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STABILITY OF NATURAL GAS IN THE DEEP SUBSURFACE

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FINAL REPORT TO THE DEPARTMENT OF ENERGY

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SUMMARY

Natural gas is an important fuel that is likely to become increasingly important in the future. The deepest parts of many sedimentary basins are unexplored and remain frontier areas for natural gas exploration. Fundamental questions on the depth limits (if any) for natural gas survival and the processes operating to produce inorganic components (such as carbon dioxide, nitrogen, and hydrogen sulfide) remain unanswered. The composition of ultra-deep gas can be calculated thermodynamically, and actual samples can be obtained from fluid inclusions that sampled gases present in the deep growth environment. Both methods were used in this study.

A computer program has been written to calculate the equilibrium composition of gases in systems with up to 70 compounds and 20 phases at specified temperatures and pressures. It uses a free energy minimization algorithm. Calculations have shown that gas composition depends critically on rock composition, with carbonates, sulfur-bearing minerals, and iron-bearing phases being especially important. Samples of deep gas can be trapped in fluid inclusions and we have designed and built a system for analyzing individual fluid inclusions in minerals. It incorporates a pair of fast-scanning quadrupole mass spectrometers that operate under computer control to provide an analysis of the burst of gas produced as each fluid inclusion thermally ruptures in vacuum. For inclusion-rich samples a large number of inclusions can be analyzed in a few hours using a 10-20 mg sample.

The capabilities of the system have been demonstrated by analyzing samples from the gas-prone Arkoma Basin of Oklahoma and Arkansas. Basin modeling of this once deeply-buried basin was used to give a self-consistent estimate of paleotemperatures, and these were then used with the thermodynamics program to calculate gas composition in the eastern and western parts of the basin. Fluid inclusions in fracture-filling calcites were methane-rich in the west, but CO₂-rich in the east, and this was consistent with the compositions calculated thermodynamically. The composition of gases in inclusions in carbonate overgrowths from the Minnelusa B sand in the vicinity of the Raven Creek Field, Powder River Basin were studied in an attempt to establish hydrocarbon migration pathways. Methane and trace C₂ contents appear to define the migration routes. Analyses of inclusions in low-grade metamorphics from central Pennsylvania have also shown the general direction of migration, with methane moving from the organic-rich Reedsville Shale up into the overlying Bald Eagle and Juniata Formations. Methane-rich inclusions are common in quartz from the Reedsville and this seems to have been the source of the reducing fluids that locally changed the color of the overlying Bald Eagle from red to green.

We have developed the capability for calculating gas composition and for analyzing individual fluid inclusions. These techniques have been used in a wide variety of geologic studies.

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1. INTRODUCTION

Natural gas is becoming increasingly important as a fuel because of its widespread occurrence and because it has a less significant environmental impact than oil. Many of the known gas accumulations were discovered by accident during exploration for oil, but with increasing demand for gas, successful exploration will require a clearer understanding of the factors that control gas distribution and gas composition.

Natural gas is generated by three main processes. In oxygen-deficient, sulfate-free, shallow (few thousand feet) environments bacteria generate biogenic gas that is essentially pure methane with no higher hydrocarbons ("dry gas"). Gas is also formed from organic matter ("kerogen"), either as the initial product from the thermal breakdown of Type III, woody kerogens, or as the final hydrocarbon product from all kerogen types. In addition, gas can be formed by the thermal cracking of crude oil in the deep subsurface. The generation of gas from kerogen requires higher temperatures than the generation of oil. Also, the cracking of oil to gas requires high temperatures, so that there is a general trend from oil to gas with increasing depth. This produces a well-defined "floor for oil", below which crude oil is not thermally stable. The possibility of a "floor for gas" is less well documented and understanding the limits on natural gas occurrence was one of the main objectives of this research.

