

CARBON AND HYDROGEN ISOTOPE COMPOSITIONS OF GEOTHERMAL GASES

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ABSTRACT

Carbon and hydrogen isotopic compositions are compared for the gases methane, hydrogen and carbon dioxide from Ngawha, Wairakei, Ohaaki-Broadlands and Tikitere (Ruahine Springs). The different areas have different isotopic compositions with some general relationships to reservoir temperature and inferred origins. The isotopic exchange of hydrogen with water was found to indicate reservoir temperatures from most spring samples but often, higher than measured temperatures in well samples. Indicated temperatures assuming ^{13}C equilibria between CH_4 and CO_2 are 100-200°C higher than measured maxima. This difference may be due to either partial isotopic equilibration or to source conditions of methane. Possible sources for carbon dioxide and methane are shallow or deep crustal (inorganic or organic) material with the possibility of some juvenile contribution.

INTRODUCTION

Studies of the light element stable isotopes of geothermal gases should have advantages in showing aspects of their origin and previous history which may be less affected by near surface conditions than would the aqueous fluids. Previous studies and reviews (e.g. Panichi and Gonfiantini, 1978; Truesdell and Hulston, 1980) have emphasised isotopic exchange and geothermometry. However, Des Marais et al. (1981a) have recently inferred that the carbon isotopic composition of geothermal methane and other hydrocarbons from North American geothermal fields have origins independent of the carbon dioxide despite CO_2 and CH_4 being approximately in isotopic equilibrium at Cerro Prieto.

The carbon isotopic composition of geothermal gases has been the subject of many studies but only a few have made hydrogen isotopic measurements. The isotopes of hydrogen can be measured in the three molecules CH_4 , H_2 and H_2O , and exchange may be at a different rate to that of carbon.

This study considers both hydrogen and carbon isotope compositions of geothermal gases from four New Zealand geothermal fields. The isotopic compositions of the gases carbon dioxide, methane and hydrogen are then evaluated for information on their origin and their usefulness for geothermo-

metry based on isotopic fractionation between species.

THE CARBON-13 GEOTHERMOMETER

Fig. 1 shows the $\delta^{13}\text{C}$ values for carbon dioxide and methane and the $\Delta^{13}\text{C}(\text{CO}_2-\text{CH}_4)$ temperatures assuming that equilibrium had occurred. Isotopic temperatures are near 400°C for the Ngawha and Broadlands samples, with no difference between wells and springs at Ngawha. These temperatures are higher than any measured well temperatures at either field. The $\Delta^{13}\text{C}(\text{CO}_2-\text{CH}_4)$ indicated temperatures at Wairakei and Tikitere, near 350°C are similar to each other, but with a wider range at Wairakei due to the variations in $\delta^{13}\text{C}(\text{CO}_2)$. Wairakei wells with heavier $\delta^{13}\text{C}(\text{CO}_2)$ values have therefore lower indicated $\Delta^{13}\text{C}$ temperatures and are those with high gas contents and higher enthalpies.

Using well data only to ensure that the fluids are well characterised the $\Delta^{13}\text{C}(\text{CH}_4-\text{CO}_2)$ indicated temperatures have been plotted (Fig. 2) against the temperatures calculated from silica solubility.

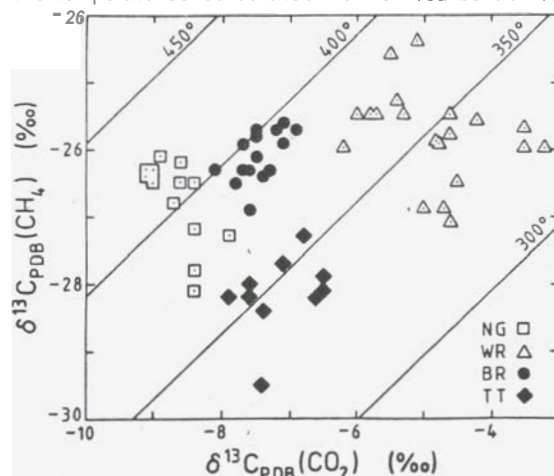


Fig. 1: $\delta^{13}\text{C}_{\text{PDB}}$ for carbon dioxide and methane from springs and wells at Ngawha (NG), wells at Wairakei (WR), Broadlands (BR) and springs at Tikitere (TT). The indicated temperatures are for equilibrium fractionation, using the data of Richet et al. (1977).

