Reports

Ammonium-Nitrogen in Green River Formation Oil Shale

Abstract. *It has been assumed that all of the nitrogen in oil shale from the Green River Formation is present as organic nitrogen and that the nitrogen in spent shale from retorting is present in the char or coke. In fact, from 41 to 84 percent of the nitrogen is present as ammonium fixed within silicate minerals in five samples of raw oil shale and between 46 and 69 percent of the nitrogen is similarly fixed in two samples of spent shale. Both organic nitrogen and fixed ammonium-nitrogen are lost during retorting by the Fischer assay procedure; the loss of organic nitrogen is greater.*

Shale oil produced from the Green River Formation is very high in N and requires upgrading before introduction into conventional refineries (*1*). Although Forsman and Hunt found 500 parts per million (ppm) of inorganic N in Mahogany and Papery shales from the Green River Formation in Utah (*2*), the tacit assumption generally has been that all of the N in oil shale is present in the kerogen (*3*). After retorting, about half the N originally present remains in the spent shale (*4*), and this N commonly has been thought to reside in the char or coke rather than in the mineral fraction (*5*).

Abundant evidence suggests that N commonly is present in sedimentary rocks as NH_4^+ proxying for K^+ (*6*). For example, Gulbrandsen found that NH_4^+ occupies up to 82 percent of the K^+ sites in authigenic feldspar in the Meade Peak member of the Phosphoria Formation (*7*). Stevenson and Dhariwal reported the substitution of NH_4^+ for K^+ in the illite of soils (*8*), and Sterne *et al.* observed up to 80 percent NH_4^+ in K^+ sites in illite in shales associated with a stratiform base metal deposit (*9*). Authigenic potassium feldspar and illite are abundant in Green River Formation oil shale (*10*); thus, it seems likely that NH_4^+ proxying for K^+ would contribute significant amounts of N to these oil shales.

Table 1. The N and K^+ contents of samples from Colorado core hole 1. Standard deviations used to estimate analytical precision are based on replicate analyses of all samples and are calculated according to the method of Youden (*21*).

Sample depth* (m)	Total N† (ppm)	Fixed NH_4^+-N		Organic N (ppm)§	Fixed K^+ (%)‖	K^+ sites occupied by NH_4^+ (%)¶
		ppm‡	Percent of N			
772.3	2589	1239	47.9	1350	0.83	29.4
781.5	6198	4080	65.8	2118	1.94	36.7
781.5 (s)	4611	3162	68.6	1449	2.44	26.7
789.3	4588	2313	50.4	2275	1.80	25.8
813.2	3876	3267	84.3	609	1.34	40.5
819.4	4438	1833	41.3	2605	1.12	31.3
819.4 (s)	2856	1329	46.5	1527	1.37	21.3

*Sample depths indicate tops of samples consisting of a 0.31-m interval; (s) denotes spent shale from the Fischer assay. †Standard deviation is estimated to be 677 ppm. ‡Standard deviation is estimated to be 193 ppm. §Calculated as the difference between total N and fixed NH_4^+-N. ‖Standard deviation is estimated to be 0.034 percent. ¶$NH_4^+/(NH_4^+ + K^+) \times 100$. Calculations are on a molar basis.

Table 2. Percentage changes in concentrations as a result of retorting. Before the percentage changes were calculated, we adjusted the concentrations of the various species determined for raw shale to a volatile-free basis by dividing the observed value by the fraction of charge remaining as spent shale. The fractions of charge remaining were 0.87 and 0.82 for the samples from 781.5 and 819.4 m, respectively.

Species measured	Sample depth	
	781.5 m	819.4 m
Total N	−35.3	−47.2
Fixed NH_4^+-N	−32.6	−40.6
Organic N	−40.3	−51.6
K^+	9.4	0.0
K^+ sites occupied by NH_4^+	−27.2	−32.0

We analyzed five samples of Green River Formation oil shale taken from Colorado core hole 1 obtained from the Laramie Energy Technology Center (LETC) (*11*). The three upper samples came from the Parachute Creek member, whereas the two lower were from the Garden Gulch member. Analysis by x-ray diffraction revealed that both illite and potassium feldspar were found in all five samples (*12*). The amounts of total N, fixed NH_4^+-N, organic N, and fixed K^+ found in each sample of raw shale are reported in Table 1. Fixed NH_4^+-N was found to comprise from 41.3 to 84.3 percent of the N in the raw shale samples, and from 21.3 to 40.5 percent of the fixed K^+ sites are occupied by NH_4^+. Thus, an important fraction of N in oil shale from the Green River Formation is present as fixed NH_4^+-N.

