MINERAL ALTERATION IN A LOW-ENTHALPY HYDROCARBON WELL. TARANAKI, NEW ZEALAND

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SUMMARY – Mineral alteration in the Eocene Mangahewa Formation sub-arkoses of Well Mn-2 is a product of millions of years of water-rock interaction in a rock-dominated environment. The thermal peak, at about 150°C, occurred 4Ma ago. Since then temperatures have fallen to about 120-130°C. Temperature, pressure, permeability/porosity, degradation of organic material, the composition of porewaters and gases and time induce alteration and deposition of new minerals in this low enthalpy hydrocarbon well. Kaolinite, illite-smectite, pyrite and carbonates may have initially formed under near-equilibrium conditions but subsequent coarsening of crystals or ion diffusion within or among crystals may be kinetically-induced. In contrast, the growth of **quartz** during the diagenetic history of the Mangahewa Formation may be entirely kinetic. Healed fractures and overgrowths in quartz indicate that earlier solutions were enriched in Cu and Zn while the later ones have high contents of Ca, K, Ni, Cl and Ge.

1. INTRODUCTION

The Taranaki Basin is a Cretaceous to Cenozoic active-margin basin located in western New Zealand. It encompasses offshore areas beneath the continental shelf, the Taranaki Peninsula and northwestern South Island (King and Trasher, 1996). Petroleum and natural gas reserves in Taranaki occur mainly in Eocene sandstone and fractured Oligocene and early Miocene limestone reservoirs (King and Trasher, 1996, Crown Minerals, 2000), sealed by marine claystones and siltstones (Collen, 1988).

Most of the exploration for hydrocarbons in New Zealand is focused in the Taranaki Basin with over 70% of oil and gas production derived from its Maui and Kapuni fields. In 1997, New Zealand had total oil/condensate reserves of 346.42 million barrels and 5.44 trillion cubic feet of natural gas (Crown Minerals, 2000).

The average conductive heat flow in Taranaki Basin is 60 mW/m^2 with values **of** 65-70 mW/m^2 coincident to the Taranaki chain of volcanoes, suggesting a causal relationship; and areas in South Island (Allis et al, 1995) where as much as 3 km of erosion had occurred in Late Miocene (Funnel et al, 1996). The highest heat flow measurement of 74 mW/m^2 is found in New Plymouth, adjacent to the Paritutu gas field (Fig 1) and the 1.74 Ma Sugar Loaf volcano remnants (Funnell et al, 1996; King and Trasher, 1996).

Gases in the Taranaki Basin are dominated by CH_4. However **CO,** concentrations are high in the onshore extension of this field, comprising as much **as** 46% of the total gas in the Kapuni field and 72% in Paritutu (Lyon et al, 1996). Giggenbach (1997) showed that the high CO, content in some Taranaki well discharges are caused by decarboxylation in some areas (Kapuni) or due to the addition **of** a magmatic component, based on C and He isotopic compositions (Paritutu). Most of the high CH_4 discharges from the rest of the Taranaki wells, however, may have been produced by cracking processes, that occur at temperatures **>120°C** or even by fluid-rock equilibrium, where temperatures are >160°C (Giggenbach, 1997).

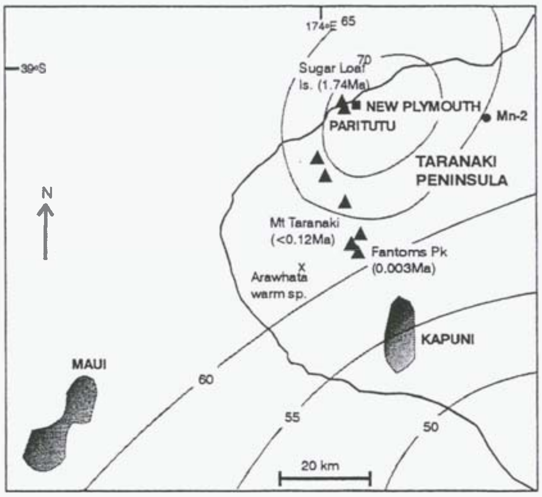

Figure 1- Map of Taranaki showing the location of place names mentioned in text, volcanic features, warm spring and heat flow contours (adapted from Trasher and King, 1996; Funnell et al, 1996).

