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[EA]Evidence for Microseepage in CO_2-EOR Monitoring and Verification*

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Abstract

A summary review of gas flux and soil gas measurements is presented for an operational CO_2-EOR project at Rangely, Colorado, and for a proposed CO_2-EOR project at Teapot Dome, Wyoming. A critical review of geochemical data from a small area of alleged leakage at a farm over the Weyburn Field in Saskatchewan, Canada is also reviewed. This work demonstrates the importance of measurement of CH_4, as well as CO_2, because of the subsurface mobility of CH_4. Considering the greenhouse warming potential of CH_4 and the probable increase in CO_2-EOR, relative to pure CO_2 sequestration for the near- to mid-term, increases the relevance of CH_4.

Direct measurement of fluxes is necessary to determine the potential transport of gases to the atmosphere, with methods proposed by various authors for shallow subsurface-, surface-, and above the land surface. Monitoring may be by chemical measurement of gases, verification by isotopic determinations, and accounting by direct measurement or estimation of gas exchange at the surface.

Introduction

The postulated role of trace gases in climate change have focused on CO_2 and to a lesser extent on CH_4. Methane has a more potent "greenhouse-warming-potential" (GWP) than CO_2 when considered on a molecule-to-molecule basis. The atmospheric concentration of CO_2 is approximately 400 ppmv, and clearly rising. The atmospheric concentration of CH_4 is approximately 1.9 ppmv, probably rising, and because of methane's potency is also considered important by those with technical knowledge.

Direct removal of CO_2 from the atmosphere is considered less practical than preventing release to the atmosphere. Collection (capture) at large sources is more viable but poses a problem in what to do with the large amounts of CO_2, considering there are limited reuses. Geologic sequestration has generally been considered a good option, but the costs are high with no direct economic return. Use of CO_2 in CO_2-EOR has a

direct economic benefit, though continues the production of petroleum and natural gas from depleted fields, partially offsetting the goal of complete sequestration.

The concerns over geologic storage are potential for leakage from a deep reservoir into shallow groundwater, or into the atmosphere. These concerns determine the necessity for Monitoring, Verification, and Accounting (MVA) of potential for leakage from a deep reservoir. Those familiar with microseepage will find MVA to be an extension of microseepage applied to oil and gas exploration. Although CO_2 is being injected, CH_4 is also important for several reasons; CO_2 is soluble in, and reactive with water; CH_4 is not soluble, nor reactive, being stable in the subsurface; CH_4 is ubiquitous in the current CO_2-EOR option; CH_4 is a more mobile molecule when overpressured; and the GWP of CH_4 is greater. At the present time, many MVA practitioners have not recognized the importance of CH_4, possibly not recognizing the above physical and chemical characteristics.

There are problems in reliable monitoring and verification research. Reservoirs are large, relatively open systems with large amounts of fluids being injected and removed, and where “equilibrium” is only approximated. There is systematic seasonal variation in surface measurements because of soil microbiology in producing/consuming carbon-containing compounds. One is searching for a small, deep-sourced signal in the presence of substantial near-surface noise. The best chance of detecting a deep-sourced signal is when the surface noise is minimal, normally winter or the dry season, necessitating an understanding of local climate. Winter-time measurements in some locations can be physically and mentally demanding.

This research summarizes work in the MVA field by the author in a transition retirement, primarily at two locations: Rangely, Colorado, USA and Teapot Dome, Wyoming, USA. Early work was done at a Test Site in central Colorado. Some minor work was done at the South Liberty salt dome, Texas, USA, and a requested critical review of others’ work at Weyburn, Saskatchewan, Canada (Figure 1).

Abbreviated Methods

If one is to determine gas flow across the earth-atmosphere interface, flux chamber or accumulation chamber methods are one approach. Open-air measurements are another method, particularly eddy covariance (EC). Flux measurements with a chamber are direct, and EC fluxes are calculated with measurements of gas concentration and three-dimensional air flows using a sonic anemometer. An important consideration in the detection of a subtle signal from the subsurface is elevation of measurement and significant dilution must be recognized when using above ground measurements.

The flux measurement is more elaborate and not normally used in exploration but can also supplement free-soil gas methods. The open-air measurement integrates the estimated flux over a substantial distance in the upwind direction, but the dilution limitation is quite real. Flux chamber and soil gas methods are measuring over a very limited area, possibly representing a limited volume. Commercial flux chambers are now available using IR measurement and Cavity Enhanced Absorption Spectrometry (CEAS) which can replace gas chromatographic measurements. The commercial chambers are generally much smaller in area than those used by this author in 2000-2005, but more portable.

Methods and results are detailed in four refereed publications for Rangely, and three refereed publications on Teapot Dome. A summary publication with an environmental orientation is Klusman (2011) and a summary publication with a geologic perspective is Klusman (2015). These also contain the reference to the earlier cited publications for both Rangely and Teapot Dome. An invited publication focused on the importance of faults as pathways for seepage of gases (Klusman, 2018).

Results and Discussion

A limited number of figures will be presented from Rangely and Teapot Dome to illustrate specific points. Figure 2 illustrates the differences and similarities between on-field and control area measurements. Obviously, not all locations on an overpressured field are anomalous. Also, methanotrophic oxidation can result in negative fluxes, even in winter when methanotrophs can operate below a frost line. In this case, the CH_4 being oxidized is being drawn from the atmosphere, as there is negligible flux from depth. One could argue that the sampling density was barely adequate to allow the differentiation.

Figure 3 shows CO_2 concentrations and $\delta^{13}C$ of CO_2 in 10-m holes for an anomalous location and a non-anomalous location. Concentration measurements alone are not adequate to rely on this separation, although summer concentrations are higher, but variable, than the concentrations in winter. In summer, the isotopic shift is similar to that observed for oxidation of organic matter in the soils. If there is no deep source of carbon-containing gas (Figure 3d), the summer and winter values are similar. If the CO_2 is from methanotrophic oxidation of a deep source of CH_4, (Figure 3b) there is an isotopic shift.

Figure 4 shows the $\delta^{13}C$ of CH_4 for 10-m holes in an anomalous and non-anomalous location at Rangely. The original thought prior to the study was that methanotrophic oxidation of CH_4 was likely to be first-order, dependent only on the concentration of CH_4 in the unsaturated zone. The curvature in Figure 4a and Figure 4b demonstrate that methanotrophy is also dependent on downward diffusion of O_2 from the atmosphere, making the reaction 2^{nd} order. The curvature is greater for the summer, showing a higher rate of oxidation than in the winter, suggesting an even higher order reaction, related to soil temperature. Note that the maximum rate of oxidation is at approximately 5 meters depth in this climate.