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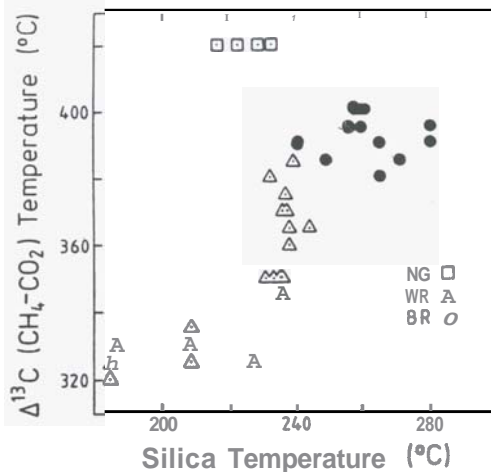
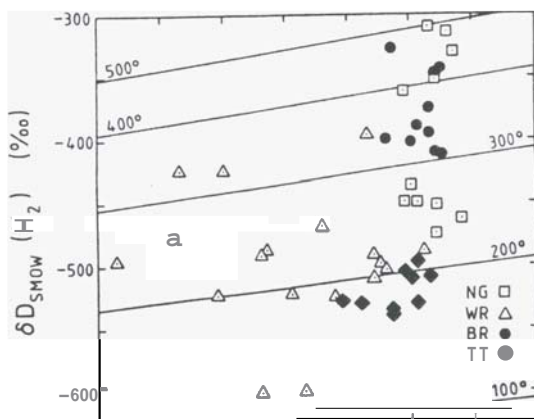


Fig. 2: $\Delta^{13}\text{C}(\text{CH}_4\text{-CO}_2)$ temperatures plotted against silica temperatures, for wells from Wairakei, Broadlands and Ngawha.

Similar patterns show if Na-K-Ca temperatures are used. There are no regular patterns for either the Broadlands or Ngawha well data, but there is a positive correlation for the Wairakei data and a less significant correlation for all the well data. Thus the $\Delta^{13}\text{C}(\text{CH}_4\text{-CO}_2)$ temperatures could be used as a guide for well temperatures, but they would not be precise. As the ^{13}C equilibration reaction is very slow by several orders of magnitude compared with the silica (or Na-K-Ca) geothermometer (Truesdell and Hulston, 1980; Giggenbach, 1982), the $\Delta^{13}\text{C}$ indicated temperature is probably not a true reflection of the conditions in the exploitable reservoir but is defined by conditions of higher temperature at an earlier period of the gas's history. However, these data appear to show that Broadlands and Ngawha, with their generally



similar reservoir temperatures, have similar $\Delta^{13}\text{C}$ temperatures, and that we can estimate that Wairakei and Tikerere reservoir temperatures may be similar.

Further, although one can argue that there are separate origins for methane and for carbon dioxide and the lack of appreciable re-equilibration of ^{13}C at geothermal reservoir temperatures (Sackett and Chung, 1979; Giggenbach, 1982), but this does not preclude there remaining records of higher, "frozen-in" temperatures.

Comparison of $\Delta^{13}\text{C}(\text{CH}_4\text{-CO}_2)$ temperatures with gas temperatures calculated assuming CH_4 forms from graphite and CO_2 according to D'Amore and Panichi (1980) show no pattern with all samples plotted, but approximate correspondence of $+200^\circ\text{C}$, when only the Ngawha results are considered. This appears fortuitous in view of those authors' unproven assumptions that CO_2 is merely a "carrier" gas, and nitrogen is wholly atmospheric.

The indicated carbon-13 temperatures for the wells at Ngawha are generally the same as for the springs, i.e. near 400°C . This shows that spring gases are reliable reflections of the deep gas ^{13}C values and $\Delta^{13}\text{C}(\text{CH}_4\text{-CO}_2)$ temperatures. Thus it is reasonable to compare Tikerere spring gas ^{13}C data with the well data from other areas.

DEUTERIUM THERMOMETERS

The three pairs of molecules $\text{CH}_4\text{-H}_2$, $\text{H}_2\text{-H}_2\text{O}$ and $\text{CH}_4\text{-H}_2\text{O}$ cannot be considered independently since a change of one molecular composition would affect two geothermometers. Water is the dominant molecular species and may be considered invariant in composition except for liquid-vapour separation. In general, the assumption is made that the surface discharge represents the isotopic composition of liquid water which is the source of the water with which methane or hydrogen equilibrates.

Fig. 3 shows the δD values for hydrogen and methane and the $\text{AD}(\text{CH}_4\text{-H}_2)$ temperatures. Isotopic equilibrium temperatures between CH_4 and H_2 and between H_2 and H_2O are detailed elsewhere (Lyon and Hulston, in press).