This paper is a study of the effects of low-enthalpy heat, with time, on rock alteration or diagenesis in one of the gas-producing sandstone formations of the Taranaki Basin, the Eocene Mangahewa Formation, exemplified by Well Mn-2. This well was drilled within the 60-65 mW/m^2 contours east of New Plymouth (Fig 1) and intersected the Eocene Mangahewa Formation sub-arkoses at 3600 to 4400m. Condensate and gas discharges from Well Mn-2 contain 85% CH_4 and **15%** CO, The CH_4/CO_2 ratio suggests a temperature of

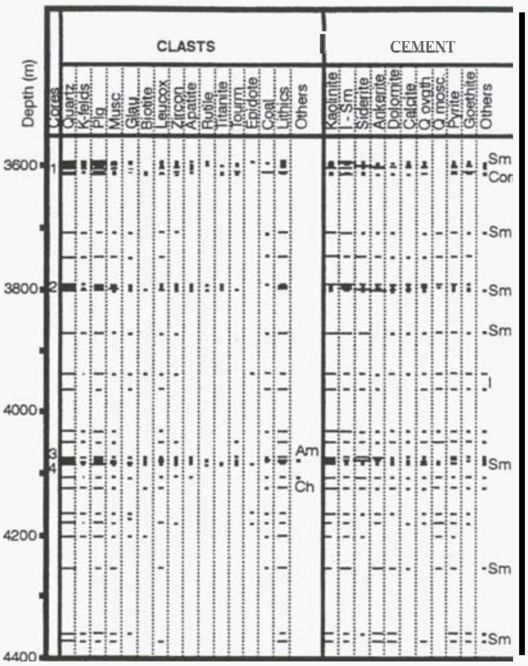

Figure **2**- Distribution and abundance of detrital and authigenic minerals in the Mangahewa Formation sub-arkoses of Well Mn-2. Abbreviations: **Am=** Amphibole, Ch= Chlorite, Corr= Corrensite, Glau= Glauconite, I= Illite, I-Sm= Illite-smectite, K-Felds= K-feldspar, mosc= mosaic, Musc= Muscovite, ovgth= overgrowth, Plg= Plagioclase, Q= **Quartz**, Sm= Smectite, Tourm= Tourmaline.

170°C (Giggenbach, unpublished results) from a source beyond drilled depths.

2. ANALYTICAL METHODS

Thirty-one samples of cores and cuttings were analysed employing light microscopy (transmitted and reflected), cathodoluminescence, particle-induced X-ray emission analysis (PIXE) using proton rather than electron beams, scanning electron microscopy with attached energy dispersive X-ray (SEM-EDX), fluid inclusion heating and freezing procedures, fluorescent microscopy to detect oil-filled fluid inclusions and stable isotope analysis of ^{13}C and ^{18}O of authigenic carbonates.

3. RESULTS

The predominant detrital materials in the Mangahewa Formation in Well Mn-2 (Fig 2), include as much as 80% **quartz** with plagioclase, K-feldspar other minor fragments and lithoclasts of igneous, sedimentary and metamorphic origins (Fig **2).** Most of the detrital materials, however, originate from granite as is commonly found in late Cretaceous and Eocene sedimentary rocks in the rest of the Taranaki Basin (Smale et al, 1999). Some of the source rocks experienced several hydrothermal and metamorphic events prior to deposition as clasts in sedimentary rocks, evinced by the presence of two-phase fluid inclusions in granitic crystals and metamorphic minerals such as epidote, actinolite, tourmaline, zoisite, chlorite and **quartz** mosaics.

Authigenic minerals form as cements and replace both clasts and cement during diagenesis. These consist of interlayered illite-smectite, kaolinite siderite, ankerite, dolomite, calcite, chalcedony, pyrite, goethite and rarely, smectite, corrensite and illite.

