STRONTIUM ISOTOPE ($^{87}SR/^{86}SR$) CHEMISTRY IN PRODUCED OIL FIELD WATERS: THE IEA CO_2 MONITORING AND STORAGE PROJECT

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Abstract: EnCana's CO_2 injection EOR project at Weyburn Saskatchewan (Canada) is the focal point of a multi-faceted research program, sponsored by the IEA GHG R&D and numerous international industrial and government partners. More than yearly strontium isotope, trace element and dissolved gas surveys were conducted by INGV in conjunction with the thrice yearly borehole fluid sampling trips performed by the Canadian partners. This paper focuses on the Sr isotope monitoring. Approximately 25 samples were collected over three years for $^{87}Sr/^{86}Sr$ analyses. At Weyburn, a water-alternating-gas (WAG) EOR technique is used to inject water and CO_2 into the Mississippian Midale reservoir. $^{87}Sr/^{86}Sr$ ratios for produced fluids fall between 0.7077 and 0.7082, consistent with published values for Mississippian fluids and carbonate minerals. A small $^{87}Sr/^{86}Sr$ component of this produced fluid is derived from waters of the Cretaceous Mannville aquifer, which has been used for water-flooding EOR since 1959. The progressively more positive Sr isotope trend from 2001 to 2003 may be due to: 1) a smaller Mannville aquifer component in the water flooding process; and/or 2) the dissolution of Mississippian host rocks during the ongoing CO_2 injection. Evidence that $^{87}Sr/^{86}Sr$ values are approaching those of Mississippian host-rock values may point towards zones of carbonate dissolution as a result of continuing CO_2 injection. This hypothesis is strengthened by i) $\delta^{13}C$ data; ii) preliminary "gross composition" of dissolved gases (H_2S, CO_2, CH_4, He, H_2) and iii) by trace elements data.

Key words: CO_2 geological storage monitoring, EOR Weyburn oil field brines, Sr isotopes.

S. Lombardi et al. (eds.),
Advances in the Geological Storage of Carbon Dioxide, 243–259.

1. INTRODUCTION

The Weyburn oil field, presently owned and operated by EnCana Resources, is located approximately 120 km SE of Regina (Canada). After the discovery of the field in 1954 and its primary depletion in middle 1964, other tools were exploited, such as horizontal wells and water flooding. Since August 2000, CO_2-Enhanced Oil Recovery (EOR) has also been performed, with around 5000 tons/day of CO_2 being injected within the Mississippian Midale Beds oil reservoir at a depth of 1300-1500 m. The "Phase A1" early injection area currently comprises around 90 oil producers, 30 water injectors and 30 CO_2 injection wells (Wilson & Monea, 2004; Tian et al., 2004). Recent studies (Tian et al., 2004) stated that after 3 years of CO_2 injection oil production increases have been relatively slow, with responses only in 30 wells and increases in the average oil production per well from around 6 to 11 m3/day and an increase in the Gas/Oil Ratio of the Phase A1 area from around 20 to 33 m^3/m^3. The CO_2-storage efficiency decreases with an increase in the amount of CO_2 produced together with oil and water. Apart from industrial exploitation, the EnCana CO_2 injection EOR project at Weyburn is the focal point of a multi-faceted research program to "co-optimise" CO_2-EOR production and CO_2-geological storage within the framework of the Kyoto Protocol. This work is sponsored by the IEA GHG R&D and numerous international industrial and government partners, including the European Community (Riding & Rochelle, 2005).

Together with reflection seismic monitoring of the evolution of CO_2 distribution at depth (recent papers on http://www.uregina.ca/ghgt7/), the geochemical monitoring tools are mainly: i) soil gas geochemistry, to discover and monitor possible CO_2 surface leakage (Jones et al., 2005) - this tool is particularly important in geo-dynamic areas where the risk assessment of CO_2 geological storage sites must be very accurate (Quattrocchi, 2003, 2004); and ii) deep-reservoir fluid geochemistry (Gunter et al., 2000; Quattrocchi et al., 2004; Perkins et al., 2004, Shevelier et al. 2004). In the Weyburn case, we are dealing with a 3-phase reservoir (water-gas-oil) requiring complex chemical equilibria, diffusion and thermodynamic models (Nitao, 1996; Czernichowski-Lauriol et al., 2001; Quattrocchi et al., 2003; Chapoy et al., 2004; Tian et al., 2004, Le Nidre and Gaus, 2004).

