analysis would be less than unity. It seems, therefore, that the only significant source of copper in these aerosol samples also results in atmospheric magnesium and sulfate. For particles collected below 2000 m, the sea appears to be the only important source of copper particles. (For samples collected above the inversion layer, copper concentrations are much lower and there appears to be no positive correlation between copper and sulfate concentrations. However, the data are few in number.)

Further support for the view that the source of atmospheric copper in the samples collected below 2000 m comes from the variation of concentration with altitude. The aluminum concentrations show no significant variation with altitude, whereas the sulfate, magnesium, and copper concentrations decrease approximately exponentially with increasing altitude. The correlation coefficient between log[Cu] and height is −0.52 (16 points), a value significant at better than the 95 percent confidence level.

The geometric mean mass ratio of $[Cu]/[SO_4]$ is 0.018 ± 0.005 compared with the oceanic value of 1.1×10^{-6} (*11*). The enrichment factor for copper relative to an ocean reference constituent Y is given by

$$E_{sea}(Cu) = \frac{(Cu/Y)_{atm}}{(Cu/Y)_{sea}} - 1$$

where in this case Y is either sulfate or magnesium. Based on magnesium or sulfate, copper is enriched by a factor of 2×10^4 during aerosol production at the sea surface.

Enrichment at the sea-air interface is consistent with measurements by Duce *et al.* (*12*), who found that at Narragansett Bay, Rhode Island, enrichments of copper of about 50 occurred in the top 150 μm of the sea surface. If when a rising bubble bursts at the water surface only the top 0.025 to 0.75 μm of the surface is stripped off (*13*) and if all the enrichment of copper occurs in this surface layer, enrichment of copper in the atmospheric aerosol is estimated to be in the range 10^4 to 3×10^5. This range encompasses our measured enhancement.

Barker and Zeitlin (*14*) also found enrichments of copper as well as iron and zinc in surface layers and marine atmospheric samples gathered off the island of Oahu, Hawaii. Copper in the atmospheric aerosol was enriched by three to four orders of magnitude. Our measurements, which were made in the Southern Hemisphere and were removed from any direct coastal influence, corroborate these results.

The evidence strongly supports the contention that copper found in atmospheric aerosols collected near Tasmania and below the inversion layer originates from the ocean. The estimated enrichment of copper is rather large but is comparable to enrichments of other heavy metals (*7*) including silver (*15*). A biogenic agent (*12*) may be responsible for the approximately 20,000-fold enrichment of copper during aerosol production at the sea surface.

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Carbon-13/Carbon-12 Isotope Fractionation of Organic Matter Associated with Uranium Ores Induced by Alpha Irradiation

Abstract. *Analyses of stable carbon isotopes from two sample suites from sandstone uranium (tabular) ores show interesting variations. Organic carbon associated with high-grade uranium ore is heavy ($\delta^{13}C = -16.9$ to -19.6 per mil, where $\delta^{13}C = {}^{13}C/{}^{12}C$ relative to the Pee Dee belemnite standard) relative to the adjacent lower-grade samples (-22.7 to -26.4 per mil). It is suggested that the heavy isotopic values for the ore samples are related to a radiation and chemical isotope effect that has occurred mainly because of an alpha-radiation dose of 10^{11} rads.*

Stable carbon isotopic fractionation in noncarbonate materials occurs mainly as a result of biological processes (*1*), catagenesis (thermal cracking) of buried organic matter (*2*), and occasionally exotic reactions such as solar proton "stripping" (*3*). We report here on a radiation-induced isotope fractionation not previously observed.

To better understand the relationship between organic matter and uranium, we have analyzed two suites of five samples each from the Kerr McGee Corporation section 30 mine near Grants, New Mexico. The uranium ore occurs in medium- to fine-grained nonmarine sandstones of the Upper Jurassic Westwater Canyon member of the Morrison Formation (*4*). The ore is of the trend or tabular type, where the ore forms blankets that are lit-

Table 1. Uranium, organic carbon, carbonate carbon, and isotopic carbon data for samples from the Kerr McGee Corporation section 30 mine, New Mexico.