Interlayered illite-smectite d-spacings range from 12 to 10.05Å in this well, with most clustering between 10.65 to 10.158, (Fig 3). From Core 1 at about 3600m to Core 4 at about 4100m, d-spacings generally decrease from 10.65 to 10.15 **A,** following an increase in measured well temperatures from about 115°C at 3600m to 130°C at 4100 m (Fig 3). The increase in illite component in the I-Sm, inferred from decreasing d-spacings, is a common pattern found in geothermal and hydrocarbon systems, where the structural and chemical reorganization of smectite to interlayered illite-smectite to illite is related to increasing temperatures and cation exchange with prevailing solutions (Steiner, 1977; e.g., Eberl, 1993). In geothermal systems like Wairakei, for example, occurrences of interlayered I-Sm with d-spacings of <10.6Å form in equilibrium with **quartz** at >180°C (Steiner 1977). However in this well, only chalcedony is deposited with I-Sm (60-*80%* illite in <2μm fraction), suggesting equilibrium with a lower temperature silica polymorph. Geothermal I-Sm temperatures recalculated using the •-cristobalite geothermometer (Henley et al, 1984) yielded temperatures of 110-150°C (labeled mineralogy in Fig **3).** Recalculated I-Sm temperatures are similar and up to 32°C higher than measured temperatures above 4200m, suggesting cooling. However, below 4200m, recalculated I-Sm temperatures are lower by about 10°C and may be due to decreased mobility of K' in low porosity rocks (Fig **3).** The maximum recalculated I-Sm temperature is similar to the highest temperature, 148°C, attained at **3600-4400m**, 4Ma ago (Funnell 1998, pers comm).

In Core 1 at **3600m**, I-Sm d-spacings decrease generally **with** increasing porosity, suggesting the strong influence of solutions in redistributing K$^+$ in the formation. Furthermore d-spacings also decrease markedly where the paleo-oil contents (oil-filled inclusions in Fig **3),** recorded in **quartz** fluid inclusions, are most abundant. Apparently the progressive transition of smectite to interlayered illite-smectite and hence to illite, in the sub-arkoses of the Mangahewa Formation, is governed by several factors: temperature, circulation of silica-saturated K+-bearing solutions in equilibrium with • -cristobalite in zones of good permeability or porosity; mobilization of Al^{3+} from the rock and the decomposition of organic matter. The smectite to illite transition is believed to be a dissolution/crystallization process wherein domains of illite grow at the expense of a shrinking parent smectite (Freed and Peacor, 1989). In hydrocarbon systems time, availability and free-flow of ions, relative water-rock ratio, and temperature induce the smectite to illite transition (Ahn and Peacor, 1986).

Book-like aggregates of kaolinite form cements prior to and after the precipitation of carbonates. During burial, as the system was heating, kaolinite preceded the crystallization of illite-smectite in the matrix (Fig **4**), suggesting changes in fluid flow and composition. It also replaces authigenic illite-smectite, often forming wispy fibers. Kaolinization of illite-smectite is accompanied by oxidation of pyrite to goethite or hematite at 3600m or the simultaneous deposition of ankerite and dolomite at 3800m. The depletion in cations, during kaolinization of I-Sm; and the release of Fe^{2+} from pyrite for subsequent incorporation in goethite, indicate reaction with slightly acid waters (Fig **3**). These acid waters may be organic acids (Shebl and Surdam, 1996) or bicarbonate waters from the reaction of CO_2 with porewater.

Siderite in the Mangahewa Formation often crystallizes around a core of goethite or hematite and rarely, glauconite (Fig **4**). Siderite becomes mantled by ankerite followed by dolomite and then, sometimes, calcite, showing depletion in Fe and an increase in Mg and Ca with time. The cycle of siderite to magnesian carbonates is repeated when detrital pyrite is oxidised to goethite later in the diagenetic history (Fig **4**). The aforementioned paragenesis is evidence for Giggenbach's (1997) thesis that Fe^{2+} and Fe'' interchange between minerals constitutes an effective buffer in controlling reduction-oxidation processes in hydrocarbon systems like Taranaki. During the early stages of diagenesis, low temperatures favor the formation of Fe^{3+}- oxides, such as hematite (Giggenbach (1997):

