normal. The hypothesis is supported by Angell (*10*), who found that the circumpolar vortex was expanded in all seasons (displaced toward the equator) during episodes of warm SST's, and Pittock (*12*), who showed that Australian rainfall in all seasons was highly correlated with tropical SST anomalies. In support of this last observation, Angell (*10*) also found that rainfall in the Indian summer monsoon over the period 1868 to 1977 was less than normal during warm tropical SST's. The correlation between tropical SST anomalies and the monsoon rainfall was significant at $P < .01$.

Further examination of the crop yield data strengthens the hypothesis. When the 15 El Niño years (case 1) with below-trend corn yields were analyzed for component climatic factors, it was found that in about half of those years the below-trend yield could have resulted from excessive precipitation during the planting season in one or more major regions of the U.S. Corn Belt, rather than from drought. For example, in 1957, a strong El Niño year, rainfall in the eastern Corn Belt during April and May was more than 200 percent above normal, delaying planting beyond the optimum time and consequently causing lower yields. Note in Fig. 1 that the percentage deviation for corn yield in 1957 is marginally below trend.

In further calculations, we analyzed corn yield separately for many of the corn-producing states to determine whether the outcome would have been different had the dependent variables been the deviation of the corn yield for any one of these states rather than for the United States as a whole. The results show little difference. For the entire United States, 34 El Niño years (case 1) showed yields at or above trend, compared with 38 for Illinois, 36 for Iowa, 34 for Minnesota, 33 for Ohio, and 29 for Indiana. Corn yields of states south of the Corn Belt showed much lower levels of association with El Niño events. The similarity in the results for individual states raises confidence in the overall finding for the United States.

These results suggest a relation between spring and summer temperatures and precipitation in the Corn Belt and El Niño years. Therefore, one of the questions raised by these results concerns the apparent lack of a significant correlation between SST anomalies and the southern oscillation index on the one hand and summer climate in the Corn Belt on the other (*2, 3*). Several explanations might account for these differences. We used a short-term moving average, whereas other researchers have used periods ranging from 25 to 80 years. Thus, fluctuations such as the warm summers of the 1930's would produce very large deviations in their data. In addition, in prior research seasonal data were used. Huff and Neill (*6*) have shown that July temperature and precipitation and June temperatures are among the most important factors in determining corn yield. With these three variables they could account for about 35 percent of the yield variance for the major states of the Corn Belt. Additional variables, such as August temperature and precipitation, did not add significantly to the explained variance. Thus, studies that rely on seasonal data might be insensitive to short-period fluctuations, which seem to have a large effect on the crop outcome.

Finally, the treatment of the data is different in this study. Other researchers have used all the years of data available for their correlations. Our study shows a strong association only for the subset of years that exhibited warm SST's. Table 1 suggests that the other years have no significant bias above or below trend for corn yield. For some recent years with warm SST's, Hanson (*13*) has shown that the westerlies are enhanced and farther south than normal in June, but as yet no coherent data for the whole growing season have been presented to our knowledge.

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Thermodiffusional Transport in Pelagic Clay: Implications for Nuclear Waste Disposal in Geological Media

Abstract. *Thermal gradient experiments in sediment-seawater systems revealed large-scale fluxes of aqueous electrolytic components away from the heat source through thermal diffusion. These findings indicate a need for similar studies in other geological materials of low permeability in order to assess the implications of this phenomenon for various nuclear waste disposal options.*

Many studies of high-level radioactive waste disposal have proposed containment within geological materials of low permeability, on the grounds that these materials can effectively minimize environmental contamination by restricting transport of waste components by fluid convection. Among the options being considered is subseabed disposal within marine pelagic clays (*1*). Desirable features of marine sediments include extremely low permeability and high plasticity, which promotes healing of fractures that may develop during emplacement of waste canisters and thus restricts fluid circulation. The high adsorptive capacity of marine pelagic clay should also inhibit diffusional release of radionuclides.

Table 1. Experimental values of the Soret coefficients.