In the case of the non-anomalous location in Figure 4c and Figure 4d, methanotropy of CH_4 from depth is not evident, only a slight isotopic enrichment with increasing depth. This suggests a very low rate of oxidation of downward diffusing CH_4 and O_2, both derived from the atmosphere.

Very large gradients in CH_4 and light hydrocarbon concentrations were observed in anomalous locations and Teapot Dome. In addition to simple plots of concentration vs. depth, a more elegant method that incorporates isotopes can be used to visualize and understand biogeochemical processes (Figure 5). Figure 5 is an Arrhenius-type plot with $\delta^{13}C$ of CH_4 on the Y-axis and natural log of $(1/CH_4)$ on the X-axis. The atmospheric science community has also used this for CO_2 and labeled it a Keeling plot. There is a near-horizontal line in Figure 5a connecting the reservoir $\delta^{13}C$ and concentration to the atmospheric δ13C and concentration (mixing line). Mixing various proportions of these two end-members with no extraneous modifications will follow this line. External processes can be discovered by deviation from this line. In Figure 5a, methanotrophic oxidation will shift the isotopic composition upward and to the right (lower concentration). The atmospheric

composition is the vertical line near the right side of Figure 5a. Methanotrophic oxidation of the low CH_4 in the atmosphere will shift the concentration to even lower values to the right and off scale. Methanogenesis shifts the isotopic ratio for carbon to lighter or depleted values and increases the concentration. There is a field low and to the left of the methanogenesis field which would represent both compositional and isotopic fractionation due to physical processes only.

Figure 5b shows the same plot with increased color transparency and the five 10-m hole locations plotted. The near-horizontal line is between the reservoir (Low-Temperature-Gas-Separation Plant, LTS) and the atmosphere. The anomalous locations 06, 17, 18 and the depth are shown. Most of these locations and depths plot in the field of active methanotrophy. Measured concentrations and isotopic shifts at Location 17 and depths of 5-, and 10-m plot below the mixing line on Figure 5b. During drilling of the 10-m hole at Location 17, increased resistance from the formation of $CaCO_3$ was noted. This effectively sealed the upper part of the profile, restricting downward diffusion of O_2. The normally less efficient process of fractionation with vertical transport is then evident for 17-5 and 17-10.

The non-anomalous locations 02 and 19 cluster near the intersection of the mixing line and the atmospheric concentration and are not visible individually. This is to be expected for data that are at or near background, and without chemical and microbiological processes evident. It is apparent that addition of stable carbon isotopic measurements has strengthened the case for recognition of microseepage at Rangely and Teapot Dome. This moves the process into verification.

The final and strongest parameter for verification used at Rangely and Teapot Dome was the measurement of carbon-14 in the soil gas of the 10-m holes. Soil gas was collected from the 10-m holes at each depth, plus three samples of the open atmosphere. This was done with larger volume, pre-evacuated containers. Since methanotrophic oxidation was occurring, the CO_2 in soil gas would serve as effectively as determining the radiocarbon age of CH_4. The CO_2 was cryogenically separated and purified on a vacuum line, and the C-14 content determined by Accelerator Mass Spectrometry (AMS). The data are returned as either % modern carbon or fraction of modern carbon, from which the radiocarbon age can be calculated.

Figure 6 shows the depth vs. fraction modern carbon (and calculated radiocarbon age) for the 10-m holes at Teapot Dome. It is clear that the 10-m holes 06, 17, and 18 had “ancient” carbon at depths >3-m. This provides the strongest verification of seepage of reservoir hydrocarbons. The non-anomalous locations 02 and 19 show ages of a few hundred years at 10-m, consistent with slow decay of humic materials not related to seepage. Not shown are the C-14 data for Rangely, though the results were similar. Interestingly, the summer and winter radiocarbon data at Rangely were similar, indicating the diminishing importance of seasonality of microbial processes at depths of 5- and 10-m.

A start on accounting of the CO_2 and CH_4 seepage from the Rangely Field to the atmosphere was made. The gross CH_4 microseepage into the atmosphere over the 78 km^2 of the field was estimated at 700±1200 tonnes/year using the measured winter on-field flux rate, which would be a maximum season. This estimate overlaps zero, but a non-parametric statistical test for the distribution gave a positive flux at a probability of 0.985. Using a simple subtraction of the background or control area from the measured on-field winter flux rate gives 400 tonnes/year. The deep-sourced CO_2 flux to the atmosphere was estimated to be <200 tonnes/year, based on isotopic shift, not direct measurement.

The saturated zone flux was estimated as part of the original Department of Energy proposal using a one-dimensional reservoir engineering code. Data were provided by Chevron, USA on porosity, permeability of the overlying section, along with static reservoir pressure. The modeled CH_4 flux from the Rangely reservoir to the top of the water table was 59. mg m^{-2} day^{-1}. The measured summer on-field flux was 4.86 mg m^2 day^{-1}, dividing by 59. = 0.08, suggesting that ≈ 92% of the seepage was oxidized in the unsaturated zone. The measured winter on-field flux was 25.1 mg m^{-2} day^{-1}, dividing by 59. = 0.43, suggesting that ≈ 57% was oxidized in the unsaturated zone. Then dividing 0.43/0.08 = 5.4, with the signal:noise ratio improved by a factor of 5 when making winter-time measurements, relative to summer measurements. This has important implications in planning of a field campaign where one is looking for a subtle signal from depth.

The Weyburn-Midale project is a CO_2-EOR project that has been operating in Saskatchewan since the 1990s. Carbon dioxide for the CO_2 flood is derived in part from a coal gasification project in Buelah, North Dakota, USA. In 2011, a surface owner raised the issue of alleged leakage on his 160-acre farm, rendering the home unlivable. An independently-funded IPAC-CO_2 study of this small area was completed using a variety of techniques and is reported in Sherk (2011).

Two geochemical techniques were used: soil gas with analysis of CH_4, light hydrocarbons, and in one study helium. The plaintiff of the Kerr farm hired Petrofind of Saskatoon, SK to make an independent sampling and analysis of soil gas, which was done in summer, 2010, and subsequently repeated in February 2011. Kathryn Romanak and Changbing Yang of Texas-BEG completed the commissioned soil gas study with summer measurements. Stuart Gilfillan and Stuart Hazeldine of the University of Edinburgh, Scotland made inert gas isotopic ratio measurements in groundwater as part of the commissioned study, which can be considered a strong verification method. Inert gas isotopes are, however, a non-routine measurement, as is carbon-14.