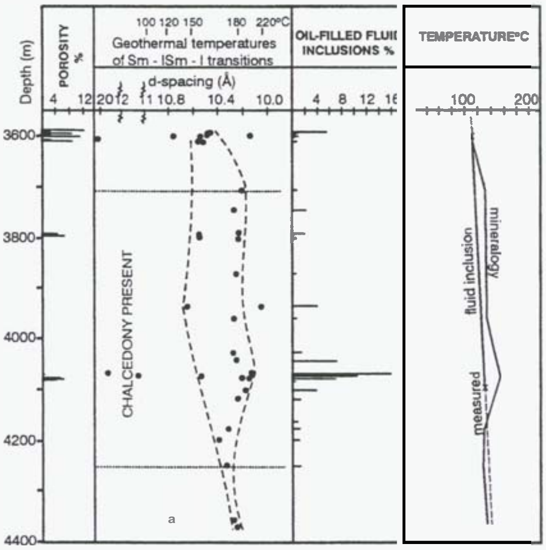

Figure **3**- Porosity, illite-smectite d-spacings. % of oil-filled fluid inclusions found in quartz grains, and measured, mineralogical and fluid inclusion temperatures. Measured temperatures are from Funnel1 (pers. comm., 1998).

$$CO_2 + 8(FeO) + 2H_2O \bullet \quad CH_4 + 8(FeO_{1.5}) \qquad (1)$$

With increasing burial and temperatures, the reaction starts to reverse and carbonaceous material is increasingly oxidised according to:

$$CH_4 + 8(FeO_{1.5}) \bullet \quad CO_2 + 8(FeO) + 2(H_2O) \qquad \mathit{(2)}$$

The increased production of CO_2 and Fe^{2+} favors the formation of siderite around the Fe-oxyhydroxide cores:

$$Fe(O) + CO_2 \bullet \quad FeCO_3 \qquad \mathbf{(3)}$$

The **low** ^{13}**C** values of siderite and dolomite from this well, at –13.6 to –8.0 ‰ suggest that much of the CO_2 involved in the precipitation of the carbonates originate from decarboxylation of coaly material, **a** common constituent of the Mangahewa Formation (Fig *2)*. At 100°C, the fractionation of ^{13}**C** during decarboxylation of kerogen is 4‰ and that between CO_2 and dolomite, 5‰ (Hoefs, 1997). This results in **a** fraction of about 75% organic C in the carbonate cement. However siderite-mantling by Mg and Ca carbonates and the absence of siderite and ankerite in some carbonate cements suggest sources of CO_2 other than reduction-oxidation processes.

Epitaxial overgrowths of quartz around detrital quartz and the healing of quartz fractures are common in the Mangahewa Formation, contributing to porosity reduction. Fluid inclusion, measured and mineralogical temperatures (Fig **3**) generally indicate temperatures below the thermodynamic equilibrium temperatures for the precipitation of quartz. However Renders et al (1995) showed that the presence of precursor cristobalite nuclei and silica concentrations in solution above the cristobalite thermodynamic saturation may cause the metastable precipitation of hydrothermal cristobalite. A similar process may occur for **quartz** in hydrocarbon systems such as Taranaki.

4. DISCUSSION

Changes in the chemical composition of the altering solutions compositions with time were determined using fluid inclusion heating/freezing measurements, detailed paragenetic analysis and cathodoluminescence of feldspars, quartz and carbonates in combination with PIXE and SEM-EDX. In this particular well, all water samples were highly contaminated by drilling additives (Crookbain, pers. comm, 1998) and hence cannot be used to ascertain the chemical composition of solutions presently circulating in the rock.

Fluid inclusions (FI) containing oil-, gas- and/or water are mainly found in quartz and feldspar grains, seldom cutting across grains except for a few instances in Cores 1 and 2. Oil- and bitumen-filled inclusions were trapped in two stages, prior to deposition of quartz overgrowths (Fig 4). Hence oil occurrences (Fig 2) record paleo-oil saturation. However, gassy FI, indicated by the formation of clathrates during freezing and the presence of liquid CO_2 in a few FI, persist in quartz overgrowths and carbonate cements suggesting that gas has been generated throughout most of the diagenetic history of the Mangahewa Formation (Fig 4).