Element	Soret coefficient (°C^{-1}) Control experiment (673 hours)	Sediment experiment (768 hours)
Chlorine	0.0041	0.0040
Sodium	0.0040	0.0037
Magnesium	0.0046	0.0109
Potassium	0.0043	0.0039
Calcium	0.0048	0.0065

Most studies designed to model the chemical environment in the immediate vicinity (near-field region) of a buried canister containing radioactive waste have been concerned primarily with the effect of temperature on solution-mineral equilibria and adsorption processes. Numerous closed-system, constant-temperature experiments have been performed with solutions and solid forms consistent with various disposal options. The near field, however, will be characterized by distinct thermal gradients, which may significantly influence pore fluid chemistry and chemical transport processes. Thus, to supplement information from constant-temperature experiments with seawater and subseabed sediments (*2*), we have modeled the mass flux in a thermal gradient system, using a titanium-lined pressure vessel designed to provide a stable temperature gradient of 200°C between a "hot" zone (300°C) and a "cool" zone (100°C) over a distance of approximately 30 cm at 600 bars (*3*).

To obtain data on diffusional processes in a thermal gradient in the absence of rock-water interaction, we performed a control experiment with 3-μm alumina as an inert matrix and sulfate-free artificial seawater (*4*). Analysis of fluid samples from the hot and cool zones indicate that substantial concentration gradients developed within the first 100 hours (Fig. 1a), with enrichment of sodium, chlorine, potassium, calcium, and magnesium in the cool zone and corresponding depletion of these components in the hot zone. The data obtained thus indicate that thermodiffusional transport (the so-called Soret effect) produced a large-scale flux of solute components down the thermal gradient. Steady-state conditions were obtained after about 600 hours, at which time the ionic strength of the hot zone was reduced to approximately half that of the cool zone. The oxidation of trace amounts of dissolved organic matter by dissolved oxygen generated a slightly lower *p*H and higher dissolved CO_2 content in the hot zone than in the cool zone.

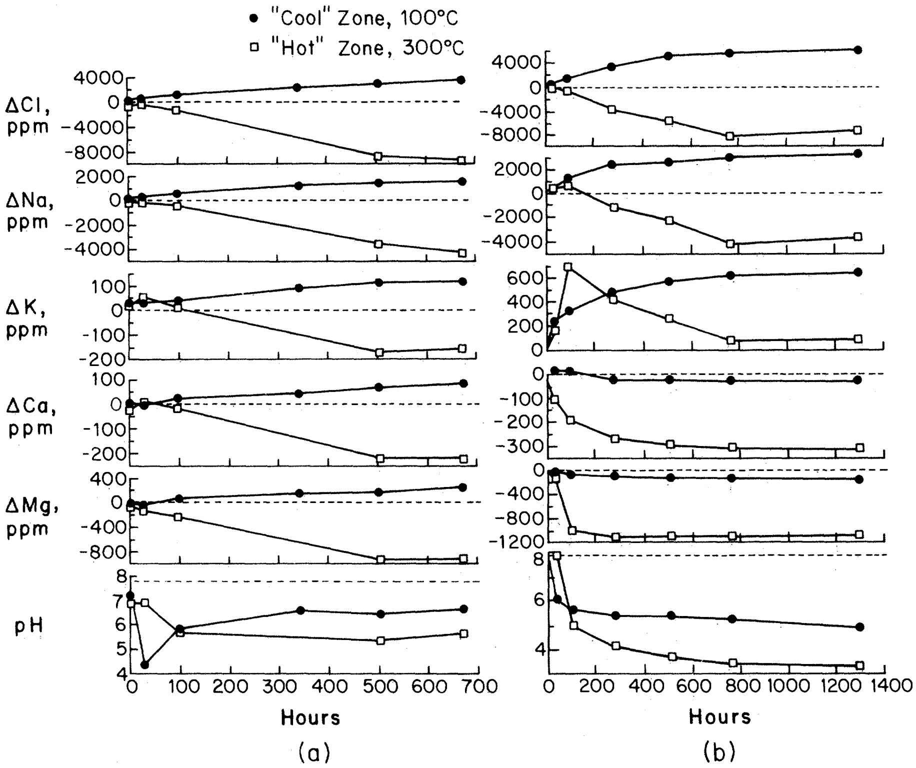

Fig. 1. Change in relative fluid composition with time of hot and cool zones of (a) control and (b) sediment thermal gradient experiments.

In addition to thermal diffusion, pore fluid chemistry is dependent on rock-water interaction. Thus, we performed an additional experiment with marine pelagic clay and seawater (*4*). The thermal gradient maintained was similar to that in the control experiment.