INGV has conducted geochemical monitoring experiments from pre-injection ("Baseline", B0, August 2000) to the present day (September, 2004, see Appendix). The purpose of produced fluid and gas monitoring was to identify and ultimately quantify water-gas-rock reactions in the reservoir; in this paper we are focusing on the Sr isotope results. These data may help in reconstructing the evolution of the fluid reservoir prior to and during the injections stages (after Sunwall and Pushkar, 1979; Smalley et al., 1988). At

Weyburn, the situation of the reservoir composition is complicated by the water-alternating-gas (WAG) EOR technique, which has been used to inject water into the Midale beds over a forty year period. Unfortunately strontium isotopic compositions of the produced reservoir oil brines prior to upper-water flooding (i.e. prior to 1959) are not available, therefore we may only record the evolution of the oil waters since the beginning of CO_2-injection. Clearly, therefore, the isotopic signature of the Mississippian Midale reservoir waters had already been modified by previous mixing with waters from the overlying, hydraulically-separated, Cretaceous, Mannville aquifer. CO_2 geological storage is mainly limited within the oil reservoir stratum (around 20-30 m thick), considering that diffusion within, and reactivity of, the cap-rock is limited, with extremely low migration rates even in the highest impact scenario of CO_2 diffusivity / advection to the surface (Czernichowski-Lauriol et al., 2001; Le Nidre & Gaus, 2004).

In mature reservoirs, Sr isotopes can be used to differentiate original formation water from injected water for water-flood surveillance (Smalley et al., 1988; Bernaby et al., 2004 and references herein). In the present work Sr isotope data (partially discussed in Quattrocchi et al., 2003) are also supported by: i) major, minor and trace element chemistry; ii) the preliminary "gross composition" of dissolved gases; and iii) carbon isotopic ratios (after Hutcheon et al., 2003).

The use of Sr isotopic ratios for this application is possible by modeling two-component mixing in the framework of Sr isotope time-tuning curves (Veizel and Compston, 1974; Burke et al., 1982; Popp et al., 1986; McNutt et al., 1990; Jones et al., 1994; Denison et al., 1994; Bruckschen et al., 1995; Romer et al., 2003; Barnaby et al., 2004). The Sr isotopic composition of formation waters could yield a significant contribution for the characterization of reservoir properties, such as connectivity between strata and reservoir heterogeneity, and thus to evaluate regional fluid flow and to interpret the evolution of fresh and saline groundwaters. Data on the Sr isotopic compositions of oil field waters from a variety of reservoir rocks are abundant in a number of recent publications (Starinsky et al., 1983; Stueber et al. 1987; Russel et al., 1988; Franklyn et al., 1991; Chaudhuri and Clauer, 1993; Russell et al., 1988; Notsu et al., 1988; Nakano et al., 1989).

Strontium isotopes thus provide a potential tracer for both static (fluid flow on geological scale) and dynamic (fluid flow on production timescale) reservoir characterization in conjunction with conventional studies using seismic, log, core, well test and production data. Strontium isotopes are especially sound to better understand formation waters patterns because the Sr isotope composition of water samples collected at the well head is known to be identical to that of the subsurface fluid (Quattrocchi et al., 2003; Bernaby et al., 2004). By using a geochemical, multi-component approach to

better understand the ongoing formation oil/brine-related processes (Fisher et al., 1987; McNutt et al., 1987; Connolly et al., 1990), we may fully and better predict the long-term storage of CO_2 in the subsurface at the Weyburn oil-field, the most studied and multi-faced CO_2-EOR project in the world at present (Wilson & Monea, 2004).

2. METHODS

The Appendix summarises the INGV geochemical surveys during the Weyburn IEA-EC Project, from August 2000 to September 2004, for strontium isotope, major, minor and trace element and dissolved gas analyses. The laboratory analytical methods, applied to the liquid phase, were used after sampling the oil waters at the oil or gas well-head within collapsible, approx. 1-gal LDPE containers and allowing them to sit for a 1-2 minutes to achieve gravity separation of water and hydrocarbons.