A major problem in establishing deep gas composition has been the availability of suitable samples. Direct sampling of deep gas is limited by the depth and location of available wells, and there have been no generally-applicable techniques for directly analyzing the composition of deep gas. Rock samples can be retrieved by drilling and coring in the shallow part of the crust which, for practical purposes, means down to depths of approximately 25,000 ft (7,620 m). In very deep holes coring is expensive and risky. The cores are flushed with drilling mud and gases are lost from samples in an unpredictable way as they are brought from the deep, high temperature, high pressure environment to the surface. For cuttings, the circulation time from bit to surface may exceed eight hours -- and during this interval nothing can be done to prevent sample deterioration. A major problem has been that the standard methods of organic geochemistry rely on analyzing rock and fluid samples, and there are no samples available from depths not yet drilled. We have tried to circumvent these problems by analyzing deep gas samples trapped in fluid inclusions in minerals and cements that crystallized deep in sedimentary basins. These microscopic cavities in crystals form as the host minerals grow, and they trap samples of the gases present in the growth environment. Subsequent deep drilling, or the geologic processes of uplift and erosion, can bring these samples to the surface. Even these samples are spatially

limited, but interpolation and extrapolation can be carried out using thermodynamic software developed to calculate deep gas composition.

2. ANALYTICAL CAPABILITIES DEVELOPED

A major emphasis of the research program has been the development of analytical techniques for analyzing the gases in individual fluid inclusions. Fluid inclusions have presented a difficult analytical problem because, in general, minerals contain multiple populations of inclusions that have formed at different times, and therefore, sampled the surrounding growth medium at different times (Roedder, 1984, 1990; Goldstein and Reynolds, 1994). Any method that involves analysis of the combined contents of a large number of inclusions will contain an unknown mixture of primaries and secondaries. For example, crushing the host mineral will release gases from both primaries and secondaries (Pavlun et al., 1986). In addition, crushing generates many new superclean fracture surfaces that remove gases by adsorption and change the overall composition (Barker and Torkelson, 1975). An alternative way to open inclusions is by heating, but again, collection of gases released over some temperature range gives a mixture of gases from both primaries and secondaries. Separate analysis of each individual inclusion, together with careful heating/freezing stage microscopic documentation, seems to offer the only way of getting compositional information for the primaries without the complications caused by the presence of later populations of inclusions.

Our philosophy has been to try and develop a technique that will permit the rapid analysis of a large number of individual inclusions so that multiple populations can be distinguished on compositional grounds. Clearly, detailed microscopic examination and careful sample selection improve the validity of the interpretations. The main disadvantage of this approach is that the gas composition for a specific, pre-selected inclusion cannot be obtained. In contrast, the commonly-used methods of laser Raman spectroscopy and microFTIR can analyze specific inclusions, but they require considerable time for set up and analysis. Using these techniques is time consuming and as a consequence only a relatively small number of inclusions is usually analyzed. Also, when individual inclusions are analyzed with these techniques there is a tendency to use the inclusions that are easiest to work with, i.e. the big ones - and these are just the inclusions that are most likely to suffer from the effects of stretching, necking, leakage, etc. However, these methods do have the advantage of being non-destructive.

In 1982 Barker demonstrated the possibility of analyzing gases in individual fluid inclusions and subsequently designed and built a computer-controlled, fast-scanning mass spectrometer (Barker and Smith, 1986). The experience gained with that system was later used to design a "second generation" system that took advantage of the vastly improved memory and computing power of the newer PCs. This dual mass spectrometer system ("DMS") used two UTI 100C quadrupole mass spectrometers operating in parallel (Figure 1). The analog output from the two instruments was digitized and stored on magnetic tape for subsequent offline processing (Barker and Underwood, 1992). The analytical system has continued to evolve, and in the last year we have made a major change in the system by replacing the 12-bit analog-to-digital converter (ADC) with a new, high-speed (200kHz), 16-bit ADC. We also took this opportunity to replace the PC-AT with a 486 model, and to move the processing carried out on the Alliant minisupercomputer, first to an HP/Apollo workstation, and then later to a PC (Pentium). These changes were not without their problems. The new ADC board appeared to suffer from cross talk and had to be shipped back to the manufacturer. The new 486 PC also developed problems that required return to the maker. All these changes consumed considerable time. The Post Acquisition Data REduction ("PADRE") program continues to provide essentially unlimited processing time that is not constrained by the high scan speeds of the quadrupole mass spectrometers. The most recent change has been to replace the 9-track tape with a CD-WORM ("Write Once, Read Many times"). CDs store approximately three times as much data as the tapes and make it possible to carry out longer heating runs. One option here is to use slower heating rates, which allows more time for the gas to be pumped away. This decreases the gas background and smaller inclusions can be analyzed.

