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Chemical Variations of CO_2 in the Rankin Trend Natural Gases, Carnarvon Basin, Australia: An Example of Mineral Sequestration?

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High-CO_2 gas fields serve as important analogues for understanding various processes related to CO_2 injection and storage. The chemical signatures, both within the fluids and the solid phases, are especially useful for elucidating preferred gas migration pathways and also for assessing the relative importance of mineral dissolution and/or solution trapping efficiency. In this paper, we present a high resolution study focussed on the Gorgon gas field and associated Rankin trend gases on Australia's Northwest Shelf of Australia. The Gorgon field is characterized by a series of stacked reservoirs (Figure 1), and is therefore well placed to characterize CO_2 migration, dissolution and reaction by looking at geochemical signatures in the different reservoirs. Hydrological data at the Gorgon field also suggests that many of the major faults possess very low transmissivities, which should prevent or limit mixing of reservoir fluids with different chemical imprints. The gas data we present here reveal correlatable trends for mole %-CO_2 and $\delta^{13}C$ CO_2 both areally and vertically as observed by Edwards et al. (2007). We suggest that the observed relationships are imparted due to mineral carbonation reactions that occurred along the CO_2 migration pathway. These results have important implications for carbon storage operations and suggest that under certain conditions mineral sequestration might occur over longer migration distances and on shorter timescales than previously thought.

The Australian NW shelf is a marginal rift setting which contains four basins, including the Carnarvon Basin. The Gorgon field, within the Carnarvon, is one of the largest gas fields in Australia (~ 40 TCF), with gases contained within an upthrown horst block defining the Rankin trend. Structurally, the Rankin horst block formed in response to late Triassic rifting, with later drowning of the system leading to formation of the intra Jurassic unconformity and deposition of the Muderong shale that forms the regional seal. The Rankin trend extends northward for more than a hundred kilometres to the Goodwyn and North Rankin fields. Gases of the Gorgon field are higher in CO_2 than surrounding fields such as the Barrow Sub-basin and on the Exmouth Plateau. Currently it is believed that the CO_2-rich Gorgon field gases migrated up and towards the southern Gorgon as a late dry charge and formed a spill chain to the north, displacing earlier, wetter gases (Longley et al, 2002).

Gases of the Gorgon field have the highest CO_2 concentrations among all gases in the Carnarvon Basin, with CO_2 up to 16% and $\delta^{13}C$ clustered between -3 to -5‰ (Figure 2). Within the Gorgon field, there is a systematic change in both the CO_2 concentration and carbon isotopic signature towards the north and up through the section (see data superimposed on Figure 1). Generally, CO_2 % decreases and becomes depleted in $\delta^{13}C$ (lighter) upsection and towards the north; a trend which also holds true for the greater Rankin trend gases in general.