- $^{87}Sr/^{86}Sr$ isotopic ratios were analysed from Sr dissolved in oil-water using standard mass spectrometry methods coupled with the following sample preparation technique (modified after Jones et al., 1994; Quattrocchi et al., 2003): 100 mL of sample is added to 50 mg of Na_2CO_3 to transform the sulphates ($SrSO_4$, $BaSO_4$) into carbonates. The final product of this reaction is filtered and washed to completely eliminate the sulphate ions. The residual on the filter was dissolved with 2.5 N HCl and the obtained solution was evaporated. The dry residue was dissolved with 2.5 N HCl and the strontium was separated from the other elements using a cation exchange resin (DOWEX resin type). This element is placed (as $Sr(NO_3)_2$) on a tantalium filament and the $^{87}Sr/^{86}Sr$ ratio is measured by a VG 54E mass spectrometer (University of Rome). The $^{87}Sr/^{86}Sr$ values were then normalised to the standard ratio of 0.1194. The analytical measurements are affected by an error expressed as 2 times the standard deviation (± 0,00002).
- The dissolved gas analytical method is based upon the partitioning of gases between the liquid and gas phase in the head-space of the sampler (Capasso & Inguaggiato, 1998). A *Chrompack*™ CP2002 portable gas-chromatograph is used in the laboratory to analyse CO_2, CH_4, H_2S, H_2, N_2, O_2, and light hydrocarbons (C_2-C_4), while He is also analysed with an ALCATEL mass spectrometer. As the dissolved gases were not sampled at borehole P,T,[X] conditions, it is necessary to correct the analytical data to the reservoir pressure of 16 MPa (1300-1500 m), considering also kinetic effects. The degassing during the rise of fluids from 16.5 MPa (reservoir pressure) to 0.1 MPa (atmospheric pressure) can be calculated following certain principles (Chapoy et al., 2004; Tian

et al., 2004; Renè Perez, personnel communication, work in progress). This can be done for each dissolved species, assuming a constant pump rate, sampling time and stripping effects before the immediate sampling of the oil waters at surface. At present we will only discuss the data gathered by sampling at 0.1 MPa pressure, as the "gross composition" of the reservoir evolution.

- Alkalinity is measured (U of C partner) by an ORION 960 titrometer (with 0.16M H_2SO_4) soon after the oil water sampling, considering $HCO_3 + CO_3$ and oily alkali.
- trace elements (partially discussed in this paper) were analysed by multi-component ELAN™ 6000 ICP for the following elements:, Be, B, Al, Si, Fe, Ni, Pb, Mn, Rb, Sr, Ag, Ba, Br, Cd, Cs, Cr, Cu, As, and Zn. Measurements are affected by an error expressed as 2 times the standard deviation.
- Major elements (partially discussed in this paper) are analysed by DIONEX HPLC; a charge imbalance of less than ± 5-10 % is considered acceptable.
- Geochemical Modeling, partially discussed in this paper (Cantucci B, PhD thesis in progress, INGV-University of Florence Italy 2004-2006), is accomplished by PHREEQC version 2.10 (Parkhurst and Appelo, 1999). The oil water composition is imposed both during kinetic evolution and in final equilibrium with the Vuggy and Marly rock compositions.
- Contour maps are created with the kriging technique within the program Surfer, while the "gross composition" of dissolved gases are discussed using normal probability plots (Sinclair, 1991).

3. RESULTS AND DISCUSSION

Approximately 25 samples were collected during the M 1 (March 2001), M 5 (July 2002), M 7 (March 2003), and M 9 (September 2003 partially analysed, not discussed) surveys for $^{87}Sr/^{86}Sr$ analyses. $^{87}Sr/^{86}Sr$ ratios found in the produced fluids from the Mississippian Midale beds fall between 0.7077 and 0.7082, consistent with published values for Mississippian fluids and carbonate minerals (approximately from 0.7076 - corresponding to 330 Ma ago - to 0.7082 corresponding to 360 Ma ago - Bruckschen et al., 1995; see Fig.1, Table 1).

Most of the sedimentary formation waters migrated over long distances prior to entrapment in the reservoir rocks from which the waters are sampled. Nearly two-thirds of the formation brines have higher $^{87}Sr/^{86}Sr$

ratios than marine Phanerozoic seawaters, whose values range between 0.7068 and 0.7062 (Veizer and Compston, 1974; Notsu et al., 1988).

Table 1. Sr isotope data for the M1, M5, M7 Weyburn oil-waters.

		Monitor 1	Monitor 5	Monitor 7
$^{87}Sr/^{86}Sr$	Min	0.70775	0.70800	0.70797
	Max	0.70825	0.70818	0.70818
	Mean	0.70798	0.70804	0.70807
$\delta^{87}Sr$	Min	-0.63	-0.28	-0.32
	Max	0.08	-0.03	-0.03
	Mean	-0.31	-0.23	-0.19
	Manville	Mississipian	1st survey	3rd survey
$^{87}Sr/^{86}Sr$	0.7073	0.7082	0.70798	0.70807