Laboratory number	Uranium (%)	Organic carbon (%)	Organic carbon $\delta^{13}C$	Carbonate carbon (%)	Carbonate carbon $\delta^{13}C$
359	0.008	<0.2*	−23.52	0.78	−12.63
360	0.39	0.4	−19.61	1.27	−11.93
361	0.69	0.8	−18.73	0.10	−13.62
362	1.08	1.4	−18.71	0.04	−16.05
363	0.016	<0.2†	−22.65	1.26	−15.74
824	0.038	0.2‡	−24.06	<0.01	
825	2.87	5.0	−17.76	<0.01	
826	2.78	4.3	−17.66‖	<0.01	
827	1.17	1.8	−16.87	<0.01	
828	0.016	<0.2§	−26.43	<0.01	

*Reanalyzed to give 0.30 by difference and 0.11 after acid leach. †Reanalyzed to give 0.23 by difference and 0.12 after acid leach. ‡Reanalyzed to give 0.19 by difference; 0.20 total combustion. §Reanalyzed to give 0.13 by difference; 0.12, total combustion. ‖Acid-treated replicate, −17.45 per mil.

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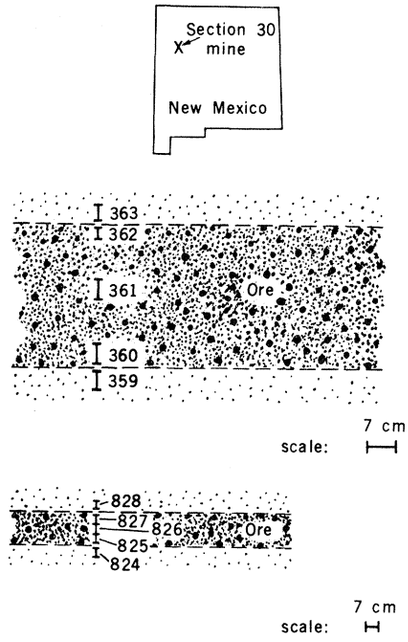

Fig. 1. Location of samples from two suites in the Kerr McGee Corporation section 30 mine near Grants, New Mexico.

erally suspended in sandstone units. Individual ore bodies range from a little less than 1 to 15 m thick, 5 m to somewhat more than 100 m wide, and a few tens to at least a thousand meters long. The richer parts of the ore commonly contain more than 1 percent uranium. The ore is intimately associated with structureless organic matter which is insoluble in organic solvents, weak acids, and bases. The ore and organic matter surround sand grains and fill interstices between grains. The samples were collected in 1960 by F. Moore of the U.S. Geological Survey and were reported by Granger (*5*). This type of ore accounts for approximately 40 percent of the U.S. ore production and reserves.

The uranium was analyzed fluorimetrically or volumetrically. The carbon contents were measured in 1961 by combustion for total carbon, by acid-gasometric analysis for carbonate carbon, and by difference for organic carbon; these analyses were repeated in 1977 with comparable results (*6*). The organic carbon was also measured directly (after acid leach) in the process of isotopic analysis. The carbon isotopic analyses were done by radio-frequency induction combustion (*7*) and measurement on a Nier type double-collector mass spectrometer (15-cm radius of curvature) (*8*).

The five samples from each suite are represented by a vertical traverse of one low-grade ore sample above, three ore samples, and another low-grade ore sample below (Fig. 1). These samples are two suites of more than 40 that were collected and analyzed in 1958–62 (*4*, *5*). We chose them for analysis because of their high organic (and uranium) contents.

