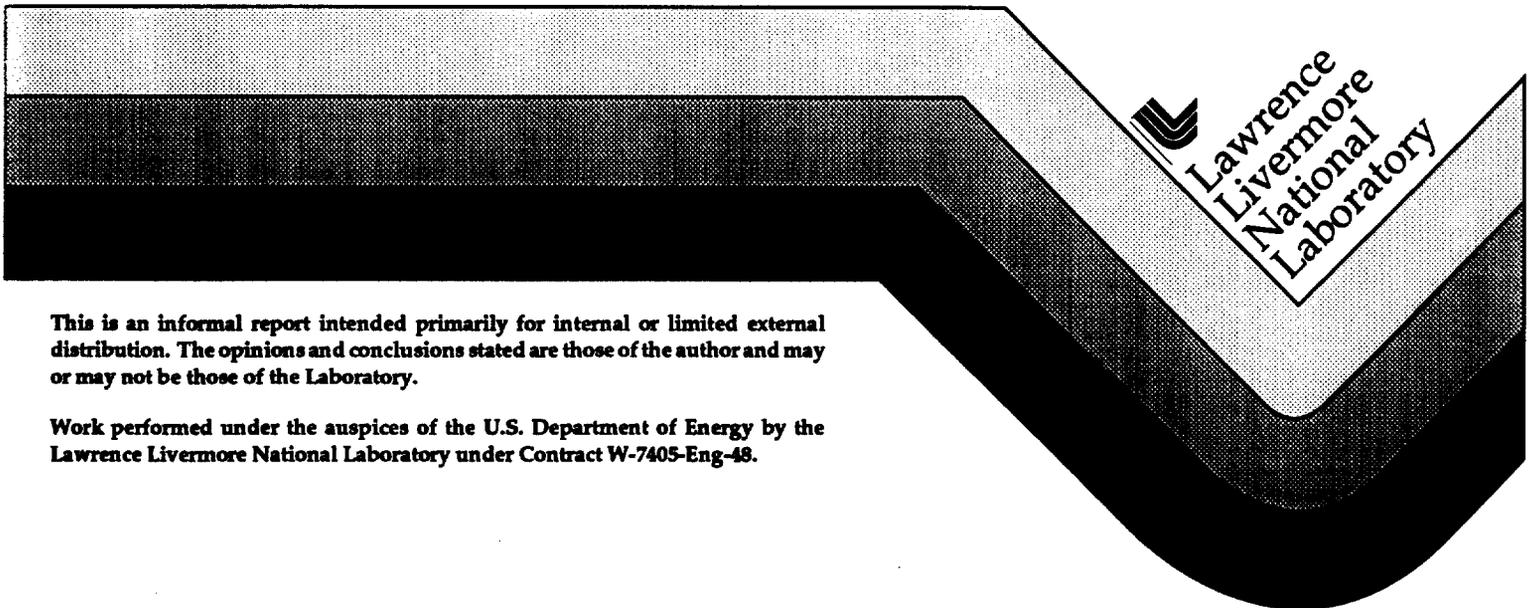


## Volatile and Fluid Transport in Deep, Arid Soils

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**Volatile and Fluid Transport in Deep, Arid Soils**

***FY97 LDRD Final Report***

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## **Introduction**

The legacy of nearly five-decades of rapid industrialization throughout the Southwest includes sites where volatile contaminants have been accidentally or intentionally released at or immediately below the surface. Understanding the mechanism and rate of volatile transport through the vadose zone is important to assessing the potential impact on groundwater resources. This is particularly significant in arid environments where the unsaturated (vadose) zone above the water table may be more than 300 m thick. While numerical models have been developed to predict the movement of volatiles through the unsaturated zone, there are only limited opportunities to verify predictions against field data. Field measurements of vadose zone transport are important in terms of constraining model parameters and can be applied to a variety of contaminant issues. This includes the ability to monitor and detect deep underground explosions in violation of nuclear test ban treaties.