The AD temperatures for Ngawha springs are about 250°C for all three deuterium pairs, but the $\delta\text{D}(\text{H}_2)$ values from the Ngawha wells are higher, with consequent $\text{AD}(\text{CH}_4\text{-H}_2)$ temperatures of $400\text{-}500^\circ\text{C}$. Broadlands AD isotopic temperatures are a mean about 380°C , which is similar to the $0/0$ temperature. This suggests that this temperature, although higher than at any drilled depths, has some significance in the history of the fluids. In contrast, AD temperatures for the gases from springs at Tikerere are generally near 200°C which is close to some chemical estimates. As the $\Delta\text{D}(\text{H}_2\text{-H}_2\text{O})$ temperatures for springs at Ngawha proved to give a reasonable estimate for the reservoir, and this geothermometer was also reasonable in Iceland (Arason, 1977), these Tikerere estimates of near 200°C should be considered in reservoir assessments there.

The Wairakei well data, however, have a much greater scatter, but with most $\Delta D(\text{CH}_4\text{-H}_2)$ and $\Delta D(\text{H}_2\text{-H}_2\text{O})$ temperatures between 200 and 300°C. A major exception is H₂ from WR81, at -600‰. This well has a very low gas content and is perhaps contaminated by hydrogen from reaction with well casing. It is suspected that the low gas content of Wairakei wells has contributed to the unusually large scatter of the $\delta D(\text{CH}_4)$ values in Fig. 3.

METHANE COMPOSITION

The deuterium and carbon-13 compositions of geothermal methane (Fig. 4), show that no consistent relationship is apparent for all samples considered together. The Wairakei methane, however, is of more variable and generally lower deuterium content than that from the other three areas.

Natural gases have been analysed for their δD and $\delta^{13}\text{C}$ compositions by Schoell (1980) and these New Zealand geothermal methanes are nearest to his TT(h) type as shown in Fig. 4. All other methanes analysed by Schoell (1980) had $\delta^{13}\text{C}$ values more negative than -30‰ and most had δD values more negative than -175‰. The TT(h) gases were North German coal-derived gases developed by high temperature reaction of humic (terrestrial) source rocks, and have low concentrations of higher hydrocarbons, as do these geothermal gases. During heating at lower temperatures, these sediments have lost higher molecular weight hydrocarbons and isotopically lighter methane. Similar methane, though with more positive δD values, has been found in the Thuringer Basin, East Germany (Runge and Wand, 1980) with $\delta^{13}\text{C}$ values ranging from -23 to -47‰.

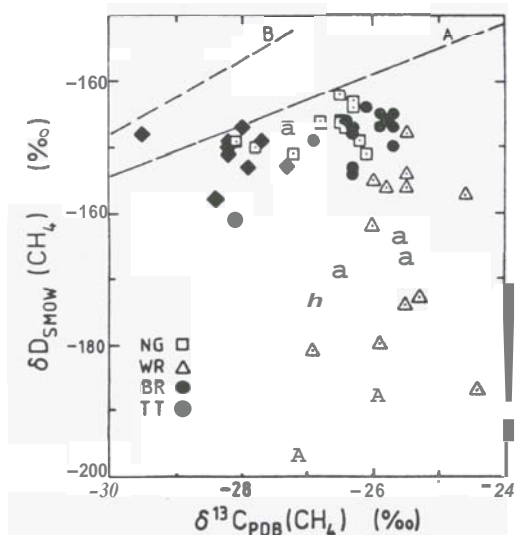


Fig. 4: Methane isotopic compositions. Geothermal samples compared with German natural gas from A: Schoell (1980), and B: Runge and Wand (1980). All other German data had $\delta^{13}\text{C}(\text{CH}_4) < -30\text{‰}$.

However, the New Zealand geothermal gases have more negative δD values than the German data. The reason is not known but Smith et al. (1982) also noted that there were more negative $\delta D(\text{CH}_4)$ values in the natural gas methanes from Australia than in Schoell's similar samples (all with $\delta^{13}\text{C} < -46\text{‰}$) from Germany.

Des Marais et al. (1981a), using $\delta^{13}\text{C}$ analysis have recently postulated that individual hydrocarbons (methane, ethane, propane, benzene) from Yellowstone, Cerro Prieto and The Geysers geothermal fields are derived from decomposition of organic matter in the sediments with a correlation of heavier methane with higher temperatures. It has also been shown that in higher temperature Cerro Prieto wells, and from longer term laboratory decomposition experiments, methane becomes more enriched in $\delta^{13}\text{C}$ (Des Marais et al. 1981b). This is probably due to decomposition of organic matter that has already lost some of its $\delta^{13}\text{C}$ depleted radicals, and therefore the methane $\delta^{13}\text{C}$ composition tends to approach that of the original organic matter.