The uranium, carbon, and carbon isotopic results are given in Table 1. The low-grade samples at the borders of the ore show $\delta^{13}C$ values (*9*) of -22.7 to -26.4 per mil, which are typical of sedimentary organic matter (*2*). The lightest values are similar to those reported for terrestrial kerogens and humic material (*10*). The ore samples have carbon isotopic values that range from -16.9 to -19.6 per mil, that is, approximately 5 to 8 per mil heavier than the low-grade samples. These values are not typical of sedimentary organic matter from the nonmarine environment (*11*), and the organic material in these samples all appears to derive from an epigenetic introduction of originally soluble organic matter. Pyrolysis–gas chromatography (*12*) of these samples and pyrolysis–gas chromatography and elemental analysis of other ore samples (*13*) show a very refractory carbon-rich, hydrogen-poor material that does not give a graphite x-ray diffraction pattern (*14*).

Because the organic matter and uranium were deposited in late Jurassic time (*15*), the uranium in equilibrium with its daughters has deposited a dose (*16*) of 10^{11} rads (*17*), which was absorbed mainly in the intimately associated organic matter. The decay of each atom of ^{238}U to lead accounts for eight alpha particles, six beta particles, and associated gamma rays. This radiation dose is 10^4 greater than that used in most radiation chemistry experiments. A dose of 10^5 to 10^9 rads applied to organic chemicals (*18*, *19*) and sedimentary organic matter (*20*, *21*) leads to dehydrogenation as well as the production of methane (*22*), ethane, and higher alkane homologs. The resulting organic material is deficient in hydrogen, and the atomic ratio of hydrogen to carbon shows a decreasing linear trend with the logarithm of the radiation dose (*23*). Radiation from uranium decay has produced optically observable effects such as microscopic halos (*24*) in coalified wood; however, our amorphous samples do not show this effect. Figure 2 shows the relationship between $\delta^{13}C$ values for organic matter and the logarithm of the uranium content (and dose absorbed). The mineralized samples show carbon which is depleted in ^{12}C, whereas the nonmineralized samples show lesser or negligible isotopic changes.

Figure 2 shows that the radiation becomes less effective in altering the carbon isotope values at high dose. A logarithmic plot has also been used to show the variation in the uranium content as a function of the hydrogen content of coaly material (*20*) and the ratio of hydrogen to carbon (*23*) of organic matter associated with uranium ores. Our modification of the explanation proposed in (*20*) is that, as the irradiation dose increases, alpha particles are absorbed in organic material that has become more radiation-resistant since it has already lost functional groups, lost aliphatic side chains, and become aromatized.

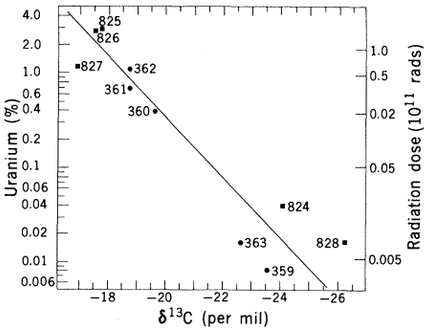

Fig. 2. Semilogarithmic plot of $\delta^{13}C$ as a function of the percentage of uranium and the calculated radiation dose (*16*). The line is for the equation $\delta^{13}C = 3.04 \log U - 30.73$ (where $\delta^{13}C$ is per mil and the uranium concentration is in parts per million), with the correlation coefficient $r = .925$, which is significant at the 99 percent confidence level (*27*).

Bond-breaking by alpha radiation and alpha recoil of the nucleus are most effective in the immediate vicinity of the uranium atom, whereas bond-breaking by beta and gamma radiation will be diffused over a much larger volume. The high linear energy transfer of the alpha radiation (*19*, *25*) gives a high density of primary ionizations that are so close together that they may be considered as continuous. This energy transfer and ionization leads to many broken bonds, radicals, ions, and excited molecules in a small volume where preferential formation of ^{13}C-deficient volatile products can occur to produce the observed isotope effect in the bulk organic material (*26*).

It is also likely that the radiation acts to catalyze the "fixation" of the uranium ore in the organic matter by creation of chemically reactive reductants (*18*) that will reduce the soluble uranyl(VI) species to insoluble UO_2. The radiation also makes the organic material more refractory (less soluble and oxidizable), and it protects the uranium ore from remobilization or solution.