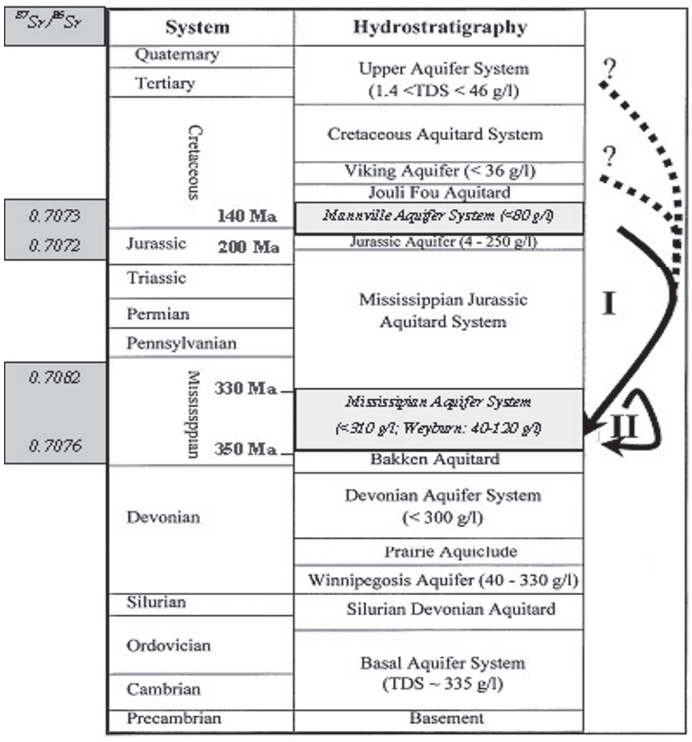

Figure 1. Williston Basin hydro-stratigraphy and nomenclature (modified from Bachu and Hicheon, 1996). Arrow (**I**) indicates that water from the Mannville Aquifer System is used for water-flooding. The symbols (?) are added to leave in question the use of upper aquifers for water-flooding. Arrow (**II**) indicates that water produced with oil is continuously re-injected.

The Pennsylvanian seawater (over the Mississippian ones) has $^{87}Sr/^{86}Sr$ values around 0.7083 (normalised to NBS 987 = 0.710255; Popp et al., 1986; Denison et al., 1994; Bernaby et al., 2004).

The Mannville aquifer, used since 1959 for water flooding of the Weyburn oil-field, is a Cretaceous arenite, with $^{87}Sr/^{86}Sr$ values between 0.7072 and 0.7073 which corresponds to an age of 140 Ma BP (Jones et al., 1994). A small component of the recycled fluid is derived from the Mannville aquifer and is re-injected into the Midale beds via a water-alternating-gas (WAG) EOR technique, as mentioned. Strontium isotopic compositions of the produced water prior to water flooding (i.e., prior to 1959) are not available. Other case histories describe the use of Sr isotopes to discriminate water-flooding injection components from the formation water (i.e., Smalley et al., 1988), mostly when the injected water has a Sr content and $^{87}Sr/^{86}Sr$ ratio which is different from the in-situ formation water. The lowest values of the Sr isotopic ratio found in the oil waters could represent a higher degree of mixing between the two aquifers (Fig. 2). We started to analyse the oil water Sr isotopes in 2001, around 40 years after the beginning of water flooding. Despite this fact we found Sr values of the oil water in the range of the Mississippian host rock (Midale reservoir), although a certain percentage of the Sr isotopic ratio could be referable to the Mannville component. Average Sr ratios and mass balance calculations suggest that as much as 25% of the produced fluid in 2001 was derived from the Mannville aquifer, decreasing to 15% in 2003.

The progressively more positive (i.e. higher) trend in the Sr isotopes from 2001 to 2003 may be due to: i) a smaller Mannville aquifer component in the water flood over the last three years and/or ii) the enhanced dissolution of Mississippian host rock during progressive CO_2 injection.

If the leaching of Mississippian host rocks is increased (as a consequence of CO_2 injection) it could shift the values towards the pre-water-flooding Sr isotopic "baseline" values, affected by 40 years of water-flooding which added a 25% Mannville component. In general terms, the lowest Sr isotopic ratio values found thus far may represent a higher "contamination" of Mississippian Midale fluids by re-injected Mannville flooding water. It may involve progressively lower Sr isotopic values which may coincide with the highest injection volumes of Cretaceous waters, as there is no natural communication or mixing between the two aquifers (no fluid pathways have yet been found in the highly impermeable Jurassic-Triassic Watrous Formation). Considering this general process, we observed instead a progressive decrease of the Mannville "contamination" from 2001 to 2003. Therefore, the more probable scenario is that the $^{87}Sr/^{86}Sr$ values are progressively approaching the Mississippian host-rock values and may point towards zones of carbonate dissolution resulting from continued CO_2

injection. Carbonate minerals within the Midale beds, which were precipitated from waters during the Mississippian, would have Sr ratios consistent with what would be considered a "baseline" isotopic composition. The leaching of strontium during dissolution of these minerals would drive the Sr composition of the produced waters to heavier values, thereby masking the Mannville aquifer contribution.