The Romanak method uses GC-determined measurements and constructs ratio plots which support a given physical, chemical, or biological process. Figure 7 shows two of the ratio diagrams with the Kerr farm data plotted as individual points. The panels of Figure 7, in particular b), support respiration of soil organic matter, not seepage.

The inert gas isotopic ratio data in Figure 8 was derived from four shallow wells on the Kerr property and an adjacent farm. Also plotted are the inert gas isotopic ratios in the injected CO_2 and from produced fluids in adjacent production wells. The data are plotted along with the isotopic ratios in air-saturated-water (ASW) at 10 and 25°C. The four groundwater samples plot closely with the ASW measurements, yet far from the injected fluids and the produced fluids. These plots, and other isotopic ratios seem to conclusively demonstrate the absence of detectable leakage on the Kerr farm. This author also suggested that the CO_2 from Buelah, ND with a $\delta^{13}C$ of approximately -23‰ reacts with reservoir carbonate of 0‰, to produce a reservoir CO_2 of approximately -12‰. The soil gas $\delta^{13}C$ of -23‰ is consistent with normal soil respiration.

This author was requested to review all of the geochemical data generated in the Sherk (2011) and Petrofind studies and write an independent analysis of the data. A critical result of the Petrofind soil gas measurements was that the winter soil gas CH_4 concentrations were significantly lower than in the summer. A few low concentration occurrences of C_2H_6 in the Petrofind data led to the Petrofind conclusion; there was seepage from the deep reservoir. This was inconsistent with the seasonal results at Rangely where both seasons were also measured. At Rangely, the winter concentrations were higher.

Figure 9 summarizes this author's independent interpretation of the Petrofind data. Figure 9a provides an alternative explanation for the Petrofind finding of high CH_4 in the summer. Acetate is converted to CO_2 and CH_4 by the well-known acetate partitioning mechanism, which is common in freshwater environments. The process would slow in the winter (Figure 9b). At Rangely, where there is no surface freshwater, the acetate partitioning for CH_4 production cannot operate. A deep source of CH_4 was previously demonstrated for Rangely. At Rangely, the methanotrophy accelerates in the summer and slows down in the winter. The net is an opposite relative seasonal CH_4 concentration from that found at Weyburn. Consequently, the Petrofind data is also consistent with a conclusion of "no detectable leakage." A final comment, the area is known as "prairie-pothole-country," with many small water-filled depressions typical of the Pleistocene glaciation and favorable to fresh-water methanogenesis. The temperature bars on either side of Figure 9a) and Figure 9b) are relative temperatures. At Rangely, it is assumed there is also a small, but possibly detectable temperature gradient associated with seepage.

Limited CO_2 and CH_4 fluxes and soil gas were measured at the "Frio Experiment" on the South Liberty salt dome after a one-time injection of CO_2 by the Texas-BEG with DOE funding. This author and Brian Strazisar of NETL-DOE made flux and shallow soil gas measurements with the same protocol as used at Rangely and Teapot Dome. The average CH_4 flux was -2.31 mg m^{-2} day^{-1} in February 2004 and -0.08 mg m^{-2} day^{-1} in February 2005. These data demonstrated a difficulty in measurements in warm, wet climates. The surface environmental noise is methanotrophy drawing CH_4 from the atmosphere, masking any evidence of deep-sourced seepage, if present. The larger negative flux in 2004 was due to drier conditions giving more aerated vertical space in the soil column for methanotropy to operate. In 2005, the water table was higher and there was substantial soil saturation.

Summary and Conclusions

An overview of previous MVA research at three CO_2-EOR projects was presented. The Rangely and Weyburn projects had been operational prior to the measurements and presumably have some degree of overpressure in the reservoir. The Teapot Dome Field was a depleted field that was proposed for a CO_2 flood. Evidence of deep-sourced CH_4 seepage at Rangely exists as determined by direct flux and soil gas measurements. In the case of Teapot Dome direct seepage was not found, but the importance of faults as future pathways was discussed. At Weyburn, a review of a detailed study over a small area where there was an allegation of leakage was found to be negative.

Monitoring protocols will need to be developed for each project that reflects climate, geology, and accommodates normal cultural and environmental interferences at the surface. No single method is likely to be completely satisfactory for most sites. Measurement of carbon-containing gases for verification must be supported by the liberal use of isotopes. Monitoring should take advantage of faults as pathways from the reservoir to the surface for early detection. Initially, seasonal variation in fluxes and soil gas concentrations will be needed. Winter- and/or dry season measurements will improve the signal:environmental noise ratio. Ten-meter holes equipped for nested sampling will provide an early indication of change from a baseline condition. In a large sequestration/injection operation such as Rangely or Teapot Dome, 10-12 holes at carefully selected locations with evidence of seepage present and seepage absent will be needed for comparison and contrast. Initially, sampling on a monthly basis for 1-2 years, and bimonthly thereafter till the project closes and the reservoir pressure declines back to hydrostatic pressure will be adequate. For strong verification in the case of regulatory or legal proceedings, non-routine methods such as carbon-14 and inert gas isotopic ratios may be required.

Acknowledgements

Rangely – U.S. Department of Energy-Basic Energy Sciences for funding; Chevron Production USA for access to confidential reservoir characterization documents, reservoir pressure and water quality data, and backhoe for soil characterization in trenches.

Teapot Dome – Rocky Mountain Oilfield Testing Center (RMOTC) for funding; Naval Petroleum Reserve No. 3 for access and data, and backhoe for soil profile characterization and fault trenching.