In all three cores, at least two major heating events have been recorded: a hydrothermal event inherited from clasts that had experienced temperatures of 190-290°C, prior to incorporation into the sediments; and a heating event, followed by cooling with time, within the sedimentary basin (Fig 4). Since the maximum heating event, recorded in FI at 145-150°C, the system had slightly cooled to about 110°C at 3600 m, 115°C at 3800m and 120°C at 4075m. These values indicate a geothermal gradient of about 26°C/km, 2°C lower than measured well temperatures (Fig 3). One source of discrepancy may be the lack of pressure corrections caused by the coupled effect of high gas and high salinities, for which published data are limited. Nevertheless, the difference between FI and well measurements is only 6 to 8%, well within the permissible error of predicted temperatures using petrographic means.

As a first approximation, the proliferation and abundance of carbonate cements, the reactions described by equations (1) to (3) and the Occurrence of authigenic pyrite in veinlets indicate the presence of CO_2, CH_4 and H_2S during diagenesis. Fluid inclusion freezing measurements show that >70% of the water-rich FI contain gas clathrates that disappear at <10°C, suggesting CO_2. Furthermore ice crystals in FI melt at –56.6°C, the triple point of CO_2 and homogenize at 31°C, its critical point. (Roedder, 1984). Deviations from the critical and triple point temperatures of CO_2, indicate the presence of H_2S, CH_4 and possibly, N_2 in FI from this well. Upon freezing, white crystals form in some FI. These do not homogenize and may indicate the presence of ?gypsum (Roedder, 1984), possibly from the oxidation of H_2S.

The proliferation of clathrates in tiny FI with average diameters of 10μm renders salinity and CO_2 gas estimates by freezing depression methods nearly impossible. However, as discussed by Giggenbach (1997) partial pressures of CO_2 (P_{CO_2}) in hydrocarbon systems can be represented as a function of temperature and geothermal gradients (Fig 5). At the height of the thermal regime (145-150°C) when the thermal gradient was about 35-40°C/km the theoretical P_{CO_2} was 10b. At present it is 5b at 125°C using a geothermal gradient of 28°C/km. In both cases,