The pulse triggering system has generally worked well. The system is phase locked to the AC power line, and operation is analogous to using a strobe light to watch a rotating object in that periodic noise related to the power line becomes stationary in the data fields. The noise is automatically removed with the background. The timing circuit initiates mass spectrometer sweep and ADC for both mass spectrometers, so that the overall effect is to reduce background noise and permit analysis of smaller inclusions.

The analytical procedure involves heating minerals containing fluid inclusions in a vacuum system that forms the inlet to the DMS system. As temperature rises, phase relationships in the inclusions may change in such a way that the pressure for the contents increases rapidly, ruptures the host mineral, and releases the gases for analysis. The release of an individual volatile component as a function of rising temperature can be monitored with a mass spectrometer by tuning it to a single value of

Figure 1 : Schematic diagram of the dual mass spectrometer ("DMS") analytical system, and the data flow through it. The design of the vacuum system is symmetrical so that pumping pathways are the same for both mass spectrometers. (Details of specific components are given in Barker and Underwood (1992), and recent changes are outlined in the text).

m/z (Delaney et al., 1978; Garcia et al., 1979; Barker and Robinson, 1984; Jones and Kesler, 1992) (see, for example, Figure 3). The detailed shape of a burst shows that the full peak width at 95% of maximum response is slightly greater than 25 msec. Thus the problem of analyzing the volatile contents of each inclusion reduces to one of getting a complete analysis within the 25-msec time constraint imposed by an individual burst. Most commercial quadrupole mass spectrometers require about 100 msec/mass spectrum. Since the UTI 100C instruments used in our system can scan from mass 1 to mass 300 in 75 msec, a mass range from 2-70 can be scanned in under 20 msec. The addition of a second mass spectrometer in parallel makes it possible to double the mass range to include 70-140 amu, or to include any 70 amu mass range up to an upper limit of 300 amu.

The composition of gases in each individual fluid inclusion can be displayed as a mass spectrum (AB of Figure 2), but a wide range of other displays are now possible (Table 1). Data are available as an ASCII file that can be transferred to a commercial plotting program (such as *SigmaPlot*) for specialized data display. Examples of 3-D plots obtained using *SigmaPlot* are shown later.

Ternary diagrams are a useful way of showing whether more than one population of inclusions is present. They also provide a check on the accuracy of the analyses by showing the amount of scatter. The option of isolating and displaying any size range separately is useful in recognizing data from very small inclusions where instrument noise becomes a significant part of the response. Often the points on ternary diagrams plot along a line showing mixing. Examples of the various display options are shown throughout this report. In general, software development is an ongoing process that responds to the needs of the particular geological studies being carried out.

Temporal resolution of inclusion ruptures is better than 50 msec and inclusion ruptures separated by greater time intervals will be recorded as separate bursts. Although it is assumed that single, sharp peaks (S, Figure 3) are due to the rupture of only one inclusion, it is possible that bursts may occur too rapidly to be recorded separately. If both inclusions have the same composition there will be no problem, but if compositions are different, an intermediate gas composition will be obtained. Complex bursts seen on monitoring traces (M, Figure 3) show pressures rising to the maximum in a series of steps and can be examined in more detail by expanding the time scale as illustrated. It is thought that when a large inclusion imbedded in a plane of secondaries ruptures, the plane "unzips" and a large number of smaller inclusions rupture in sequence to give a complex burst shape. The monitored release of water (18 amu) and hydrogen sulfide (34 amu) from a Smackover calcite shown in Figure 3 has both complex (M) and simple (S) bursts. In this case the PADRE software will treat

Figure 2 : (Center) Schematic diagram showing the scanning of sequential mass spectra through time (= temperature); (Top) Mass spectrum corresponding to an individual fluid inclusion burst; (Bottom) Release of water as a function of time showing bursting inclusions over approximately one minute.