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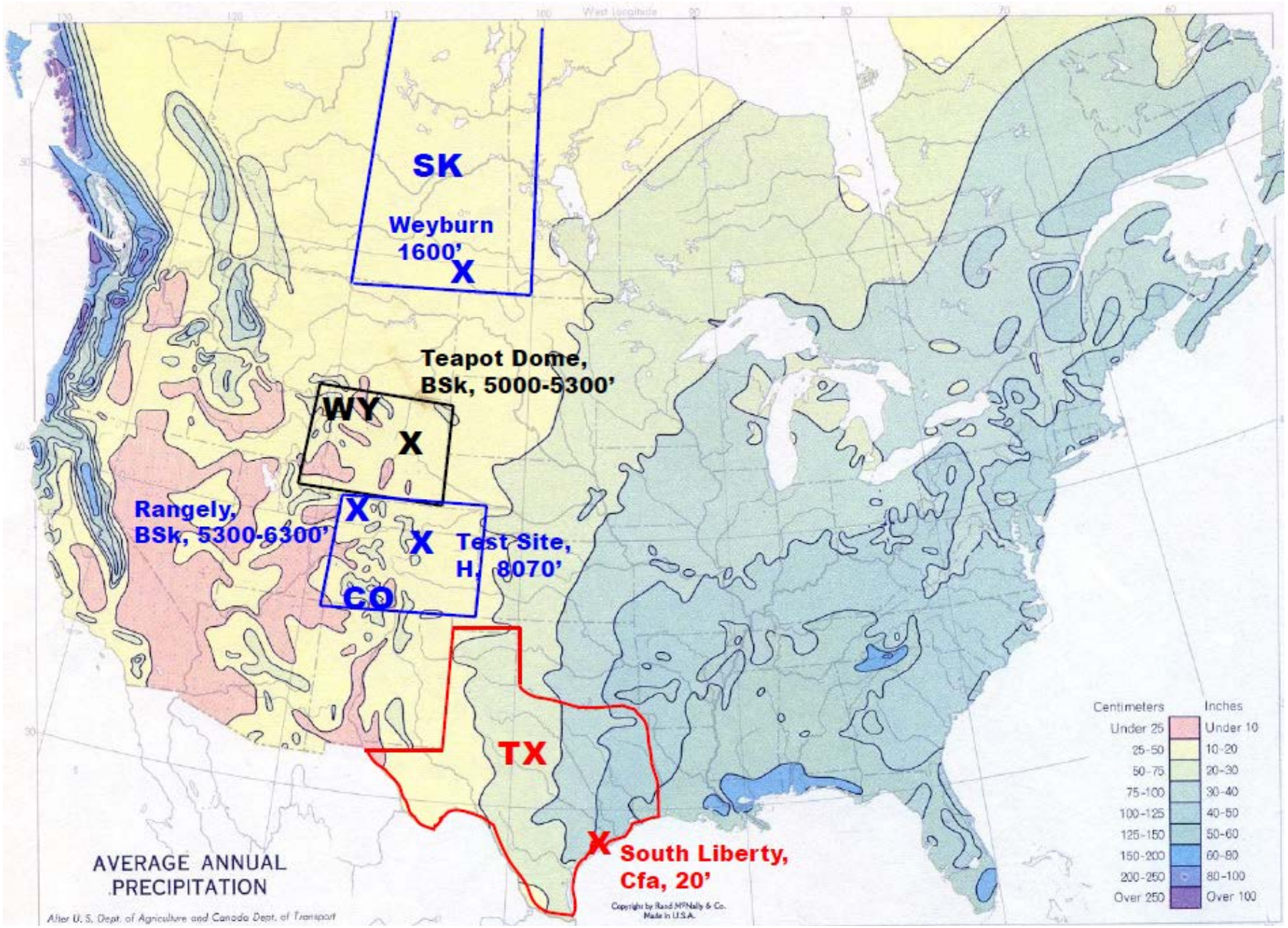

Figure 1. Map of the areas of interest, showing the annual precipitation and elevation of the locations to be discussed. The soil types at Rangely and Teapot Dome are "BSK"; dry steppe kalt (cold).

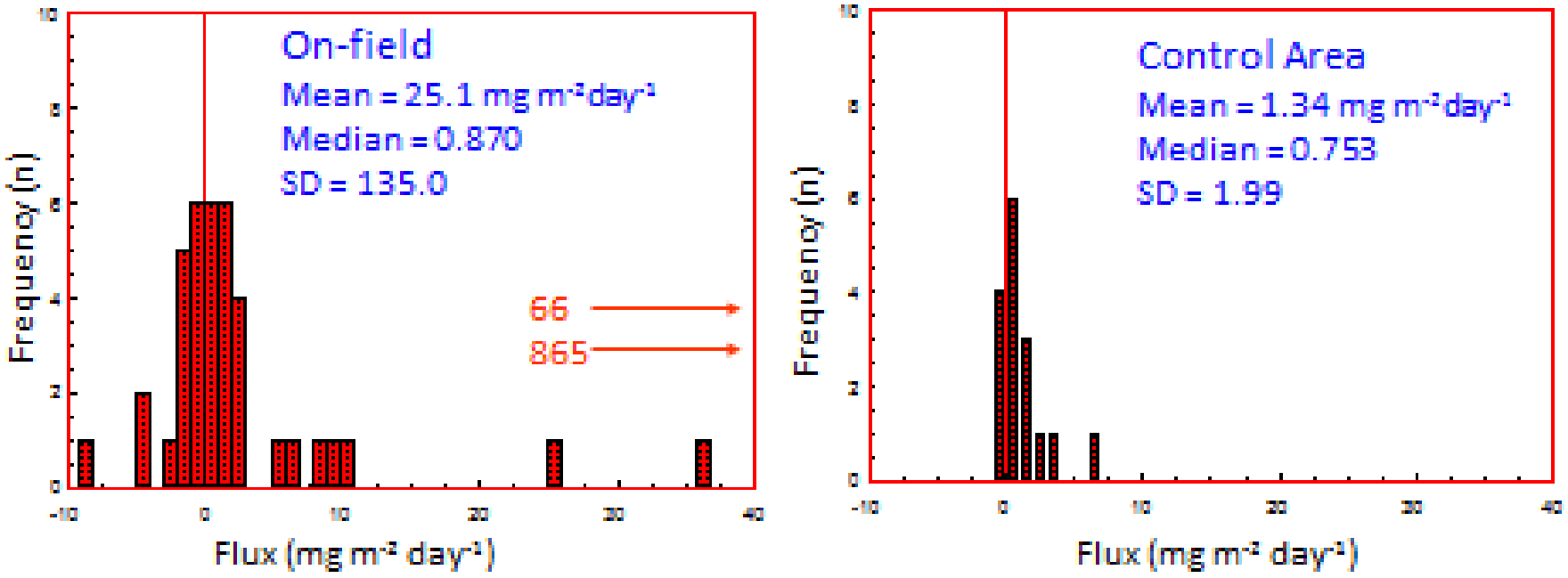

Figure 2. Winter 2001/02 CH_4 fluxes on the Rangely Field and in the Control Area.