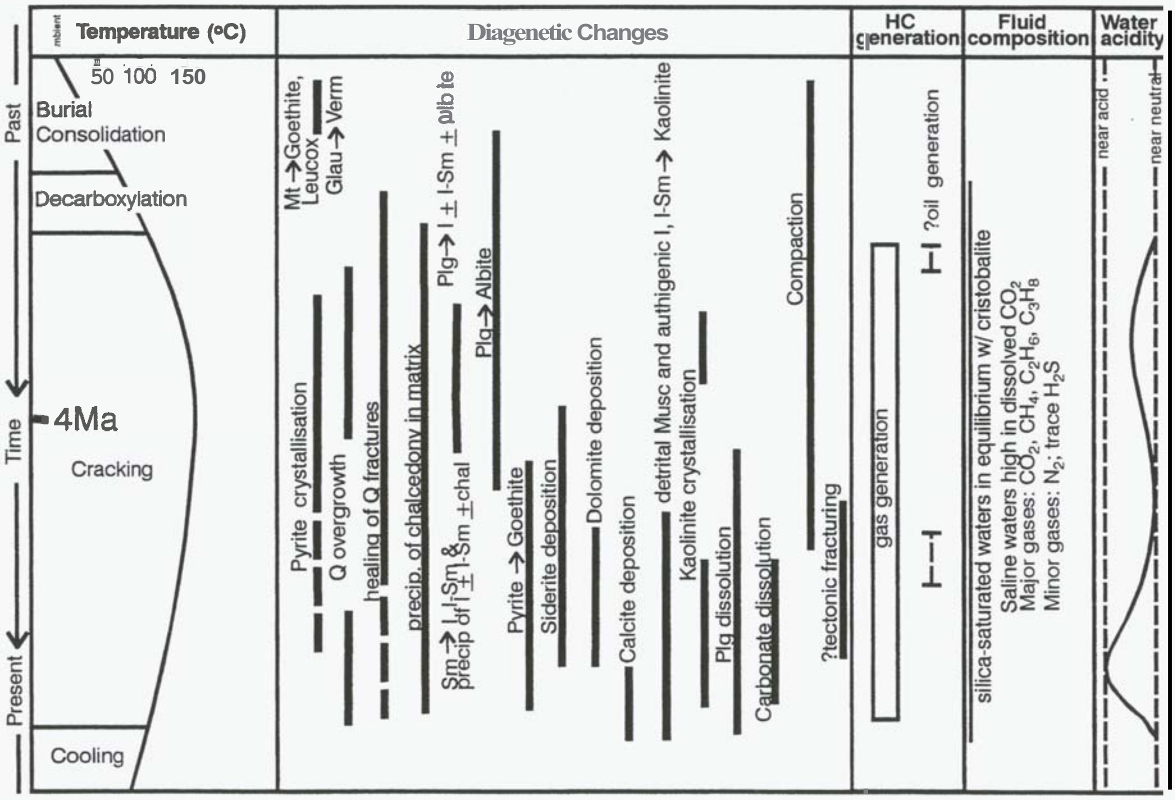

Figure 4- Diagenetic history of Mangahewa Formation sub-arkoses in Well Mn-2. Refer to Figure- 2 for mineral abbreviations. HC= hydrocarbons, precip= precipitation, chal= chalcedony, Verm= vermiculite, • = alteration to.

kaolinite, illite-smectite and calcite are in equilibrium (Fig 5), an assemblage corroborated by petrographic observations (Figs 2 and **4).** However, the presence of nearly pure CO, FI, the abundance of clathrate-containing FI and the temperature of homogenization of some clathrates (Barton and Chou, 1993) indicate much higher P_{CO_2} than thermodynamically predicted. Fluid inclusion results corroborates the conclusion from carbonate petrography, as discussed previously, that some of the CO, gas produced during the diagenetic history of the Mangahewa Formation is not in equilibrium with the source rock and may be kinetically-generated.

A combined cathodoluminescence (CL) and **PIXE** analyses show that healed fractures and overgrowths in detrital quartz contain different trace elements. Older healed fractures have orange to brown CL colors associated with relatively **high** values of Cu, Zn and Co. Younger healed fractures and **quartz** overgrowths are less luminescent. They contain high concentrations of Ca, K, Ni, Cl, and Ge relative to older healed fractures but lower contents of **V,** Cr, Mn, Co and Zn. **Thus,** with time, the metal contents of porewaters, and possibly the original quartz grains decrease as the alkali contents become dominant. Ions apparently diffuse through quartz grains enabling quartz to record the migration of major and trace elements during diagenesis.

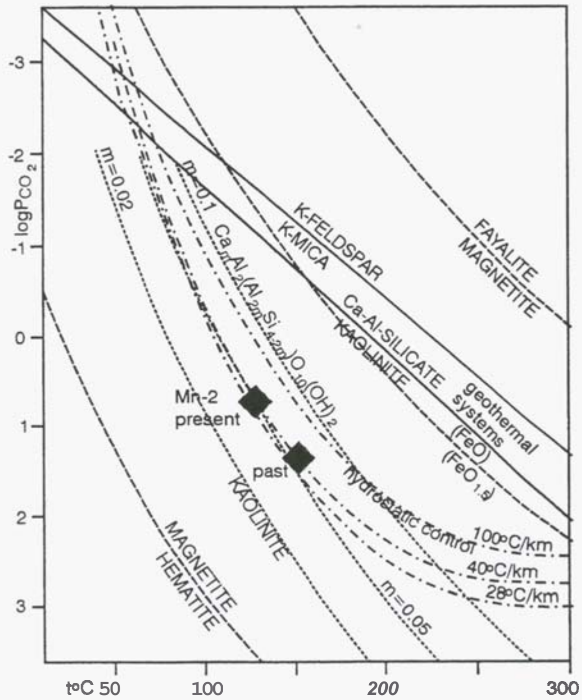

Figure 5- Fig 2 of Giggenbach (1997) showing control of P_{CO_2} by buffers involving K-feldspar/K-mica and Ca-Al-silicate/ kaolinite (solid lines), by Ca-montmorillonite/ kaolinite as a function of the mol-fraction m of margarite (dotted lines) and hydrostatically for regional heatflows of 28 and 40°C/km (dash-dot lines) to represent the recent and past thermal regimes, respectively, in Mn-2.