We have investigated the movement of vadose zone gases in a deep alluvial basin at the Nevada Test Site. The opportunity to study the migration of soil gases in this setting is unique due to the access afforded by the Joint Test Organization's U-1a tunnel complex, mined at a depth of approximately 300 m below ground surface in the alluvium of Yucca Flat (Allen, 1995; Allen, 1996). The tunnel complex is more than 180 m above the standing water level (Figure 1). In this portion of Yucca Flat the alluvium is poorly sorted and consists of channel cut and overbank deposits that contain a mixture of Tertiary volcanic and pre-Tertiary sedimentary detritus locally derived from nearby volcanic and sedimentary sources. The porosity of the alluvium ranges from 31 to 35%. Although high angle faults dissect other portions of Yucca Flat, there are no surface expressions of faults in the immediate vicinity of the U-1a tunnel complex.

During mining of the tunnel we emplaced stainless steel sampling tubes approximately 30 m into the formation to allow discrete sampling of soil gases as well as continuous monitoring of gas pressure. The tubes were emplaced such that there was no exchange between the air ventilated through the tunnel and the soil gas; sealants applied to the walls maintained pressure differences between the tunnel air and the formation gas. Similar sampling tubes were also inserted in 10 m deep holes bored vertically from the surface over the tunnel complex.

Continuous monitoring of gas pressure and  $^{222}\text{Rn}$  concentrations in the formation was used to assess the effect of barometric pressure on the movement of the soil gas. Analyses of bulk ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ) and noble (He, Ne, Ar, Kr, Xe) gas compositions and  $^{14}\text{C}$  activities permitted a comparison between soil-gas and atmospheric compositions. In addition carbonate veins and void fillings exposed during mining were sampled for petrographic analysis and measurement of oxygen and carbon stable isotope ratios to determine the origin of the fluids from which these deposits precipitated.

## Gas Movement

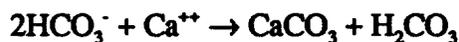
The barometric pressure of the soil gas measured in the formation at the tunnel level exhibits cyclic fluctuations that correspond to changes in surface barometric pressure. High pressure winter-time atmospheric instability is clearly observed in barometric fluctuations of surface and formation pressure. There is less than 0.5 day lag between the arrival of atmospheric pressure fronts and corresponding changes in deep formation gas pressure. The difference in pressure between measurements at ground surface and those made at tunnel depth can be modeled by the use of a hydrostatic equation.  $^{222}\text{Rn}$  concentrations monitored inside the tunnel similarly display cyclic variations that correlate to changes in barometric pressure, but which are opposite in magnitude. A time series plot

of both the  $^{222}\text{Rn}$  concentration and the formation barometric pressure is shown in Figure 2. As the barometric pressure in the formation decreases,  $^{222}\text{Rn}$  in the formation migrates from the formation into the tunnel. Cyclic variations in barometric pressure result in gases being drawn out of permeable geologic media during periods of lower atmospheric pressure and air being forced into the same media during periods of higher atmospheric pressure. This phenomenon is referred to as barometric or atmospheric pumping. These data provide unique confirmation of the ability of formation gases to be "pumped" (concentrated or dispersed) by this process. Weather-related variations in soil-gas radon concentrations have been reported for shallow soil profiles (Clements and Wilkening, 1974; Schumann et al., 1992). Atmospheric pumping has also been invoked to explain the vertical transport of gases away from the site of buried explosions in fractured media (Nilson et al., 1991; Carrigan et al., 1996) and observed fluctuations of water levels in wells constructed in deep unconfined aquifers including those at the Nevada Test Site (Weeks, 1979).

Soil gas compositions collected from alluvium at the level of the tunnel are distinct from atmospheric compositions. While the composition of the soil gas mimics normal air concentrations for  $\text{N}_2$ ,  $\text{O}_2$ , and Ar, soil gas  $\text{CO}_2$  is enriched ~ 500% over normal air concentrations. Soil gas  $\text{CO}_2$  samples were analyzed for their  $^{14}\text{C}$  activities which are reported as percent modern (pre-fallout) carbon (pmc). The  $^{14}\text{C}$  activities of two different samples of the soil-gas are 9 and 11 pmc. By contrast, the  $^{14}\text{C}$  activity in the air ventilated through the tunnel is 107 pmc. The deep formation gases also exhibit > 5% enrichment in the heavy noble gases (Kr, Xe) relative to normal air compositions with little enrichment in the light noble gases ( $^4\text{He}$ , Ne, Ar) (Figure 3).  $^{222}\text{Rn}$  concentrations in the soil gas are approximately 500 pCi/L. Since  $^{222}\text{Rn}$  is produced by  $\alpha$ -decay of  $^{238}\text{U}$  incorporated in the volcanic sediments, the lack of a significant  $^4\text{He}$  excess is notable. Soil gas measured from the stations above the tunnel complex is also enriched in  $\text{CO}_2$  although the concentrations

are approximately one half of those observed deeper in the formation.  $^{14}\text{C}$  activities of the soil gas from the two 10m deep stations are 66 and 62 pmc.