Figure 3 : Monitoring of water (18 amu, top trace) and hydrogen sulfide (34 amu, bottom trace) from bursting inclusions in a Smackover calcite cement. (This trace corresponds to Trace XY of Figure 2.) The horizontal scale is 100 sec. The upper part of the figure shows an expanded trace across a complex burst ("M"). (From Barker and Underwood, 1992.)

point A of the multiple burst M as the top of the peak, and will subtract the preceding background and store the resulting mass spectrum. Since there is a built-in delay before PADRE begins searching for the next inclusion burst the rest of complex burst M will be ignored.

TABLE 1 : Data Display Options

MASS SPECTRA (2-70 amu, or 2-140 amu)

Individual	-- linear abundance scale
	-- log abundance scale
Summary	-- sum of all individual mass spectra
Format	-- raw spectrum
	-- background-corrected rupture

TERNARY PLOTS (any three amu's as corners)

Total population
 Subpopulations selected by size
 (size of max. peak, size of specific amu, or size of burst)
 Subpopulations selected by temperature
 Specific spectra/specific bursts
 Raw spectra or background-corrected bursts

3-D PLOTS ("SIGMAPLOT") (any three amu's can be selected)

Plot ratios of components
 Combine populations from different analyses

MONITORING (any three amu's plotted together)

Entire heating range
 Any subrange (down to individual bursts selected
 by temperature or spectrum number)

Quantitative analysis by mass spectrometry requires calibration data for both cracking patterns and relative sensitivities of the gases being analyzed (Landis and Rye, 1989). In some cases natural minerals with suitable fluid inclusions can be used for calibration. This has the important advantage that the calibration data are acquired in exactly the same way as the analytical data. For example, the 16 amu-17 amu-18 amu cracking data for water has been obtained from water-dominated inclusions in Arkansas quartz, and Barker and Sullivan (1989) reported methane cracking data

obtained using quartz samples that had inclusions containing methane in large excess over water (so that the water contribution at 16 amu was negligible). A calibration line (Figure 4) has been built to provide samples of pure gases and gas mixtures of known composition. It contains cylinders of pure gases attached to a stainless steel line by double valves and a capacitance manometer that gives the pressure as each additional gas component is added to a mixture. The most difficult problem in calibration is establishing the relative sensitivity of water and we have used two different methods. The most direct involves the thermal decomposition of cesium bicarbonate (Figure 5) to give a 2:1 mixture of carbon dioxide and water:

The other method involves determining the mass spectrometer response to the water in a magmatic glass that had been well-studied using FTIR (Figure 6). Weighed amounts of glass and lead carbonate were then heated together to give a known water-carbon dioxide mixture. The first method has several advantages and is the method of choice.

Water can be treated like any other gas over the time scale of a bursting inclusion and adsorption does not seem to be a problem. This is confirmed by detailed examination of burst shapes, especially for the pumpdown segments. These show that the shape is essentially the same for methane (which is not likely to be adsorbed) as for water and hydrogen sulfide. Even at the high scan speeds being used, the mass spectrometer and associated interfacing are capable of generating and processing high quality data. Examples illustrating system performance are given below.

Optical examination of fluid inclusions in support of the mass spectrometric gas analysis is extremely important and samples are routinely examined before analysis. We have used a Linkam THMS 600 Heating/Freezing stage installed on a Nikon Optiphot2-pol microscope. Heating is controlled by a TMS 92 Programmer with the temperature measured by a 1/10th Din standard Class A platinum resistor that has a resolution and accuracy of 0.1 °C. Cooling is controlled by a Linkam TLNP2 system using liquid nitrogen as the coolant. The stage has been calibrated with synthetic fluid inclusions with known phase transition temperatures, and with ultrapure chemical compounds that have well-documented melting points.

3. THEORETICAL PROCEDURES

At intermediate depths the reactions that generate oil and gas (together called petroleum) occur at relatively low temperatures and are *kinetically controlled*. In

Figure 4 : Calibration line that provides pure gases and known synthetic mixtures. It is attached to the mass spectrometer system when required for calibration.