In summary, the sectors (Fig. 2) characterised by the lowest Sr isotopic ratio values represent "contamination zones" of Mississippian Midale fluids by re-injected Mannville flood water. These zones exhibit lower Sr isotopic values that may coincide with the highest injection volumes of Cretaceous water. Concurrently, the average field-wide $^{87}Sr/^{86}Sr$ values are approaching Mississippian host-rock values and may point towards sectors of the field (Fig. 2) characterised by higher carbonate dissolution, as a result of continued CO_2 injection.

This hypothesis is strengthened by the $\delta^{13}C$ data available up to September 2004, as well as by other chemical data of previous surveys (Hutcheon et al., 2003 and papers in http://www.uregina.ca/ghgt7/). Using $\delta^{13}C$ values of produced bicarbonates and CO_2, the University of Calgary has outlined both injected CO_2 and carbonate mineral dissolution in the reservoir.

The available Sr-C isotopic ratios in the produced fluids (up to September 2004) corroborate the hypothesis of chemical and isotopic input from dissolved carbonates, although further surveys could modify this statement relative to early stages of the water-rock interactions in the oil reservoir. Initially, the injected CO_2 had a distinctive $\delta^{13}C$ signature of –35‰., however since 2002 CO_2 recycling and re-injection has changed this signature to between –20 to –25‰. Therefore the second strontium isotope scenario outlined above fits well with the $\delta^{13}C$ data. The Sr isotopic ratio in produced fluids tends to increase with time, suggesting input from dissolved strontium bearing carbonates.

Sr isotopic ratios of minerals (anhydrite, dolomite, calcite of the Midale and Vuggy Formations) from the Weyburn reservoir Phase A1 area are available from Queen's University. These data are consistent with the produced Mississippian brine because they range from 0.70567 to 0.708995, with an average value of 0.708134 ± 0.0001563. It is possible to assume that the dissolution of these minerals would push the Sr isotopic ratio of the oil waters from values closer to 0.7073 (Cretaceous Mannville aquifer) towards the reservoir values of 0.7076-0.7082 (Mississippian Midale-Vuggy), again strengthening the second Sr isotope theory mentioned above.

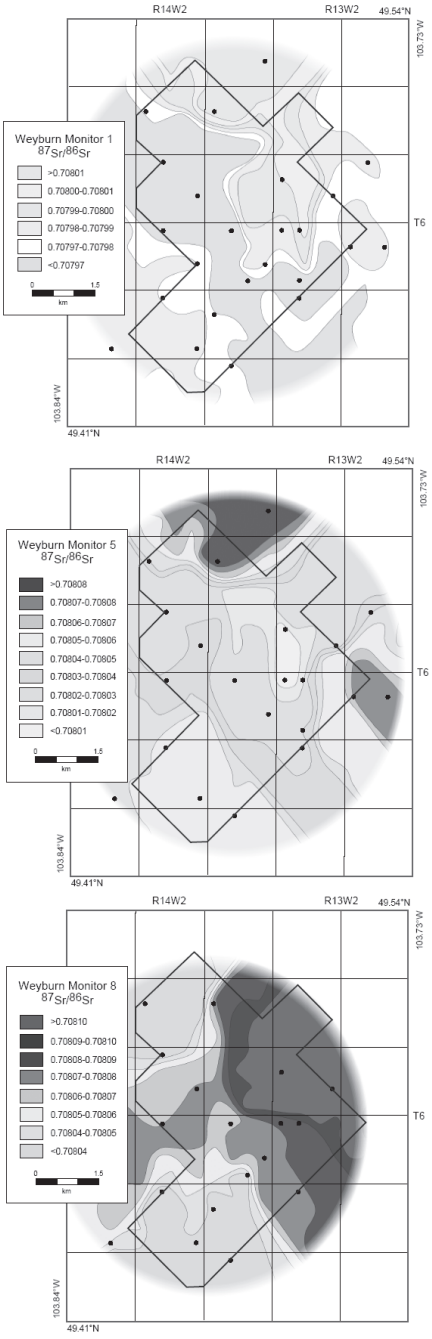

Figure 2. Contoured Sr isotopic ratio maps (a_1, b_1, c_1) from 2001, to 2002, up to 2003.