The samples from 781.5 and 819.4 m were retorted according to the Fischer assay procedure, and samples of the spent shale were provided by Dale Lawlor of LETC. Yields from these samples were, respectively, 19.9 and 35.6 gallons of oil per ton, and 87.2 and 82.3 percent of the raw shales charged were recovered as spent shale. Fixed NH_4^+-N makes up, respectively, 68.6 and 46.5 percent of the N in the spent shale, and NH_4^+ proxies for K^+ in 26.7 and 21.3 percent, respectively, of the sites (Table 1). Fixed NH_4^+-N, therefore, contributes substantially to the N content of spent shale as well as raw shale.

Percentage changes in the contents of N types and K^+ due to retorting are presented in Table 2. Both fixed NH_4^+-N and organic N were lost; the loss of organic N was greater. The K^+ content of the 819.4-m sample was unchanged; however, there was an apparent increase in the sample from 781.5 m. This increase we attribute to incomplete release of K^+ from the raw shale sample because of protection of the silicate minerals from HF by organic matter, just as Stevenson found to be the case in the determination of fixed NH_4^+-N (*6*). The decrease in the percentage of fixed K^+ sites occupied by NH_4^+ in the spent shale (Table 2) indicates that NH_4^+ is lost from silicate lattices relative to K^+. Hallam and Eugster found that ammonium illite (ammonium muscovite) and ammonium feldspar (buddingtonite) exist in equilibrium with various clay phases and NH_3 (*13*). Thus, it is conceivable that the mineral phase could serve as a source of or sink for NH_3 during retorting. The results presented here show that, under the conditions of the Fischer assay (500°C), the mineral matter serves as a source of NH_3. Under the higher temperatures and different oxygen tensions typical of other processes, the position of the equilibrium between NH_3 and the minerals would shift.

Stevenson pointed out that the Kjeldahl method, which traditionally has been used to determine N in both raw and spent oil shale, measures inorganic N along with organic N; thus the results of any soil or rock analysis by the Kjeldahl method should be reported not as organic N but as total N (*14*). Stevenson and Cheng measured total N and inorganic N (the sum of fixed NH_4^+-N and exchangeable NH_4^+-N) and calculated organic N by the difference (*15*). We have adopted their analytical procedures except that we determined NH_3 in the final step of each procedure by distilling it into a boric acid–indicator solution and titrating with 0.005N H_2SO_4 (*16*). In this study, exchangeable NH_4^+-N was insignificant for all samples and therefore is not reported.

The key to understanding the distribution of the types of N is proper determination of the fixed NH_4^+-N—that is, NH_4^+ that cannot be extracted with 1M KCl and that is thought to occur within silicate mineral lattices as a proxy for K^+ (*6*). The most likely source of error would seem to be reporting organic N as fixed NH_4^+-N; thus, we have incorporated several steps into the procedure to minimize this risk. (i) A pretreatment with KOBr is used to oxidize the N contained in organic matter and exchangeable NH_4^+ to elemental N (*17*). The treatment with 5N HF and 0.1N HCl used to break down the silicate lattice does not release NH_3 from organic matter, even from compounds as labile as amino acids or amino sugars (*18*). In fact, Stevenson found that organic matter not removed by oxidation tends to interfere with the fixed NH_4^+-N determination by protecting the minerals from HF-HCl, thereby preventing release of NH_4^+ rather than contributing NH_3 (*6*). (ii) The NH_3 is steam-distilled from a solution buffered at pH 8.8 with borate in order to avoid base-induced release of NH_3 from organic matter (*18*). Thus, we believe that the N reported here as fixed NH_4^+-N occurs as a proxy for K^+ within the crystal lattice of silicate minerals.

We determined the fixed-layer K^+ by removing exchangeable K^+ by extraction with NH_4Cl solution, breaking down the silicate lattice with HF, and analyzing the solution with an atomic absorption spectrophotometer (Perkin-Elmer model 403).

We propose that the N occurring as fixed NH_4^+-N is derived from the organic matter during early diagenesis. Oil shale of the Green River Formation is thought by some to have formed in a stratified lake with highly anoxic bottom waters (*19*). Because this is precisely the type of environment in which significant quantities of NH_3 would be generated (*20*), NH_4^+ should have been available for incorporation at the time authigenic minerals were forming. This model is consistent with the suggestion of Gulbrandsen that in the Phosphoria Formation NH_4^+ derived from the decomposition of organic matter was incorporated in feldspar as it formed from volcanic glass or intermediate alteration products of glass such as smectite or zeolites (*7*).

