n^2k^2}$$

Because of the low magnitude of the absorption indices, this quantity is nearly insignificant in the calculation of refractive indices. However, the interdependence of the two indices was taken into account by successive alternate calculations of refractive indices from the above equation and of the absorption indices from

$$k = \frac{2.303\,\lambda\,A}{4\pi x n}$$

where λ is the wavelength of light in centimeters, A is the absorbance, and x is the sample thickness in centimeters.

The experimental reflectivity curve remains smooth throughout the spectrum, with no sharp discontinuities. One weak, broad shoulder appears at 2650 A. The reflectivity and refractive index spectra decrease appreciably at short wavelengths in the ultraviolet region. This decrease may be due to changes in absorption properties in this region, but it is more probably due to increased scattering of the coal substance at these wavelengths.

Reflectivity measurements were made on polished pieces of Bruceton vitrain with a Cary spectrophotometer equipped with a specular reflectance attachment; a front-surface aluminized mirror was used as the comparison, and reflectivity values for fused quartz were used as spectral standards.

Aromaticity of coal. In regions of strong spectral absorption, an increase is expected in both the refractive index and the absorption index, and hence in the reflectivity. In coal, such marked increase in absorption does not occur anywhere in the ultraviolet-visible spectrum (*3*). As can be seen from the data for reflectivity and refractive index, there also is no substantial increase in these values at any place in the spectrum.

These data are of particular significance in view of the recent reevaluation of x-ray measurements (*5*) which indicate that the ring sizes of aromatics that may be in Bruceton vitrain should be 1-to-3 and 2-to-4 rings. Thus the possible condensed aromatic nuclei are limited to 2-to-4 rings such as are found in naphthalene, phenanthrene, fluorene, chrysene, and other compounds. The strongest absorptions of all of these are confined to a narrow region of the short-wavelength ultraviolet, so that both reflectivity and absorption should show marked increases with definite spectral fine structure in this narrow region, but they do not. Most of the 16 2-to-4-ring polynuclear condensed aromatics, naphthalene through pyrene, have their strongest band in the region 2100 to 2550 A with K values from 205 (fluorene) to 1230 (anthracene). Five of the 2-to-4-ring group have their maximum absorption band between 2550 and 2750 A with K values from 360 (2,3-benzofluorene) to 1640 (naphthacene). On the basis of K values, the allowable percentages of these compounds that could be present in Bruceton vitrain varies from 1.4 to 14 percent. These maximum percentages of individual aromatics are not additive owing to considerable overlapping interference in this short spectral region.

If the principal structures in bituminous coal vitrain are not polynuclear condensed aromatic in nature, the predominant structures may be aliphatic and alicyclic and/or benzenoid. The shortage of hydrogen, oxygen, and other elements may require that the saturated structures contain extensive systems of tetrahedral carbon-carbon bonds—that is, quaternary carbon atoms in diamond-like structures of small size or in amorphous carbon structures like the "vitron" suggested for glass (*6*).

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24 February 1959

On the Presence of Fixed Ammonium in Rocks

Abstract. From one-fourth to one-half of the nitrogen in some granite rocks, and up to two-thirds of that in some paleozoic shales, occurred as ammonium ions held within the lattice structure of silicate minerals. The results provide greater insight into the origin of the earth's atmosphere.

It has been assumed by many scientists that practically all of the nitrogen in rocks occurs in organic combination. Evidence for this assumption has been based on the fact that only a small fraction of the nitrogen in rocks could be recovered as ammonia or nitrate by leaching with base-exchange reagents. Research conducted recently by my coworkers and me (*1, 2*) has shown that soils contain considerable amounts of fixed ammonium (ammonium ions held within the lattice structure of silicate minerals), and it seemed reasonable to postulate that some of the nitrogen in rocks is fixed ammonium. The purpose of this study was to test this hypothesis (*3*).

A procedure based on the ability of HF to remove fixed ammonium from clay minerals has been developed by Dhariwal and Stevenson (*1*) for the determination of fixed ammonium in soils. This method was modified for the determination of fixed ammonium in rocks. The procedure adopted was as follows: a 0.5- to 1.0-g sample of finely ground rock (100 mesh) was treated with 20 ml of boiling 1N KOH for 6 hours. The residue was recovered by centrifugation in a polyethylene tube, washed free of KOH with ammonia-free water, and treated with 10 ml of a solution consisting of 7.5N HF and 1.0N HCl. For granite rocks, the mixture was transferred to a polyethylene beaker and heated on a hot plate at 80°C to near-dryness. The ammonium released by HF was distilled with alkali into standard acid. The ammonia was estimated colorimetrically, by means of Nessler's reagent.

Total nitrogen in the samples was determined by a micro-Kjeldahl procedure. The digestion time was 3 hours.

The specimens included several Paleozoic shales and granite rocks. The shales were from Illinois. Shales A, B, and C were from Mississippian horizons; shale D was from a Pennsylvanian horizon. Granite rocks A, B, and C were from outcrops. Rock A was from New Hampshire, rock B was from Maine, and rock C was from Vermont (from the Rock of Ages quarry). Granite rocks D, E, and F were Pleistocene boulders from glacial till of Wisconsin age. They were obtained from Vermilion County, Ill. (*4*).

The total nitrogen and fixed ammonium nitrogen contents of the speci-

Table 1. Fixed ammonium nitrogen in shales and granite rocks.