If a number of sources exist, evolving from varied mixed compositions, it could be represented by binary diagrams as 1/Sr versus $^{87}Sr/^{86}Sr$ (Fig. 3 a), where coexistent linear trends are often found (Chaudhuri and Clauer, 1993). An isotopic trend with a very high positive slope could be explained in terms of the mixing of Sr derived from two sources which are markedly different in both their isotopic composition and Sr contents. On the other hand a low positive slope in the isotopic trend could be explained by either mixing between two sources of Sr or dilution of a single source of Sr. In the Weyburn case, considering only the first two analysed surveys (Sr available only for M1-2001 and M5-2002; see Fig. 3 a), it is clear that a unique "gross" population effectively changed in terms of mixing from 2001 (lower $^{87}Sr/^{86}Sr$ ratios and higher Sr concentrations closer to the Mannville component) to 2002 (higher $^{87}Sr/^{86}Sr$ ratios and lower Sr concentrations closer to the Mississippian component). A small group forms an anomaly of relatively low Sr values (WEY 35, 42 and 45 - wells corresponding to the vertical EnCana wells 12-25 (6-14), 14-23 (6-14), and 12-19 (6-13), respectively), which may have been caused by dilution, considering also the slightly lower salinities as a whole. Alternatively a local differential immobilization by sulphates-carbonates could be possible ("short term" geochemical modelling considering kinetic parameters is in progress, while "long term" modelling has been partially completed; Perkins et al., 2004). The WEY 5 well (corresponding to the vertical EnCana well 1-11 (6-14)) seems to be pertinent to slightly deeper strata.

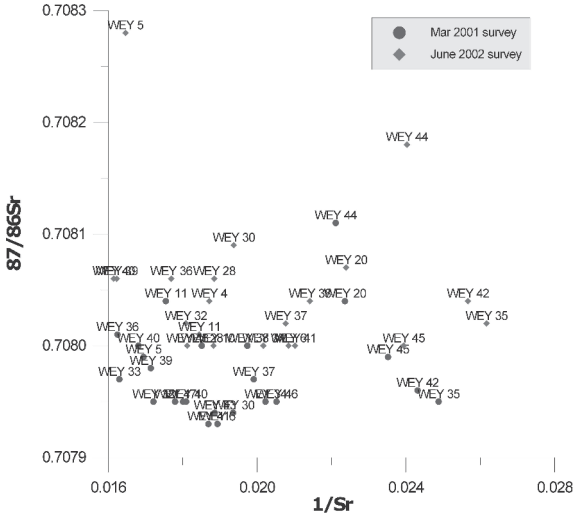

Figure 3. Binary diagrams of (a) $^{87}Sr/^{86}Sr$ versus 1/Sr; (b) $^{87}Sr/^{86}Sr$ versus Na/Cl of the Weyburn oil-brines (M1 and M5 surveys).

Albitization of K-feldspar has been used (Chaudhuri and Clauer, 1993) to explain high-slope points in the graph, in other words direct replacement of K-feldspar or replacement of K-feldspar by some other minerals (calcite, anhydrite, etc…) which in turn are replaced by albite. This effect of albitization would result in an elevation of the Sr isotopic ratio in the waters without any significant change in the Sr content of the water. In the Weyburn case the "end member" component (as defined by Chaudhuri and Clauer, 1993) common to all the analysed waters may be identified as one whose $^{87}Sr/^{86}Sr$ ratio is closer to the Mannville component used for water flooding, progressively changed during the CO_2 injection and consequent rock dissolution. This is also suggested by the $^{87}Sr/^{86}Sr$ versus Na/Cl binary diagram (Fig 3 b), where the Na/Cl ratio is higher as a whole for the M1-2001 waters than for the M5-2002 waters and vice versa for the $^{87}Sr/^{86}Sr$ ratios. As a whole, the Weyburn data do not display a trend of higher $^{87}Sr/^{86}Sr$ ratios if the Na/Cl molar ratio approaches 1:1, as found in the literature (i.e., solutes are increasingly dominated by halite dissolution, as could also occur for the Weyburn oil brines; Burke et al., 2004). Moreover the past water-flooding modified the original $^{87}Sr/^{86}Sr$ and Na/Cl binary relationship, now affected by the host rock dissolution linked to the new industrial CO_2 injection.