Aqueous concentrations of chlorine, sodium, magnesium, and calcium from the sediment experiment were depleted greatly in the hot zone (Fig. 1b) compared to both seawater and the fluid of the cool zone. Magnesium and calcium were removed from solution largely through smectite and anhydrite precipitation, respectively, and sodium and chlorine depletions resulted from thermal diffusion. Potassium increased rapidly in the hot-zone fluids owing to illite dissolution and was transported to the cool zone by thermal diffusion. Rapid transfer of silica to the cool zone was also noted early in the experiment and undoubtedly inhibited smectite formation in the hot zone during the first 100 hours. Thus, silica diffusion down the thermal gradient in response to thermal and concentration gradients permitted hot-zone fluids to remain initially at a *p*H near that of unreacted seawater. However, because of the limited extent to which irreversible migration of silica can occur, the concentrations of these species in solution subsequently increased in hot-zone fluids, smectite formation accelerated, and *p*H decreased dramatically.

Fluid chemistry from the experiments may be used to compare the relative magnitude of the Soret and rock-water interaction effects. The total flux of solute in a system is the algebraic sum of the flux due to chemical gradients (chemical or Fickian diffusion), the flux produced by thermal diffusion, and a flux resulting from chemical exchange during rock-water interaction:

$$F = -D\left(\frac{dC}{dz} + sC\frac{dT}{dz}\right) + R \qquad (1)$$

where F is the net flux of a solute component, D is the coefficient of chemical diffusion, s is the ratio of the coefficient of thermal diffusion to the coefficient of chemical diffusion, C is the concentration of a solute component, T is temperature, z is distance, and R is the component of flux attributed to rock-water interaction (*5*). The symbol s ($°C^{-1}$) is called the Soret coefficient and is defined as a positive quantity by Eq. 1.

If a system is at steady state and $R \sim 0$, the fluxes generated by thermal and chemical diffusion will be balanced and the net flux will be zero. Thus, Eq. 1 will become

$$s = -\frac{1}{C}\frac{dC}{dT} \qquad (2)$$

Rearranging this expression and integrating over the limits of concentration and temperature, we find that

$$\Delta \ln C = -s\,\Delta T \qquad (3)$$

Values of the Soret coefficient for chlorine, sodium, magnesium, potassium, and calcium computed for the two experiments from Eq. 3 are presented in Table 1. The values from the control experiment may be regarded as "pure" values since rock-water interaction was not involved, while the values from the sediment experiment are "apparent" because of a flux contribution associated with rock-water interaction (that is, $R \neq 0$ in Eq. 1). Thus, comparison of these values permits an assessment of the extent to which rock-water interaction contributed to the net flux in the sediment experiment.

The Soret coefficients of sodium and chlorine for the two experiments are similar, suggesting that these elements were fractionated between the hot and cool zones primarily by thermal diffusion and were involved only to a minimal extent in rock-water interaction in the sediment experiment. Potassium was released from the sediment to hot-zone fluid during sediment-seawater interaction (Fig. 1b) and subsequently migrated toward the cool zone by chemical and thermal diffusion. The similarity of the potassium Soret coefficients in Table 1 indicates that contribution of potassium through rock-water interaction in the sediment experiment had ceased by 768 hours and the component had been redistributed between the zones. The large apparent Soret coefficients of magnesium and calcium from the sediment experiment relative to the pure values from the control experiment may be attributed to continuous depletion of these elements in the hot zone of the sediment experiment. This is consistent with observed formation of clay and anhydrite alteration phases.

Results of the hydrothermal experiments show that the fluid chemistry in the vicinity of a heat source in pelagic clay or other geological media of low permeability will be influenced by a combination of rock-water interaction and diffusional effects. In particular, a thermal gradient in this environment indicates thermal diffusion which results in large-scale and relatively rapid fluxes of aqueous components from the hot zone toward the cool zone. This "unmixing" serves to decrease the ionic strength in the hot zone by removing a large proportion of sodium and chlorine and may inhibit development of acidity in the near-field region through the removal of silica. The effect on rates of canister corrosion and radionuclide transport requires further evaluation. Magnesium, calcium, potassium, and sulfate, as well as a variety of minor elements, show a strong tendency to participate in temperature-dependent rock-water interaction processes as well as thermal diffusion. The extent to which this occurs depends greatly on the initial rock or sediment composition, solution chemistry, and time. Assessment of these processes is critical for modeling of the near-field chemical environment and mass transport from the near to the far field. The role of thermal diffusion, in particular, must be thoroughly evaluated in any program involving the disposal of high-level radioactive waste in geological media of low permeability.