Methane produced from organic matter decomposition would have an isotopic composition independent of that of the geothermal carbon dioxide. Fig. 4 shows that our samples are somewhat similar to other natural gases and implies they could be formed in a similar way.

Magmatic gases are dominated by carbon dioxide and hydrogen which should react to form methane in increasing amounts as temperature decreases but kinetically this does not occur very fast (Giggenbach, 1982). However, methane of unusual isotopic composition ($\delta^{13}\text{C}$ about -16‰) has been reported from the East Pacific Rise by Welhan et al. (1981) and sedimentary sources are lacking there. The recent discovery of bacteria capable of living at 250°C and of the biological production of methane in deep sea geothermal springs (Baross and Deming, 1983; Baross et al., 1982) casts further doubt on purely inorganic explanations for the origins of geothermal methane. Therefore, as low temperature biogenic methane forms in an apparent $\delta^{13}\text{C}$ equilibrium fractionation with carbon dioxide, then this could also be the case with high temperature organisms.

CARBON DIOXIDE COMPOSITION

The New Zealand geothermal CO_2 have $\delta^{13}\text{C}$ values which are significant heavier than soil carbon dioxide (typically -24‰; HENDY, 1971). Within a field (e.g. at Wairakei), some variations from the average discharge may also arise from phase separations in the aquifer. Thus one gas sample from a field may not necessarily be typical, nor represent the composition of the total gas.

Carbon dioxide from thermal decomposition of sedimentary carbonate would have $\delta^{13}\text{C}$ values of 0 ± 2‰ and could be a significant source of some geothermal CO_2 . Juvenile carbon dioxide, however, is estimated to have $\delta^{13}\text{C}$ values between -5 and -8‰ (see e.g. Allard et al. 1977). Mixtures of

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these two sources ("crustal" and "juvenile") could account for geothermal gas compositions between 0 and -8‰ and recently Allard (1980) has suggested that $\delta^{13}\text{C}$ enriched CO_2 is due to increasing proportions of crustal CO_2 .

Most of the geothermal carbon dioxide analysed in this study has a carbon-13 composition in the range -7 to -8.5‰ which is consistent with other estimates of magmatic carbon. Wairakei, however, has heavier carbon, with a wider range, the range (toward lighter values) which can be explained by successive outgassing. The average Wairakei CO_2 has $\delta^{13}\text{C}$ values about -5‰ so that probably

Wairakei has a substantial component of carbon dioxide from crustal (greywacke) carbonate decomposition. Ewart and Stipp (1968) reported North Island greywacke carbonate concentrations of about 0.1% (as CO_2) but no isotope measurements are available.

CONCLUSIONS

Comparison of the carbon-13 isotopic compositions of methane and carbon dioxide in geothermal gases suggest that there is some correlation with underground temperatures. The temperatures derived from isotopic equilibrium considerations are generally 100-200°C higher than measured or silica temperatures in the areas considered. However, although carbon dioxide is the dominant species and its isotopic composition would not be much affected by exchange with methane, the methane may have an isotopic composition which is independent of that of the CO_2 , or of the observed geothermal reservoir characteristics. It is not possible at this stage to assume any one process for the isotopic composition of methane, and in fact the collected samples could have a mixture of methanes of different origins, with the relative proportions varying between different fields.

The hydrogen-water isotopic exchange would appear to be the most useful as a geothermometer but it has proved difficult to analyse consistently in our laboratory and, we suspect, also in other laboratories. This exchange is well calibrated experimentally and theoretically and appears to have the best potential for estimating underground temperatures, particularly from surface manifestations where, at Ngawha it reliably predicted temperatures found by nearby drilling to depths of 500-1500 metres. Thus the AD estimate of near 200°C is considered valuable for Tikitere, although $\delta^{13}\text{C}$ data suggests the possibility of high temperatures.

Hydrogen isotopic temperatures estimated from the well samples are often higher than those estimated from the surface and from well silica temperatures. The exception to this is at Wairakei where (except for a few early analyses) a very good correlation is obtained between $\Delta D(\text{H}_2-\text{H}_2\text{O})$ and the silica temperatures. The higher isotopic temperatures found in other areas may be due to a frozen equilibrium indicating temperatures at greater depth or possibly a corrosion reaction with the steel of the newer well casings at Broadlands and Ngawha.

The latter suggestion does not however appear to be substantiated by excess hydrogen in terms of the chemical equilibrium between hydrogen, water, carbon dioxide and methane.

Thus, although it appears that these gases contain geothermometric information, it is not possible to say that these isotopic relationships are not fortuitous. It may be that each gas and its observed isotopic concentrations is of independent origin.

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