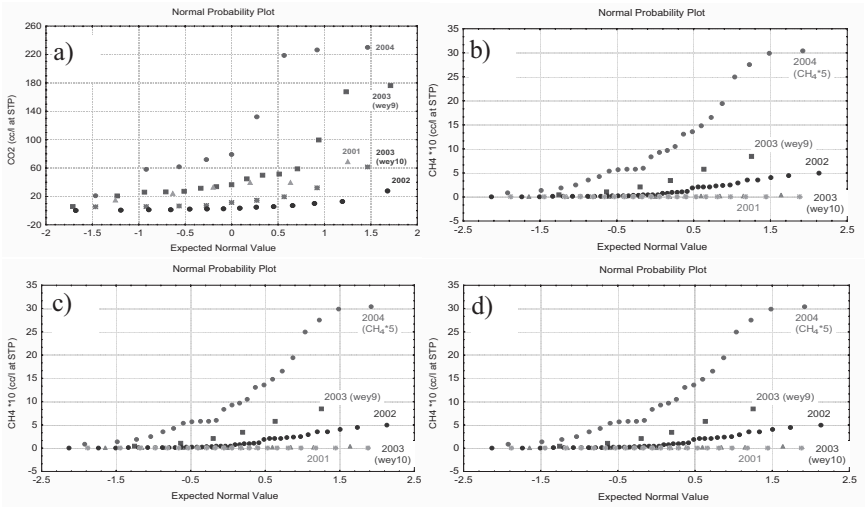

Figure 4. Normal probability plots (after Sinclair; 1991) for the Weyburn "gross composition" of dissolved gases (atm. P.); (a) dissolved CO2; (b) dissolved CH4; (c) dissolved H2S; (d) dissolved H2. All data are reported as cc/L (STP), except H2S which is reported as composition % in the head-space (not as total dissolved concentration).

Also the available "gross composition" of the dissolved gases (see the limitations in the methods paragraph detailed in Quattrocchi et al., 2003 and in Riding & Rochelle, 2005) are helpful in jointly interpreting the Sr isotopic data. Available dissolved gas data strengthens the second hypothesis, i.e. enhanced Mississippian rock dissolution. In oil brines CO_2 solubility is dependent on T, P, fugacity coefficient, salinity (eq. NaCl), and detailed chemical composition. Theoretically, from chemical equilibria calculations (Czernichowski-Lauriol et al., 2001; Perkins et al., 2004), more than 1 mole of CO_2 can dissolve into 1 kg of water for typical Weyburn reservoir brines (50°C, 14 MPa, salinity range from 35 to 110 g/l).

The steep salinity gradient in the Weyburn area will greatly affect CO_2 solubility, migration and reactivity as demonstrated by the regional 2D modelling of natural fluids in the Mississippian aquifer (BRGM deliverables within the EC Weyburn Project, Riding & Rochelle, 2005). Normal probability plots (Sinclair, 1991) of the 2001-2004 dissolved gases in the Weyburn oil-waters (Fig. 4) exhibit, as mentioned, the "gross composition" evolution, before the "degassing correction". We found a general increase of the main dissolved gases (CO_2, CH_4, H_2S) for the different surveys (2001-2004), parallel to the increase of the Sr isotopic ratio increases. In particular progressive increases of dissolved CO_2, CH_4 and H_2S were observed, while H_2 initially increased then it decreased after 2002. Dissolved He, after an abrupt early increase, decreased after 2003; the initial increasing stage was very probably due to the release of accumulated crustal He from the rock-matrix during CO_2-driven dissolution (Torgersen & Clarke, 1987).

Our dissolved CO_2 data are essentially consistent with the Tian et al. (2004) calculations, performed following the Material Balance Equation method (MBE). These authors stated that approximately 86% of injected CO_2 can be dissolved into reservoir oil, 7% into water and 7% will occur as free gas. This occurs mainly in the early stages of CO_2 injection (Gunter et al., 2000). Moreover with the increase of CO_2 injection time, the percentage of CO_2 dissolved in oil decreased by a small degree and the percentage of CO_2 dissolved in reservoir water and as free CO_2 increased slightly. This is because progressive oil recovery will result in a decrease in the average oil saturation and increase in the average water saturation. As a result, for the authors, the injected CO_2 had more chance to contact (dissolve in) the water phase than the oil phase, even though under reservoir conditions the solubility of CO_2 in oil is larger than that in water (b factor).

The increase of both dissolved gases and selected trace metals (Quattrocchi et al., 2003, reported in Riding & Rochelle, 2005) during the Phase 1 A is consistent with the second Sr isotope scenario outlined above, which highlights host-rock dissolution as the main process during the B0-M1-M9 (i.e. injection) period. During the first year of CO_2 injection

preliminary trace element data in the Weyburn oil waters showed an initial increase of Al, Be, Ba, Fe, Cr and a decrease of Ni, Cu, Zn. This different behaviour among trace metals depends mainly on redox/acidic geochemical barriers (Perel'man, 1986) developing within the reservoir and mainly around the injection wells during CO_2 injection.