The response of soil gases to changes in barometric pressure in the U-1a complex indicates that formation gases can be concentrated or dispersed at considerable depth in alluvium by atmospheric pumping despite the absence of fractures or faults which might provide a preferential transport path. Changes in formation pressure and  $^{222}\text{Rn}$  concentration at a depth of 300 m below the surface of Yucca Flat indicate the unsaturated zone is a dynamic reservoir for soil gas that rapidly responds to changes in barometric pressure.  $^{14}\text{C}$  activities of approximately 10 pmc correspond to apparent  $^{14}\text{C}$  ages of >15,000 years and imply the soil gas does not readily exchange with the atmosphere. Enriched heavy noble gas and depleted  $^{14}\text{C}$  abundances in the soil gas deep the basin may be the result of fractionation of a static gas body that has not mixed with an atmospheric gas reservoir. However because soil gas concentrations and  $^{14}\text{C}$  abundances mimic those of present day Yucca Flat groundwaters collected from wells north of the U-1a complex, sub-surface transport in arid environments more likely involves the upward flux of gas exsolved from deeper waters. One possible mechanism for generating high  $\text{CO}_2$  concentrations at depth is the precipitation of calcite from groundwaters. Precipitation reactions liberate  $\text{CO}_2$  gas:



Lower  $\text{CO}_2$  concentrations and higher  $^{14}\text{C}$  activities in the shallow 10 m boreholes above the tunnel complex is likely due to dispersion of the groundwater-derived soil gas signature near the surface.

## Fluid Movement

Secondary calcite is abundant within the alluvial sequence. In particular euhedral calcite spar occurs as fracture fillings and void coatings within the alluvium. Petrographic and stable isotope analysis of calcite suggests that carbonate-rich fluids dissolved in groundwater precipitated into void spaces in the alluvium. These observations confirm stratigraphic interpretations (Drellack et al., 1989). The sparry calcite shows textural evidence of repeated dissolution and re-precipitation. However, the  $^{14}\text{C}$  activity of the last crystallized calcite spar is 0 pmc. The oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and carbon ( $^{13}\text{C}/^{12}\text{C}$ ) stable isotope ratios of U-1a calcites are plotted in Figure 4. The isotope ratios are reported in conventional delta ( $\delta$ ) notation as permil deviations from SMOW (oxygen) and PDB (carbon) reference standards. The calculated isotopic composition of calcite in equilibrium with an average present-day Yucca Flat groundwater at 30°C is shown for comparison. The carbon isotopic ( $\delta^{13}\text{C}$ ) composition predicted for calcite in equilibrium with Yucca Flat groundwaters is consistent with the range of variation in the natural samples. This suggests a common source of carbon in both the calcites and the Yucca Flat groundwaters. In contrast, the oxygen isotope ( $\delta^{18}\text{O}$ ) compositions of the U-1a calcites are all higher in  $\delta^{18}\text{O}$  than the predicted equilibrium composition and suggests the U-1a calcites precipitated from water that was higher in  $\delta^{18}\text{O}$  than Yucca Flat groundwaters. This type of enrichment occurs naturally when waters undergo evaporation. At the same time, the concentration of dissolved solids will gradually increase and eventually reach saturation with respect to calcite. The range in  $\delta^{18}\text{O}$  values of the U-1a calcites likely reflects the relative amount of open-system evaporation of the water from which the calcite precipitated. Evidence of distinct and repeated dissolution and precipitation of calcite, the enrichment in carbonate  $^{18}\text{O}$  signatures, and the absence of  $^{14}\text{C}$  activity in last crystallized phases suggests that groundwaters which flowed into Yucca Flat after the deposition of the alluvium repeatedly precipitated calcite during higher stands of the water table more than ~ 40,000 years ago.