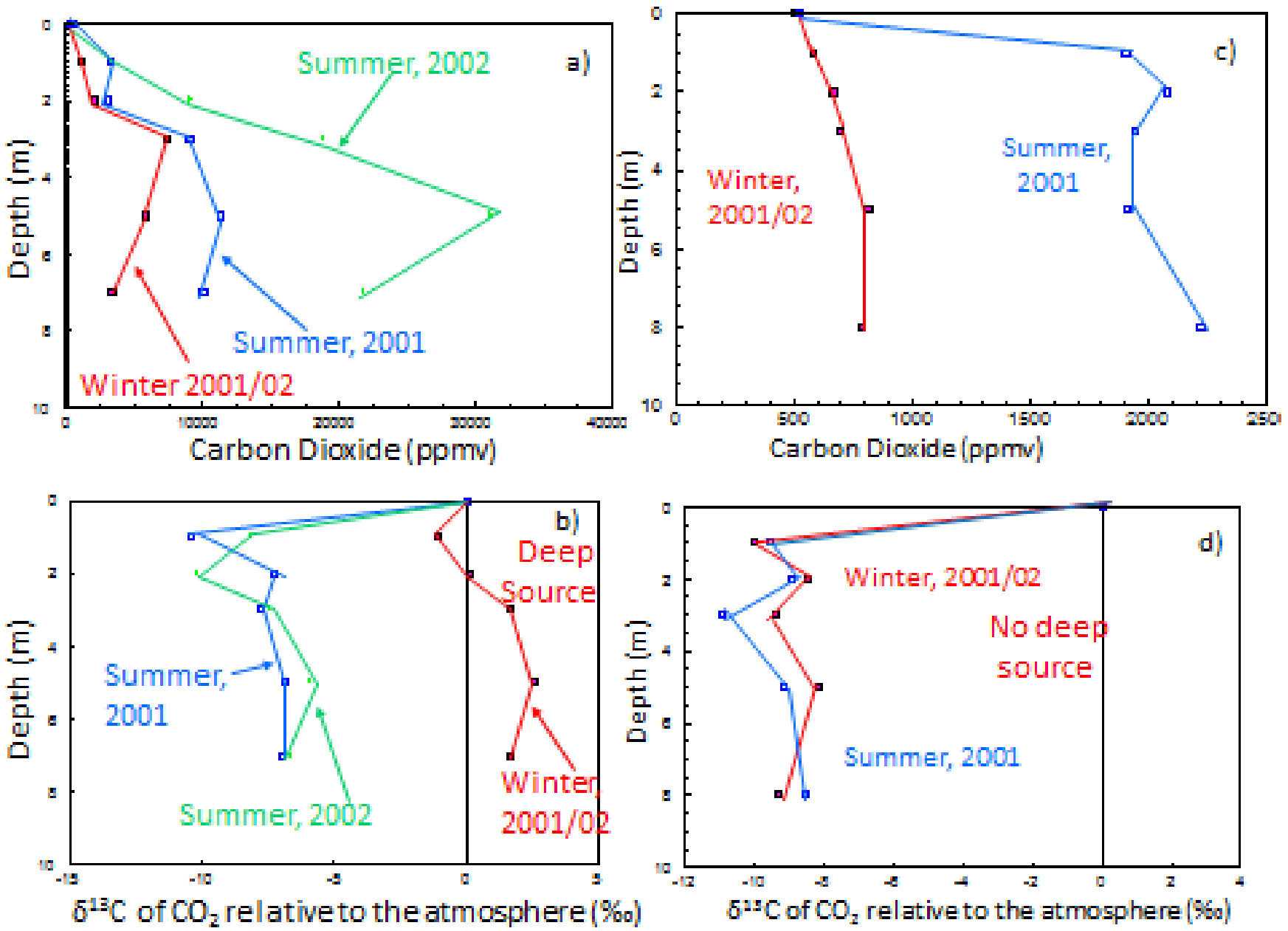

Figure 3. Carbon dioxide concentration and isotopic shift of CO_2, relative to the atmosphere at Rangely; a) and b), anomalous Location 01; c) and d), non-anomalous location 28.