Our available trace metals data for the Weyburn oil-field could be interpreted within the framework of the Basinal Brine Theory (Kharaka et al., 1987), such that high dissolved metal concentrations in the presence of aqueous sulphide species require acidic solutions with pH values lower than those generally obtained in basinal brines. Very acidic solutions in some sectors of the reservoir are assured by CO_2 injection. From the mixture it will lead to non-equilibrium in the reaction: H_2S (gas) > H_2S (aqu) and will result in the transfer of gas to the water phase (Kharaka et al., 1987) in agreement to our dissolved H_2S data. This process will continue until essentially all the metals are precipitated as sulphides, as suggested by early PHREEQC chemical equilibria calculations (in progress and outlined in Quattrocchi et al., 2003). We suggest, in the frame of future Weyburn field monitoring, to merge more strictly the periodically measured parameters pertaining to different phases, i.e., dissolved H_2S together with the H_2S "free gas phase" (U of C data), as well as with the trace metal contents, to also study the sulphide precipitation/dissolution equilibria. Both chemical dissolution of the Mississippian Midale-(Marly)-Vuggy oil host-rocks and CO_2 dissolution as part of "solubility trapping" (Gunter et al., 1993; 1997, 2000) are clearly outlined by merging the Sr isotopic ratio evolution with other isotopic and chemical data collected for Weyburn oil waters (Hutcheon et al., 2003; Perkins et al., 2004; Shevelier et al., 2004).

4. CONCLUSIONS

From the Sr isotopic data of the Weyburn oil brines collected during the CO_2 EOR early injection period spanning from March 2001 to September, 2003 we found an evolution of the water-rock interaction processes. The progressively more positive (i.e., higher) trend in the Sr isotope ratios from 2001 to 2003 is suggested to be due to the dissolution of the Mississippian host rock. Carbonate minerals within the Midale beds precipitated from waters during the Mississippian, and therefore would have Sr ratios consistent with what would be considered a "baseline" isotopic composition. The leaching of strontium from the dissolution of these minerals would drive the Sr composition of the produced waters to heavier values, thereby masking the Mannville aquifer contribution. This hypothesis is strengthened by the $\delta^{13}C$ data, by the Sr isotopes of the reservoir rocks as well as by the

evolution of other chemical data (dissolved gases, trace metals, major element chemistry).

In summary the Sr isotopic ratio in produced fluids corroborates the hypothesis of chemical and isotopic input from dissolved carbonates, strengthening the foreseen prevalent solubility trapping of CO_2 during the 2001-2004 Weyburn early CO_2 injection phase.

Results of this work suggest the usefulness of the Sr geo-chronological curves for the study of evolving CO_2 geological storage studies. The comparison between newly produced oil brine data and the data of Bruckschen et al., 1995, relative to the Dinatian Sr isotope record, show the potential of the Sr isotope geo-chronological curve, together with all the literature data.

ACKNOWLEDGEMENTS

We are grateful to the European Community which funded the Weyburn Project (Contract N. ENK5-2000-00304). A particular thank you is extended to Ken Ferguson and Dan Fradette working at the Weyburn EnCana oil field.

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APPENDIX

Table 2. INGV geochemical surveying in the frame of the Weyburn IEA-EC Project, from August 2000 to September 2004. At the end of the M 8 survey the injected CO_2 amount since the beginning of the Phase A1 was around 1.7 Ml m^3 CO_2.

Survey	Dissolved gases	Chemical analyses	$^{87}Sr/^{86}Sr$ ratio
Baseline (B 0), Aug. 2000	no	no	partially
Monitor 1 (M 1), March 2001	yes (few)	yes	yes
Monitor 2 (M 2), July 2001	no	no	no
Monitor 3 (M 3), Sept. 2001	no	no	no
Monitor 4 (M 4), March 2002	no	no	no
Monitor 5 (M 5), June 2002	yes	yes	yes
Monitor 6 (M 6), Sept. 2002	no	no	no
Monitor 7 (M 7), April 2003	no	no	yes
Monitor 8 (M 8), June 2003	yes	no	no
Monitor 9 (M 9), Sept. 2003	yes	partially	partially
Monitor 10 (M 10), March 2004	yes	partially	partially
Monitor 11 (M 11), Sept. 2004	yes	partially	partially