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Behavioral Competition: A Mechanism for Schedule Interactions

Abstract. *Rats pressing a lever for food reinforcement showed large positive-contrast effects when provided with the opportunity for a competing wheel-running response. Positive and negative behavioral contrast may reflect reallocation of competing interim and terminal responses between schedule components following changes in the reinforcement conditions in one component.*

The level of operant behavior that a given rate of reinforcement will maintain in a given situation is usually affected by the amount of reinforcement obtained in other situations. A much-studied example of this dependence is behavioral contrast (*1, 2*). The standard demonstration of contrast involves food-reinforced key-pecking by pigeons at two distinct visual stimuli presented in alternation (multiple schedule). If reinforcement for pecking at one stimulus (the changed component) is discontinued, responding to the other (the unchanged component) usually increases (positive behavioral contrast). Conversely, if pecking at one stimulus is reinforced more frequently, rate of responding to the other (unchanged) stimulus decreases (negative behavioral contrast).

The necessary and sufficient conditions for contrast have not yet been fully defined. The best generalization is that contrast results from changes in relative reinforcement rate (*2*). In recent years, several interpretations of contrast have been offered that depend upon the phenomenon of autoshaping: the elicitation, presumably by mechanisms related to Pavlovian conditioning, of food-related behaviors (specifically key-pecking by pigeons) in the presence of, and often directed at, stimuli that predict food (*2–4*). For example, Staddon (*3*) proposed that key-peck contrast results because pecking is an induced terminal response that typically occurs in the presence of stimuli that predict food. The stimulus in the unchanged component of a multiple variable-interval schedule is made more predictive when food delivery in the changed component is abolished. Hence pecking is likely to be facilitated (positive contrast). Conversely, if an instrumental response incompatible with pecking (such as treadle-pressing) is chosen, the facilitation of pecking by the contrast manipulation may interfere with the instrumental response, yielding a decrease in response rate (negative induction). These and other predictions of what has come to be termed "additivity theory" have been generally confirmed, and the adequacy of the contrast manipulation to produce autoshaping has been independently demonstrated (*2, 5*).

Despite these successes, additivity theory has its limitations. For example, it offers no straightforward account of negative contrast. Moreover, recent demonstrations have shown that it is possible to obtain positive contrast with responses such as treadle-pressing by pigeons and bar-pressing by rats that are not in any sense induced by food-related stimuli (*6, 7*).

There is a commonsensical mechanism that may contribute to contrast effects, which seems to have escaped attention despite its simplicity. It relates to constraints imposed by limitations of time on the animal's ability to engage in different activities. In any periodic-food situation it is possible to identifiy two mutually exclusive classes of activity, one class related to food reinforcement (terminal responses) and a complementary class (interim responses) (*8, 9*). There is evidence that interim and terminal responses compete for the available time; the most obvious is the observation that an enforced decrease in one class of activities usually leads to an increase in the level of the other.

Behavioral competition sets the stage for behavioral contrast in the standard two-component procedure. In the first (prediscrimination) condition, with equal reinforcement in both components, interim activities compete with terminal responses in both components, leading to an intermediate level of terminal responding in both. In the second (discrimination) condition, however, there will be no terminal responding in the changed component, as a result of the absence of reinforcement; hence interim responding is free to increase. With this reallocation of interim activity into the changed component, the level of interim activity in the unchanged component is likely to decrease, reducing its inhibitory effect on the measured (terminal) response. This results in disinhibition of terminal responses in the unchanged component, thus producing positive behavioral contrast. A similar, symmetrical account can be offered for negative contrast: an increase in reinforcement rate in the changed component increases instrumental responding in that component, thus displacing interim activities into the unchanged component and depressing instrumental responding there (*10, 11*).

We now describe a simple test of this theory using the standard contrast paradigm and an instrumental response, barpressing by rats, that has shown equivocal contrast in previous reports (*2, 5–7*). The key difference between this experiment and others is the explicit manipulation of opportunities for an interim activity (wheel-running) that is incompatible with reinforcement-related (terminal) activity.

Subjects were four male albino rats, approximately 120 days old, maintained on freely available food and 23.5 hours of

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