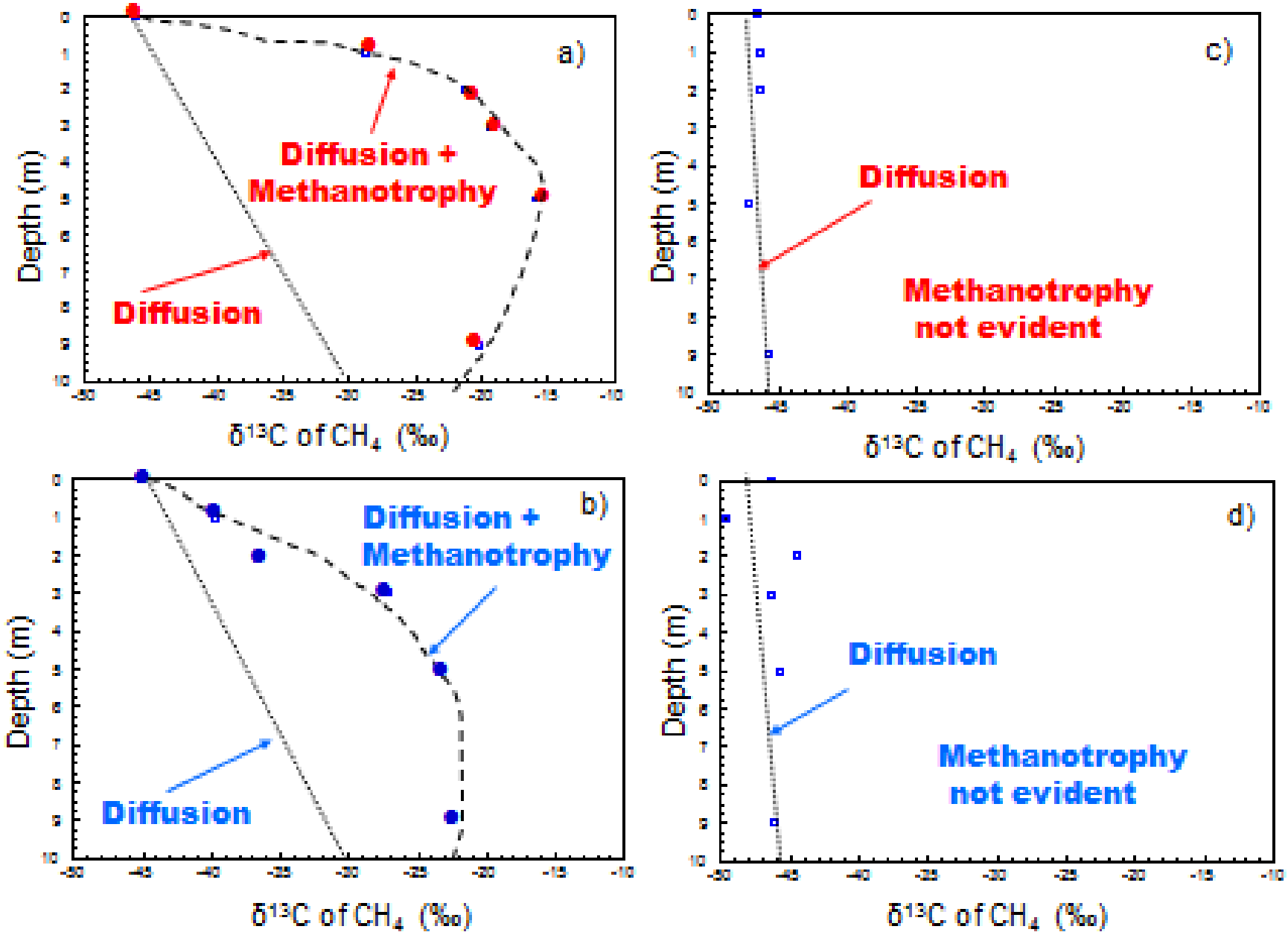

Figure 4. $\delta^{13}C$ of CH_4 at Rangely for anomalous location 03, a) summer 2002, (b) winter 2001/02, c) $\delta^{13}C$ of CH_4 for non-anomalous location 34 in summer 2002, d) winter 2001/02.

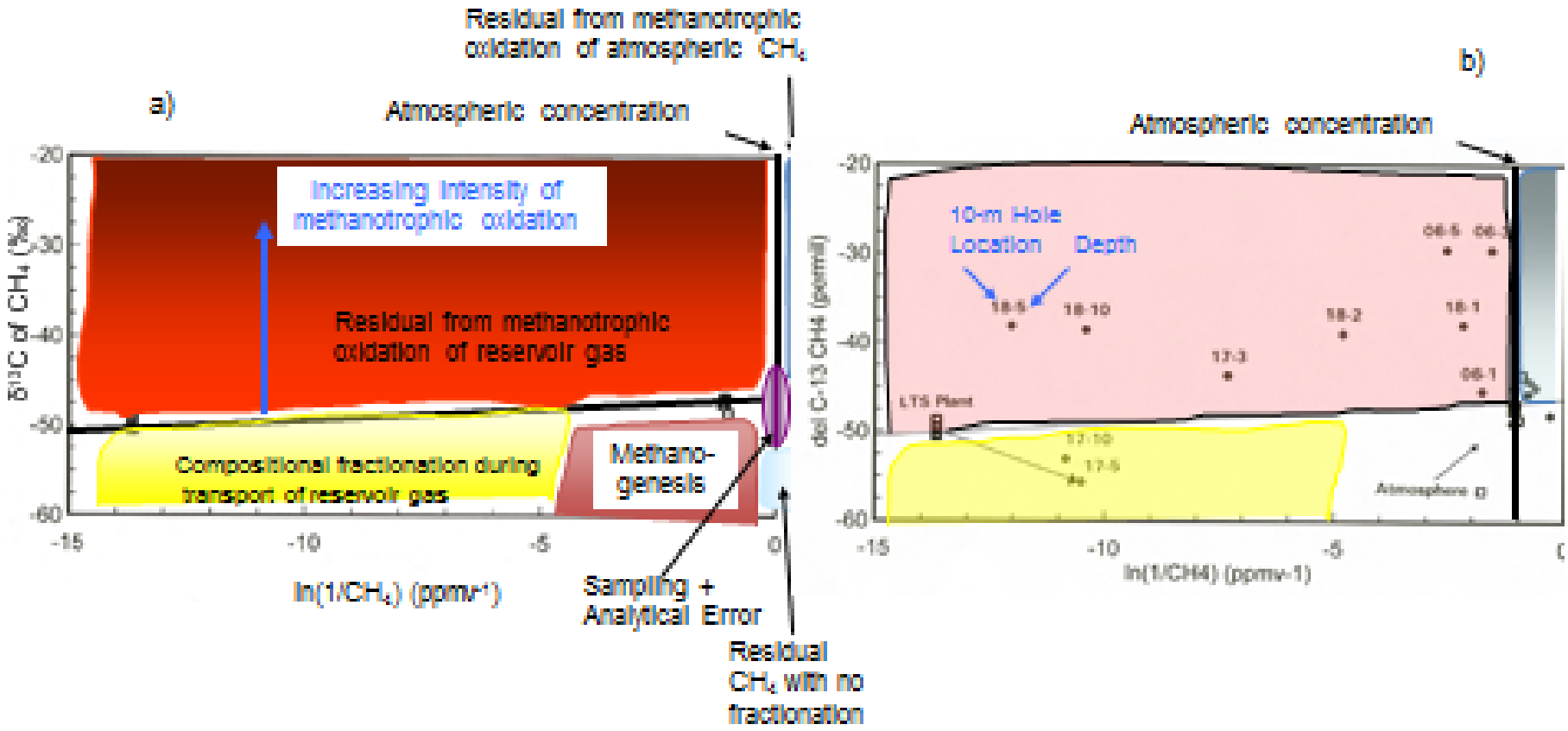

Figure 5. Arrhenius-type plot for CH_4 in 10-m holes at Teapot Dome, showing the importance of methanotrophy in the consumption of seepage from the underlying reservoir.