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6. Supported by Sandia National Laboratories under contracts SANDIA 74-1158 and SANDIA 16-3105. We thank L. H. Brush, D. R. Janecky, and R. E. McDuff for advice during manuscript preparation. R. L. Knoche assisted in fluid analysis. This is publication 1055 of the School of Earth Sciences, Department of Geology and Geophysics, University of Minnesota, Minneapolis 55455.

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The Tunguska Explosion of 1908: Discovery of Meteoritic Debris near the Explosion Site and at the South Pole

Abstract. *Submillimeter-sized metallic spheres extracted from soil in the Tunguska region of central Siberia contain noble metals in cosmic proportions. The trace element composition and geographical distribution of these spheres suggest that they are from the 30 June 1908 Tunguska explosion and not meteoritic ablation products falling continuously on the earth. Debris from this explosion was also discovered in a South Pole ice core; this discovery indicates that the Tunguska object exploded in the atmosphere with subsequent stratospheric injection and transport of the debris. The celestial body that exploded over Tunguska weighed more than 7 million tons, was more than 0.16 kilometer in diameter, and may well have been a stony meteorite. This discovery offers a new precision time marker in polar ice strata for the year 1909. The steady-state influx of cosmic matter at the South Pole is estimated to be* 1.8×10^{-8} *grams per square centimeter per year, which corresponds to a global influx of* 4×10^5 *tons per year.*

On 30 June 1908 at 7:17 a.m. local time (12:17 U.T.), a great explosion occurred in the sky over the basin of River Podkamennaya Tunguska in central Siberia (60°55′N, 101°57′E). Since then, many expeditions have been undertaken to the site and many books and reports published (*1–5*). No crater has ever been discovered during any of these expeditions, a mystery that has generated considerable speculation. The explosion was enormous. It was observed over a radius of 600 to 1000 km in central Siberia, sunlight reflected from the debris lit up the night sky for several days over Europe and western Asia, and trees were blown down over an area of several hundred square kilometers near the epicenter. Because of the lack of obvious clues expected from the impact of a celestial body (an impact crater or identifiable meteorite fragments), various explanations for the origin of the explosion have been proposed.

Careful, painstaking fieldwork by Soviet scientists eventually uncovered some important clues. Soil samples from several areas were subjected to density and magnetic separations and were found to contain black and shiny microscopic metallic spheres (*1, 2*). When scientists examined the geographical distribution of the spheres, they noticed an increasing concentration of spheres northwest of the epicenter (1, 14, and 33 spheres per unit area at 25, 40, and 70 km, respectively), whereas the concentration in the southeast direction was 7, 3, and 10 per unit area (*3*). They concluded that the Tunguska object exploded in midair and that the metallic spheres were carried by the prevailing wind, producing the observed distribution. [The wind direction of the day was from southeast to northwest (*1, 2*)].

I have examined eight of these spheres by high-sensitivity neutron activation analysis with an intent to answer the following questions: Are they truly extraterrestrial? Are all the spheres related to each other as would be expected if they originated from the 1908 explosion? Can these spheres be distinguished from the normal cosmic ablation products of iron meteoroids? (*6*). The abundances of all the elements measured in these spheres are shown in Table 1. Iridium, a reliable indicator of extraterrestrial matter, is unmistakably enriched in all eight spheres. In addition, they all contain nickel and cobalt, two other "metal-loving" elements always found with iridium in cosmic matter. Five of the eight spheres have lower and similar concentrations of iridium, nickel, and cobalt; three are characterized by very high concentrations of these elements. The iridium content of sphere H is 56,900 parts per billion (ppb) [only one iron meteorite is known with a comparable iridium content (Negrillos meteorite with 45,000 ppb iridium and 5.32 percent nickel (*7*))]. The average Ni/Ir ratio (by weight) in the first six spheres listed in Table 1 is identical to the cosmic ratio, 2.0×10^4 (Fig. 1). For the last two spheres the Ni/Ir ratio is