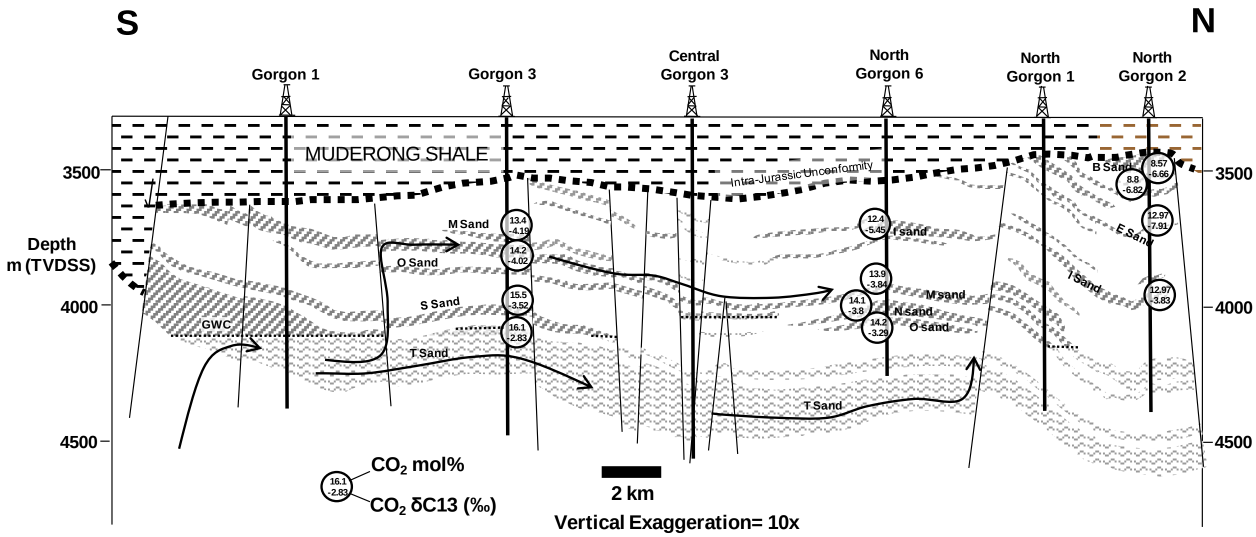

Figure 1. Schematic cross-section through the Gorgon field (Modified from Thornton, 1999)

The data plotted on Figure 2 shows that there is also a moderately strong correlation between CO_2 content and carbon isotopic signature for gases of the Rankin trend, something that is not observed for gases in the surrounding sub-basins (here, gases with ^{13}C $CO_2 > 0$‰ are affected by biodegradation.)

The spatial variation of CO_2 content and $\delta^{13}C$ and the interrelationship between the two suggests that processes were active to alter the two in tandem. We propose that these variations were driven by the precipitation of a carbonate phase. In the Gorgon area, a number of late stage carbonate cements have been identified including a late stage siderite cement in North Gorgon 1 that is observed as a pervasive, albeit minor late stage mineral. The Rayleigh distillation curves for siderite precipitation, using fractionation factors from Carothers et al (1988), are plotted on Figure 2, assuming that the initial CO_2 -rich gas charge contained 16 mol% CO_2 . The data from the Rankin trend closely follow the distillation pathways for siderite precipitation at temperatures between about 100 and 200°C. The distillations curves for other carbonate phases would fall on similar trajectories as shown in Gilfillan et al. (2009).

Other options for the observed chemical and isotopic trends are dissolution trapping of CO_2 from the migrating gas as suggested by Gilfillan et al. (2009), or mixing of two gases with different signatures. For dissolution trapping to effectively explain the data, fluid pH in excess of 7 would be needed to drive carbon to the light isotopic values observed. Furthermore, in the absence of effective mineral buffers, CO_2 dissolution would rapidly decrease pH; an effect that would prevent $\delta^{13}C$ from attaining lighter values. As for gas mixing, we find a strong positive correlation between CO_2 % and $\delta^{13}C$ CO_2, $\delta^{13}C$ methane, $C_1/C_2{+}C_3$ whereas $\delta^{13}C$ ethane remains invariant for the Rankin trend gases. The latter is consistent with ethane contribution predominantly from the initial wet gas charge while the later charge is CO_2-rich dry gas. However, there are two main factors that might go against such a hypothesis. Firstly, the theoretical mixing curve between the highest (CO_2 = 16.3%; ^{13}C CO_2 = -3.24‰) and lowest CO_2 (CO_2 = 1.4%; ^{13}C CO_2 = -14.8‰) values on the Rankin trend gases shows very little change in $\delta^{13}C$ at high CO_2 levels and therefore is not a very good fit to the Rankin trend data (Figure 2). Furthermore, if the late CO_2-rich gas charge entered the system from the south as described by Longley et al (2002) and migrated north, a mixing curve should show similar characteristics to a dispersion curve in spatial terms. However, when the CO_2 data is plotted as a function of distance from the source (assumed to be Gorgon 1), the trend is linear negative and not representative of a mixing front. We acknowledge that further data is needed to confirm our model and rule out the two alternative processes just described. Currently, carbon isotope data on carbonate cements and more gas analyses with noble gas isotopic measurements are planned to further constrain the origin(s) of and alteration process(es) within the Rankin trend gases.