Groundwater  $\text{HCO}_3$  concentrations in the Halfpint Range immediately to the east of Yucca Flat are in excess of 800 mg/L (Rose et al. 1997) and may be a source for some of this water (Kenneally, 1996).

## Conclusions

The U-1a tunnel provides unprecedented access to the vadose zone to study fluid and gas transport as analogs of volatile contaminant species. Data on gas pressure and composition indicates that, despite the absence of fractures and other means for a "fast path" to the surface, the vadose zone is a dynamic environment that responds rapidly to fluctuations in barometric pressure while retaining a gas composition that is incompletely exchanged with the atmosphere. The aridity of the soil facilitates gas movement; because soil moisture does not block pores in the soil, gas permeability is not attenuated (Schumann et al., 1992). The present measurements confirm the ability of formation gases to be "pumped" (concentrated or dispersed) at depth by changes in barometric pressure. Differences in  $\text{PCO}_2$  at the water table and  $\text{PCO}_2$  at the surface drive an upwards diffusive flux of gas exsolved from these waters. This flux is clearly seen in Figure 5 which plots of  $\text{CO}_2$  concentrations in the soil gas versus formation depth. The flux of  $\text{CO}_2$  from the deeper groundwater to the soil gas is ~ 7000 times greater than the flux of xenon. Enrichments in heavy noble gas compositions (relative to air) and with little enrichment of  $^4\text{He}$  at the tunnel level allows for gravitational settling of the noble gases. Severinghaus et al. (1996) discuss the effect of gravitational, thermal diffusion, and water vapor flux fractionation effects on noble gas concentration profiles in soil; the present data suggests that gravitational settling may be important in fractionating noble gases in deep unsaturated zones. Evidence for the movement of fluids through the vadose zone is provided by secondary carbonate minerals which may be related isotopically to precipitation of bicarbonate rich groundwater which

flows into Yucca Flat. Together these data suggest that the movement of fluids and gases may occur within deep, arid, and structurally undisturbed sedimentary basins.

### **Acknowledgments**

The cooperation of Los Alamos National Laboratory in arranging access to the U-1a / Lyner complex early in 1995 and in drilling holes for soil gas sampling made this project possible. In particular, we are indebted to Karl Hahn for all his interest in and support of this work. The assistance of Brian Allen of Bechtel-Nevada in the identification and collection of calcite throughout the U-1a complex is acknowledged. Don Jackson of Bechtel-Nevada fielded the  $^{222}\text{Rn}$  detector and pressure transducers as well as collected all gas samples.

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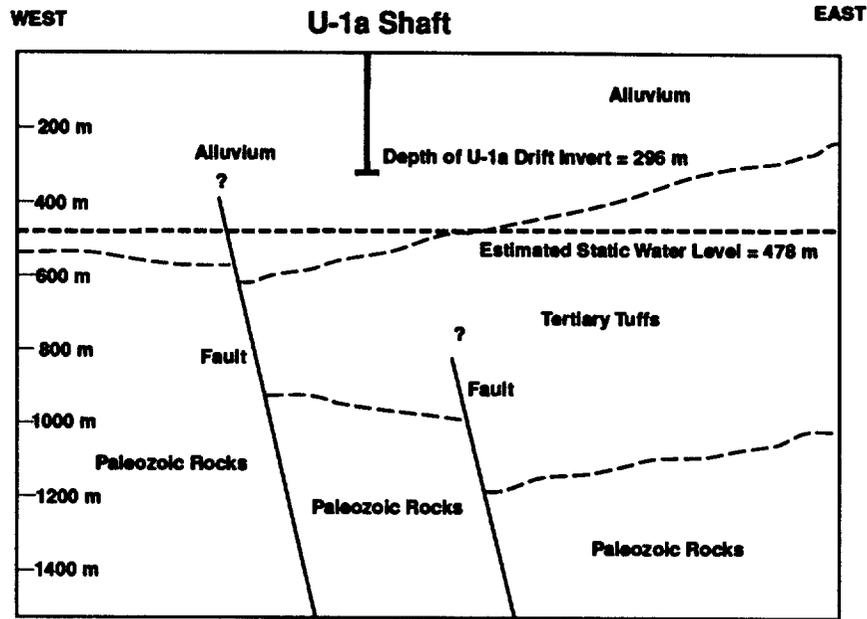


Figure 1. West-east geologic cross-section looking north along Yucca Flat. The U-1a tunnel complex is mined at depth of 296 m in the alluvium. The tunnel floor is 182 m above the estimated static water level.