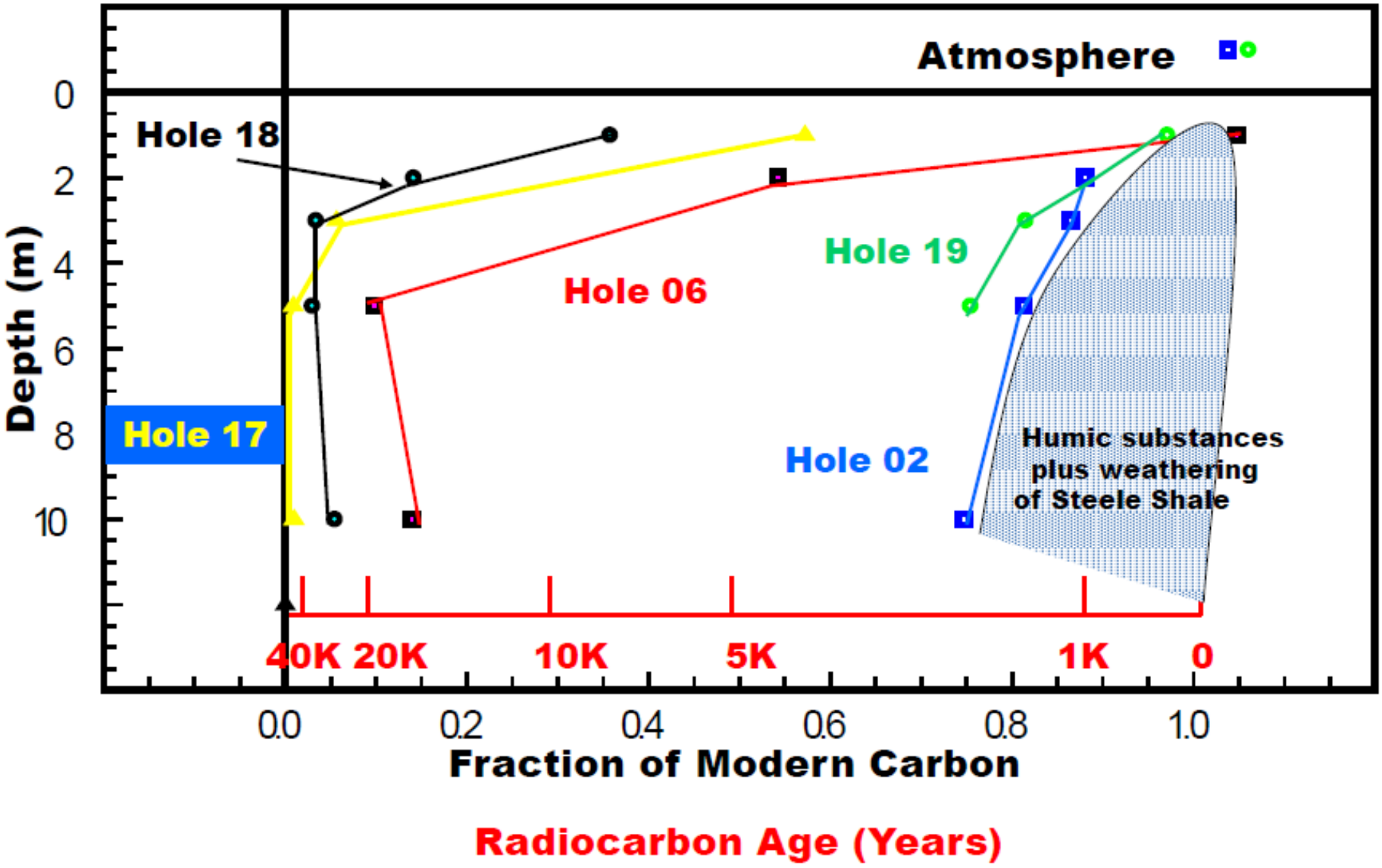

Figure 6. Radiocarbon ages of soil gas from 10-m holes at Teapot Dome.

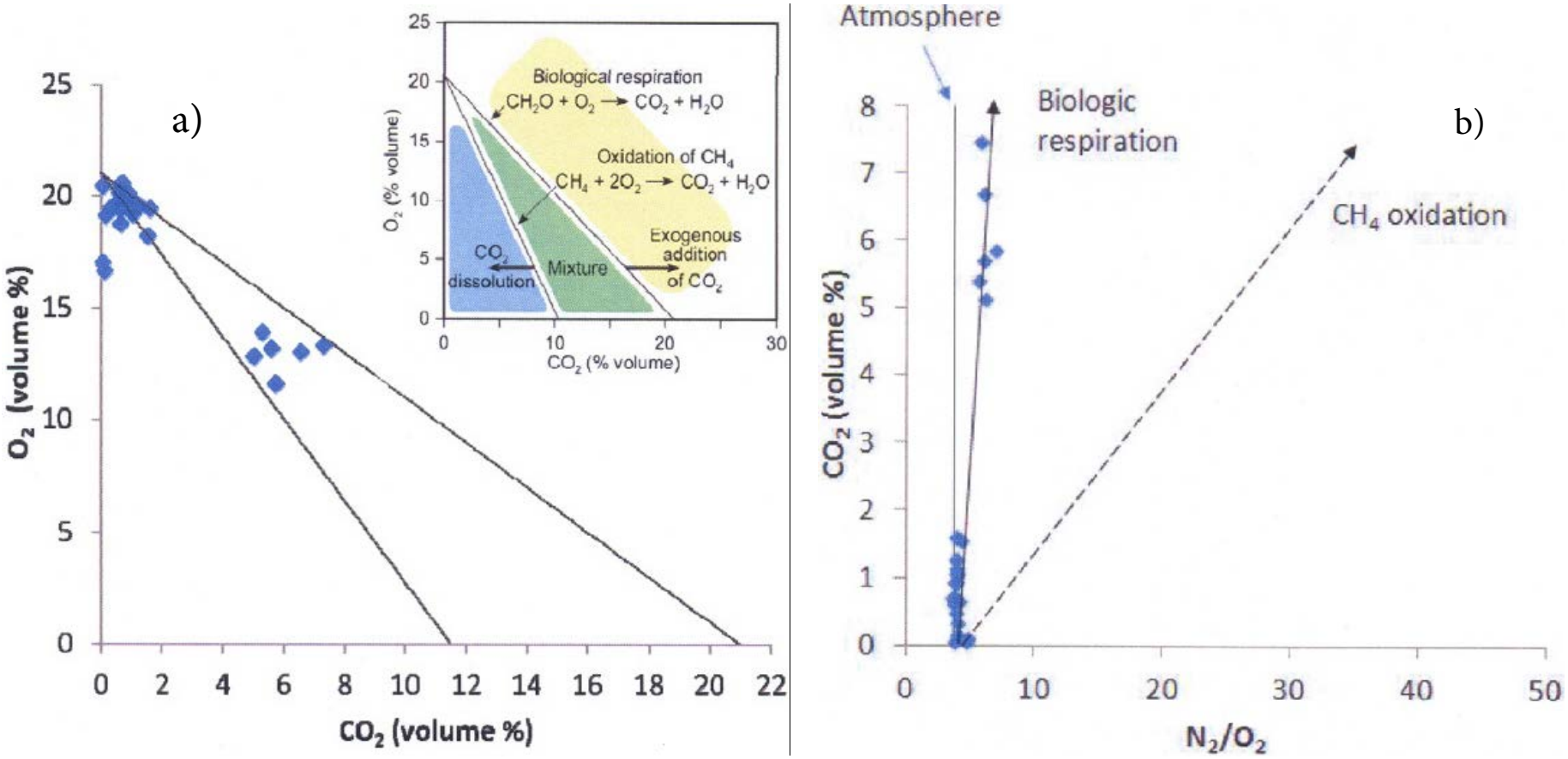

Figure 7. Romanak and Yang plots for a) O_2 vs. CO_2, b) CO_2 vs. N_2/O_2 on the Kerr farm.