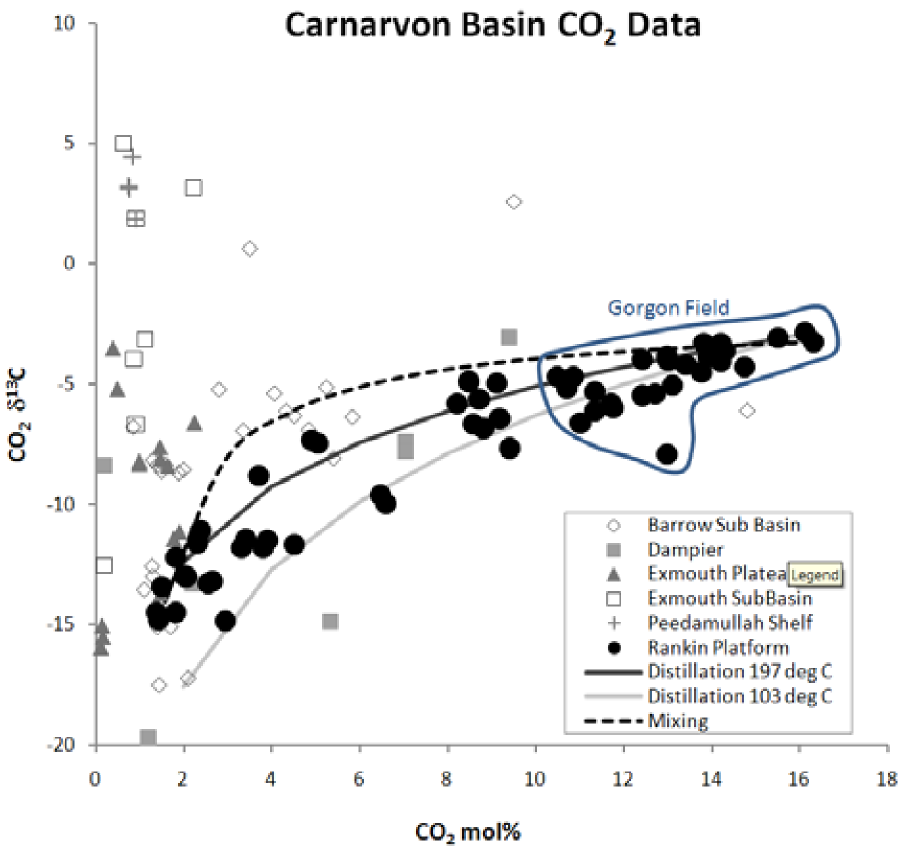

Figure 2. $\delta^{13}C$ *as a function of* CO_2 *for gases of the Carnarvon Basin. Gases of the Rankin trend fall very close to the Rayleigh distillation curves associated with siderite precipitation. Two distillation curves have been calculated at temperatures of 103°C and 197°C (fractionation factors determined at these temperatures).*

Limited $^3He/^4He$ data (R/Ra=0.02) on Gorgon field gases (Watson et al., 2004) indicate a purely crustal source for helium, which would imply that CO_2 gas in the Gorgon field was nonmagmatic in origin but resulted from carbonate breakdown at high temperatures. Once this CO_2 entered the stacked reservoir system at lower temperatures, reactions were initiated with primary Fe bearing labile phases leading to the formation of siderite. This reaction caused CO_2 to decrease concomitant with the carbon isotopes of the residual gas becoming lighter. We suspect that the structural high of the Rankin trend was responsible for channeling the CO_2 gas northward and preventing the gas from migrating into the bounding sub-basins to the east and west. Gases that migrated furthest from the source would have reacted the most and therefore be expected to show the greatest change in molecular and carbon isotopic compositions of CO_2, which is indeed the case. Within the Gorgon field, CO_2 concentrations decrease by nearly 50% from south to north along a distance of approximately 30 km. If the dynamics of CO_2 migration in the Gorgon field are similar to the far-field rates of movement for injected CO_2, then our results have important implications for the fate of injected CO_2 and suggest that mineral sequestration rates under certain conditions are more rapid than previously thought.

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