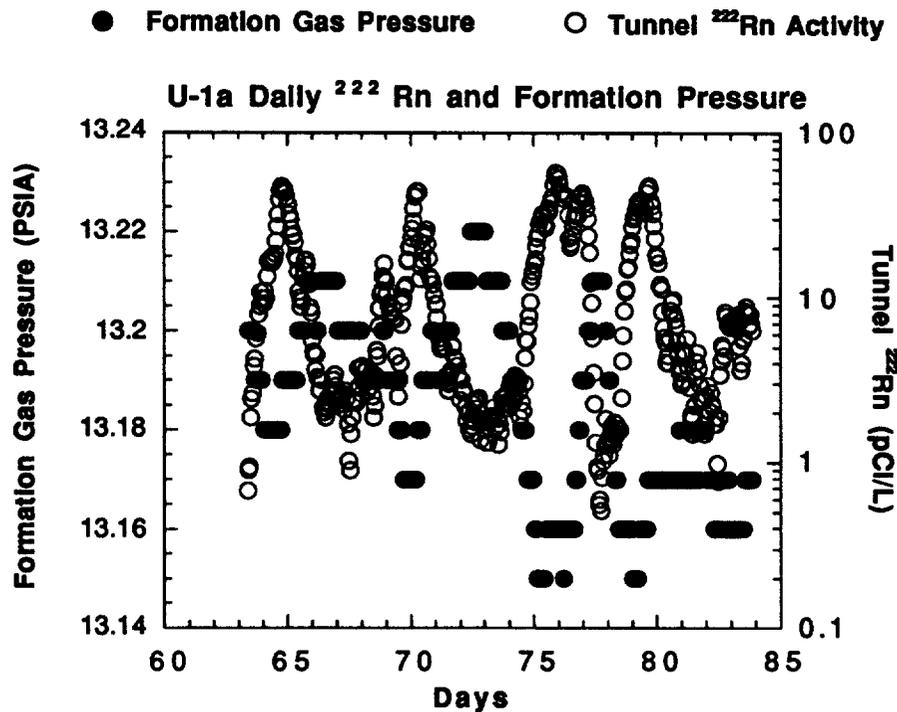


Figure 2. Time series cyclic fluctuations of formation barometric pressure and  $^{222}\text{Rn}$  concentration measured in the U-1a tunnel complex located beneath Yucca Flat at the Nevada Test Site.

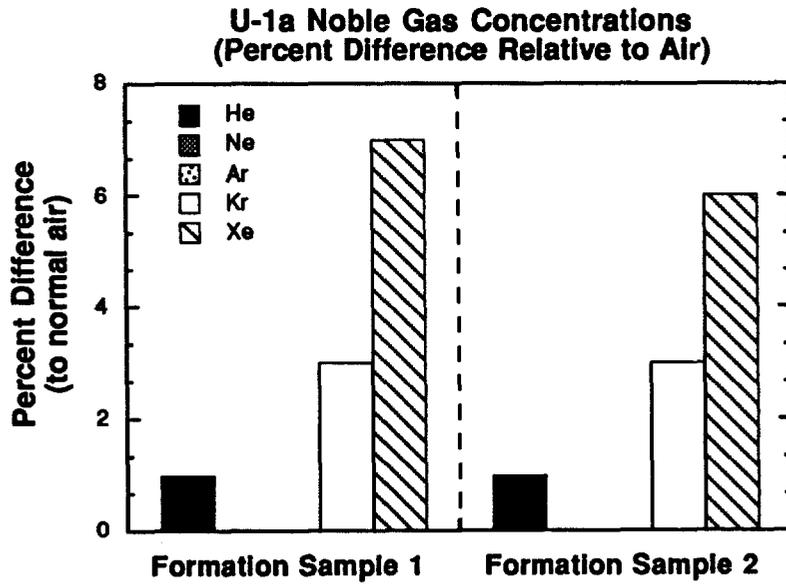


Figure 3. Noble gas composition of soil gas collected from alluvium in the U-1a tunnel complex. Note enrichments in heavy noble gases relative to normal air; these enrichments follow solubilities of noble gas concentrations in adjacent deeper groundwaters.