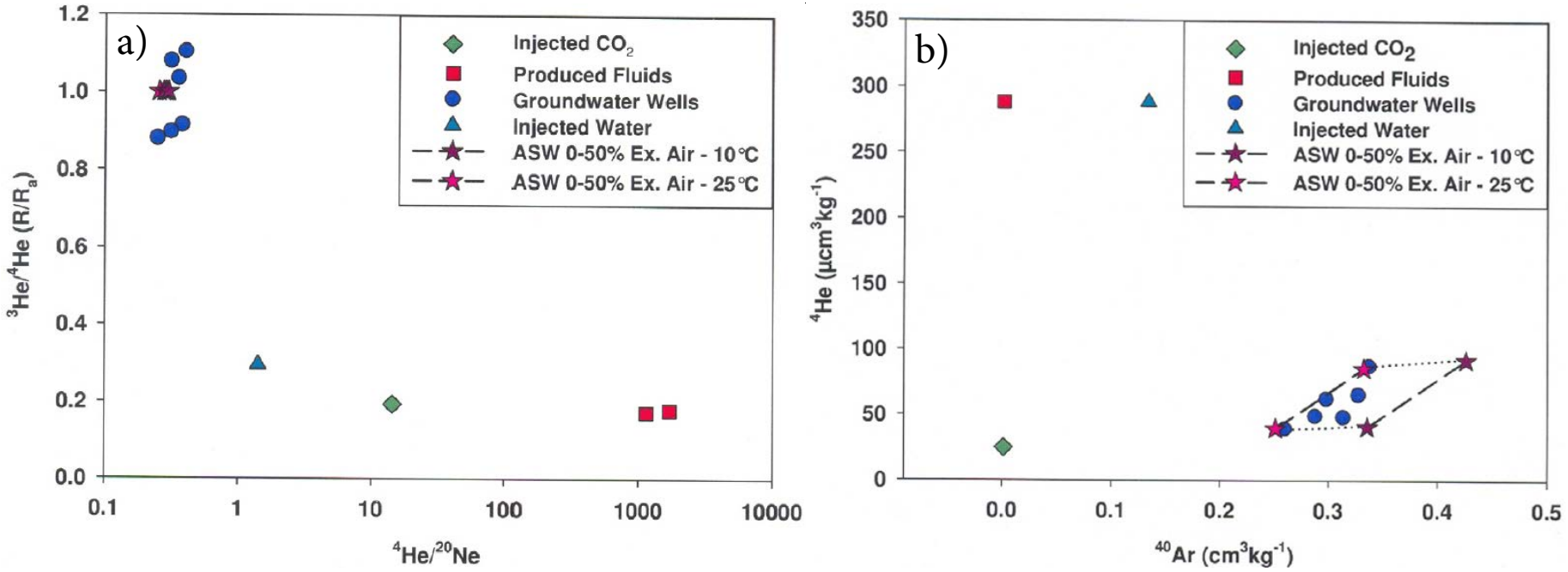

Figure 8. Selected inert gas isotopic ratios in groundwater in the Kerr farm study.

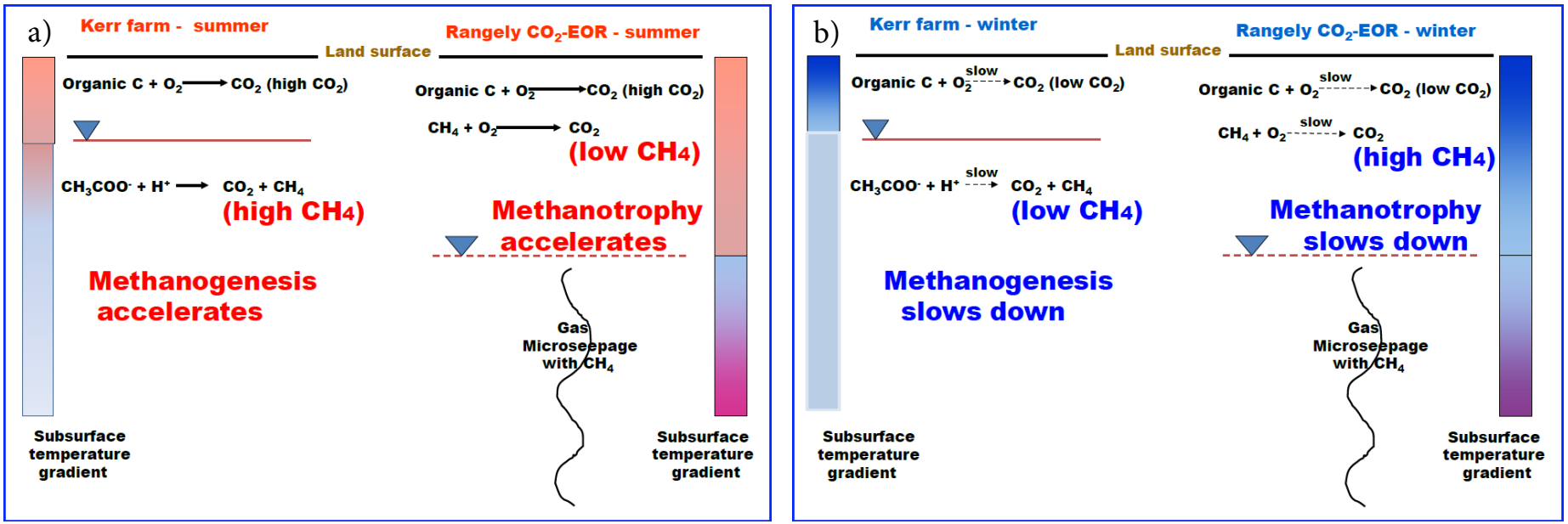

Figure 9. Klusman interpretation of geochemical processes operating on CH_4 in the shallow subsurface.