Elemental mapping of cements and detrital minerals, using PIXE, show that altering fluids introduce Si, K, Ca, Rb, Sr, Zn, Cu, Br, Ge and *S* into the rock. Iron, Mn, Ti and perhaps Ba, Ca, K and **Si** may also be locally mobilised from feldspars, muscovite, magnetite and pyrite.

The diagenetic history of the Mangahewa Formation, exemplified by this well, is closely linked to the maturation of organic matter, oxidation-reduction processes leading to gas generation and oil saturation, mobilization of elements from existing silicates, oxides/ oxyhydroxides and sulfides, and changes in water chemical compositions with time. However excess CO, gas concentrations may indicate sources other than thermodynamically controlled inorganic mineral and hydrocarbon reactions. Mineral alteration and deposition in Mn-2 are characterised by (a) dissolutionlcrystallization transformations of smectite to illite-smectite to illite, or kaolinite to illite-smectite; (b) grain coarsening of kaolinite and I-Sm with time; (c) advancing fronts of nucleation sites causing deposition of epitaxial quartz overgrowths; (d) ion diffusion and mobilisation in minerals; (e) reduction-oxidation reactions; and (f) shifts in acidity of porewaters.

5. CONCLUSIONS

Burial diagenesis of sub-arkoses, exemplified by the Mangahewa Formation, is a more complex and prolonged process than hydrothermal alteration in a geothermal system. Mineral alteration in the Eocene Mangahewa Formation sub-arkoses of Well Mn-2 is a product of millions of years of water-rock interaction in a rock-dominated environment. The thermal peak, at about 150°C, occurred 4Ma ago. Since then temperatures have fallen to about 120-130°C at present. Authigenic minerals such as siderite and iron oxides and oxyhydroxides, together with organic matter decomposition, partly govern the evolution of CH_4 and CO, in the Mangahewa Formation. However excess CO,, from sources other than oxidation-reduction processes and organic matter degradation, are indicated by FI clathrate contents, the presence of nearly pure CO, FI and the occurrence of carbonate cements other than siderite and ankerite. Thus the production of gases in the Mangahewa Formation may be partly controlled by mineral-fluid reactions under thermodynamic near-equilibrium conditions, partly by kinetic reactions. Illite-smectite is deposited at near-equilibrium with a low-temperature silica polymorph such as *-cristobalite at 110-150°C and may be induced to form kinetically during the transformation of kerogen to oil. However illite-smectite, as well as kaolinite, is metastable. Kaolinite books may be altered to illite-smectite or illite to illite-smectite, depending on the availability of cations, provided by pore water and the dissolution of detrital and pre-existing authigenic minerals. Healed fractures and overgrowths in quartz, and the distribution of elements in cements and detrital minerals show that earlier solutions in the Mangahewa Formation were relatively enriched in Cu and Zn while later ones have higher concentrations of Ca, K, Ni, Cl, and Ge. Iron, Mn, Ti, Ba, Ca, K and Si are mobilized from rock and porewaters circulate and introduce K, Ca, Rb, Sr, Zn, Cu Br and Ge into the rock.

Temperature, pressure, permeability/porosity, degradation of organic material, the composition of porewaters and gases and time induce alteration and deposition of new minerals in a low enthalpy hydrocarbon well such as Mn-2. Kaolinite, illite-smectite, pyrite and carbonates may have initially formed under near-equilibrium thermodynamic conditions but subsequent coarsening of crystals or ion diffusion within or among crystals may be kinetically-induced. In contrast, epitaxial growths of quartz during the diagenetic history of the Mangahewa Formation may be entirely kinetic.

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