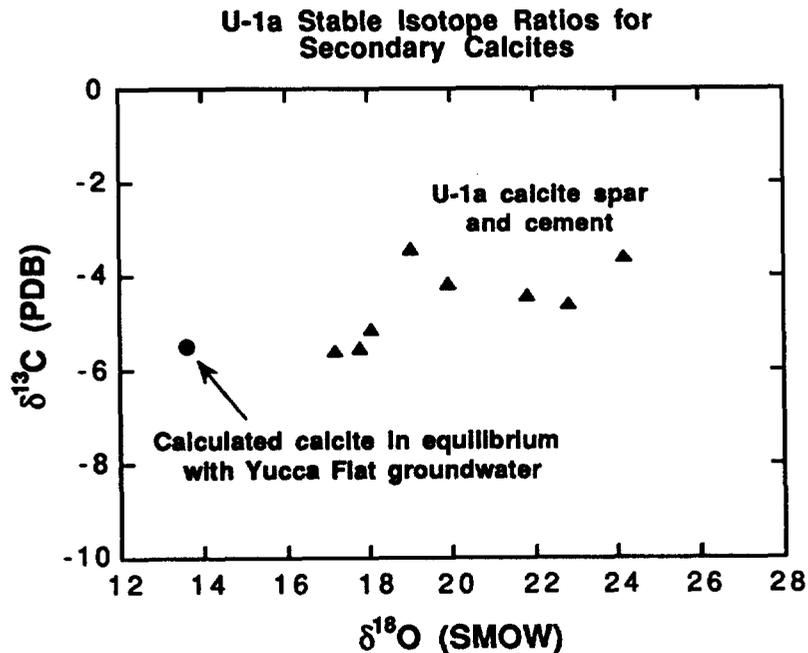


Figure 4. Oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and carbon ( $^{13}\text{C}/^{12}\text{C}$ ) stable isotope ratios of U-1a secondary calcites. The calculated isotopic composition of calcite in equilibrium with an average present-day Yucca Flat groundwater at 30°C is shown for comparison.

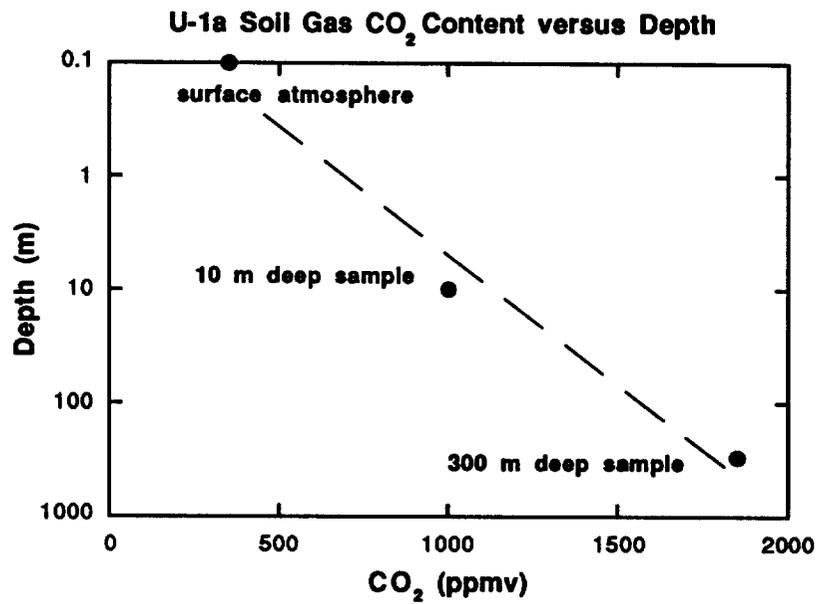


Figure 5. CO<sub>2</sub> content in U-1a soil gas samples plotted versus formation depth. Best fit line emphasizes upwards diffusive flux of concentrated CO<sub>2</sub> derived from deeper groundwaters towards lower concentrations at the surface.