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References and Notes

1. N. J. Wasilk and E. T. Robinson, in *Oil Shale, Tar Sands, and Related Materials*, H. C. Stauffer, Ed. (ACS Symposium Series 163, American Chemical Society, Washington, D.C., 1981), p. 223.
2. J. P. Forsman and J. M. Hunt, in *Habitat of Oil*, L. G. Weeks, Ed. (American Association of Petroleum Geologists, Tulsa, 1958), p. 747.
3. J. W. Smith, *U.S. Bur. Mines Rep. Invest. 5725* (1961).
4. ——, *U.S. Bur. Mines Rep. Invest. 5932* (1962).
5. A. K. Burnham, in *Oil Shale, Tar Sands, and Related Materials*, H. C. Stauffer, Ed. (ACS Symposium Series 163, American Chemical Society, Washington, D.C., 1981), p. 39.
6. F. J. Stevenson, *Geochim. Cosmochim. Acta* **26**, 797 (1962).
7. R. A. Gulbrandsen, *J. Res. U.S. Geol. Surv.* **2**, 693 (1974).
8. F. J. Stevenson and A. P. S. Dhariwal, *Soil Sci. Soc. Am. Proc.* **23**, 121 (1959).
9. E. J. Sterne, R. C. Reynolds, Jr., H. Zantop, *Clays Clay Miner.* **30**, 161 (1982).
10. W. A. Robb and J. W. Smith, in *Guidebook to the Energy Resources of the Piceance Creek Basin, Colorado*, D. K. Murray, Ed. (Rocky Mountain Association of Geologists, Denver, 1974), p. 91.
11. Colorado core hole 1 was drilled in the Piceance Basin in the NW/4 NE/4 SE/4 of section 13, T 1 N, R 98 W, Rio Blanco County, Colorado (*10*).
12. W. S. Evans, thesis, University of Texas at Arlington (1982).
13. M. Hallam and H. P. Eugster, *Contrib. Mineral. Petrol.* **57**, 227 (1976).
14. F. J. Stevenson, *Geochim. Cosmochim. Acta* **19**, 261 (1960).
15. —— and C.-N. Cheng, *ibid.* **36**, 653 (1972).
16. J. M. Bremner, in *Methods of Soil Analysis*, C. A. Black, Ed. (American Society of Agronomy, Madison, Wisc., 1965), part 2, p. 1149.
17. J. A. Silva and J. M. Bremner, *Soil Sci. Soc. Am. Proc.* **30**, 587 (1966).
18. F. J. Stevenson, G. Kidder, S. Tilo, *ibid.* **31**, 71 (1967).
19. G. A. Desborough, *Geol. Soc. Am. Bull.* **89**, 961 (1978).
20. D. C. Thorstenson and F. T. Mackenzie, *Nature (London)* **234**, 543 (1971).
21. W. J. Youden, *Statistical Methods for Chemists* (Wiley, New York, 1951), p. 15.
22. We are grateful to D. L. Lawlor of the Laramie Energy Technology Center for providing the samples of raw and retorted shale.
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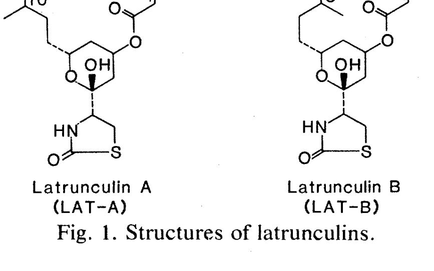
Latrunculins: Novel Marine Toxins That Disrupt Microfilament Organization in Cultured Cells

Abstract. *Two toxins, latrunculins A and B, which contain a new class of 16- and 14-membered marine macrolides attached to the rare 2-thiazolidinone moiety, were purified recently from the Red Sea sponge* Latrunculia magnifica. *The effects of these toxins on cultured mouse neuroblastoma and fibroblast cells have been evaluated. In both types of cells, submicromolar toxin concentrations rapidly induce striking changes in cell morphology that are reversible upon removal of the toxin. Immunofluorescence studies with antibodies specific for cytoskeletal proteins reveal that the toxins cause major alterations in the organization of microfilaments without obvious effects on the organization of the microtubular system.*

Among the most prominent sponges in the Gulf of Eilat (the Red Sea) are colonies of the branching red-colored *Latrunculia magnifica* (Keller), which are found at depths of 6 to 30 m and are clearly visible from long distances. Unlike most Gulf of Eilat sponges, colonies of this sponge grow exposed and appear never to be damaged or eaten by fishes. Furthermore, when squeezed manually, the sponge exudes a reddish fluid that causes fish to retreat from its vicinity. Squeezing *Latrunculia magnifica* into an aquarium is lethal, causing agitation of the fish in seconds, followed by hemorrhage, loss of balance, and, after 4 to 6 minutes, death (*1*).



Latrunculin A (LAT-A)   Latrunculin B (LAT-B)

Fig. 1. Structures of latrunculins.

Two toxins, latrunculin A (LAT-A) and latrunculin B (LAT-B) were recently isolated and purified from two *Latrunculia magnifica* species (or specimens), and their structures were determined by