Sample	Total N (μg/g)	Fixed $NH_4^+ - N$	
		(μg/g)	(% of N)
	Shales		
A (1445–1449 feet)	500	330	66.0
B (1976–2018 feet)	810	420	51.9
C (2318–2329 feet)	680	420	61.8
D (596– 600 feet)	610	410	67.2
	Granite rocks		
A (highly weathered)	86	27	31.0
B (slightly weathered)	35	10	28.6
C (unweathered)	32	18	56.3
D (moderately weathered)	26	9	34.6
E (moderately weathered)	21	5	23.8
F (moderately weathered)	37	10	27.0

mens are given in Table 1. The nitrogen contents of the granite rocks were generally lower than the values reported by Rayleigh (*5*) for igneous rocks. The results show that all of the samples contained nitrogen, which was not removed by boiling 1*N* KOH but was released as ammonia by HF. As hydrofluoric acid dissolves silicate minerals, there can be little doubt that the nitrogen occurred as fixed ammonium. Indirect evidence for the presence of fixed ammonium in rocks is provided by the study of Rayleigh (*5*), who found that the nitrogen in igneous rocks was liberated as ammonia by heating with caustic soda, but not with caustic potash. It is now known that caustic soda expands the *d* (001) spacing of silicate minerals, thereby allowing the ammonium ions to escape; caustic potash contracts the *d* (001) spacing, thereby preventing their release (*1*).

The origin of the fixed ammonium in the granite rocks must be regarded as a subject for speculation. The silicate minerals in granite rocks have crystal lattices that are contracted and incapable of fixing ammonium. I am of the opinion that ammonium was present in the substrate at the time the minerals were synthesized and competed with potassium for the pockets formed by the hexagonal oxygen rings in the crystalline nuclei of the minerals.

The nature of the nitrogen in the granite rocks that was not recovered as fixed ammonium is not known. Ammonia was liberated from rocks A, B, D, E, and F during the treatment with boiling 1*N* KOH. This nitrogen could have been in the form of exchangeable ammonium produced through the release of fixed ammonium from silicate minerals during weathering. The observation of Engols and Navarre (*6*) that substantial concentrations of ammonia nitrogen occur in unpolluted surface and ground waters of the uplands of northern Georgia as a result of the leaching of granite rock undergoing rapid weathering can be attributed to the liberation of ammonium ions from silicate minerals through weathering.

It is of interest to consider some possible inplications of the results obtained from this study. First, they indicate that a vast reservoir of nitrogen exists in the terrestrial areas of the earth as ammonium ions held within the lattice structure of silicate minerals. The amount of combined nitrogen in the silicate phase of the primary lithosphere of the earth has been estimated to be about 50 times the amount present as gaseous nitrogen in the atmosphere (*5, 7*); the amount of nitrogen in sedimentary rocks has been estimated as about one-sixth that in the atmosphere (*7, 8*). If it is assumed that an average of one-third of the nitrogen in igneous rocks, and one-half of that in sediments, is fixed ammonium, the amount of nitrogen present as fixed ammonium in the earth's crust would be almost 20 times that present as elemental nitrogen in the atmosphere.

Second, the results provide a clue to the origin of nitrogen in the atmosphere. Scientists generally believe that the nitrogen content of the atmosphere increased during geologic times, presumably through de-gassing of the earth (*7, 9*). It has been known for a long time that nitrogen is given off during the heating of igneous rocks. This has led to the conclusion that the nitrogen in volcanic gases is primary and thus is a new addition to the atmosphere. Scott *et al.* (*10*) found that fixed ammonium ions in some clay minerals were released at temperatures as low as 400°C; this is well below the temperatures reached in volcanoes.

Third, the results afford an explanation of the chemical nature of the nitrogen in stony meteorites. Biddhue (*11*) found that the fusion of meteorite powder with caustic soda and mercuric nitrate resulted in the production of ammonia. This ammonia was believed not to be entirely in the free state. Nitrogen is liberated from stony meteorites during entry into the earth's atmosphere, and I postulate that some of it originates as ammonium ions held within the lattice structure of silicate minerals.

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Changes in Soluble Citrate of Pigeon Bone during Egg Laying

Abstract. Accompanying the structural changes in medullary bone during the egg-laying cycle there are local increases in the concentration of soluble citrate. Since citrate can form both soluble and insoluble compounds with calcium, it is suggested that this anion may have a regulatory function in bone apposition and resorption.

Bone is a highly organized aggregate composed mainly of a protein matrix, apatite, water, and electrolytes. Like other tissues, it responds readily to changes in the composition of the surrounding body fluids and to the metabolic activities of the neighboring cells. Notable examples of this lability are the metaphyseal dissolution which follows the administration of parathyroid extract and the changes in avian medullary bone during egg laying.

We have suggested that resorption of bone could be initiated by the accumulation of intermediate metabolites formed by the contiguous connective tissue cells (*1, 2*). In support of this theory it was shown that, after the administration of parathyroid extract in the rabbit, dehydrogenase activity of bone slices was diminished and respiration was impaired (*2*). In this circumstance, the anions of di- and tricarboxylic acids could accumulate at physiologic *p*H, dissolving calcium from the apatite crystal and competing for calcium with the fixed colloidal anions of the bone matrix (*3*). The formation of these soluble calcium complexes would thus contribute to the dissolution of the structure.

We agree with others that, of the tricarboxylic acid anions, special attention should be accorded to citrate (*4–7*). There are several reasons for this emphasis. (i) The dissociation constant of calcium citrate is very low, and hence