Figure 5 : Monitoring curve showing the release of water and carbon dioxide from thermally decomposing cesium bicarbonate.

Figure 6 : Water measured mass spectrometrically and by FTIR for 5 MORB glass samples of different weights.

contrast, at the temperatures and pressures encountered in deep reservoirs, gas composition closely approximates *thermodynamic equilibrium* (Figure 7), and then the actual composition is controlled by reactions involving water and the surrounding minerals. Gas that is currently in shallow reservoirs, but has migrated up from depths greater than about 25,000 ft (7,620 m), will have a gas composition controlled by the mineral assemblage present during the deep burial. At depths greater than X in Figure 7 gas composition is controlled thermodynamically, and so depends on temperature, pressure, and rock composition. On uplift the rate at which reequilibration is achieved will steadily diminish, until at some point the kinetics become so unfavorable that the reaction is "frozen in". During uplift from depth Y to depth X (Figure 7) gas composition continues to adjust rapidly and remains in thermodynamic equilibrium at each transient set of ambient conditions. Thus, for a given bulk composition, the actual composition at depth X will be the same regardless of the depth represented by Y. This suggests that the gas composition in shallow reservoirs that were once deeply buried is not controlled by the greatest depth of burial, but rather by the shallowest depth at which the gas composition was in thermodynamic equilibrium with the local mineral assemblage (Barker and Takach, 1992). The depth where gas composition becomes thermodynamically controlled is not well constrained, but the approach to equilibrium is favored by high temperatures and long time intervals, and it is likely to be at depths in excess of 25,000 ft (7,620 m) for an average geothermal gradient.

Over the last few years, we have developed a computer program for calculating equilibrium compositions in multicomponent systems (Takach et al, 1986; Barker and Takach, 1991, 1992, 1994). It is a modified version of the one described by Dayhoff, et al (1964), and can handle assemblages with up to 70 compounds and 20 phases. Compound free energies and elemental compositions are used as input parameters. The amounts of the various compounds are adjusted by the program until a set is obtained which yields the minimum free energy for the system consistent with overall elemental composition, and the stated temperature and pressure. The original code was written for a mainframe computer (Honeywell), but was later rewritten in standard Fortran 77 and moved to a workstation (HP-Apollo). We are currently modifying it to run on a PC (Pentium).

Thermodynamic calculations using the free energy minimization approach show that equilibrium gas composition in the deep subsurface depends strongly on reservoir mineralogy. Calculations have been carried out for a wide variety of clastic reservoirs (Barker and Takach, 1992) and carbonate reservoirs (Tabibian, 1993; Barker and Takach, 1994). Systems with and without graphite (see, for example, Figure 8) have been investigated to simulate the differences between (i) reservoirs that were initially filled with oil but were subsequently cracked to gas, and (ii) reservoirs that originally

Figure 7 : Schematic burial history of a gas reservoir (that is now relatively shallow) showing how the change from kinetic to thermodynamic control of gas composition has influenced gas composition at various stages. (From Barker and Takach, 1992.)

Figure 8 : Variation of calculated, equilibrium gas composition with depth for a silica-feldspar-clays-iron oxides-calcite-sulfur system. Gas composition is given as cumulative volume percent (on a water-free basis). Calculations were made for an average geothermal gradient of 25 °C/km and a hydrostatic pressure of 0.47 psi/ft. LEFT : No graphite. RIGHT : Average graphite. (From Barker and Takach, 1992.)

contained just gas. In clean sands with few accessory minerals, equilibrium methane concentration drops to zero at about 25,000 ft (7,620 m), but in the presence of graphite additional methane is generated, and at 40,000 ft (12,192 m) the gas still contains nearly 10 percent methane. The gas is generated because graphite reacts with water to give carbon dioxide and methane. When no graphite is present the absolute amount of methane (i.e., moles) drops because it is oxidized by water to give carbon dioxide and hydrogen. However, in high graphite systems methane survives at high concentrations to the greatest depths studied.

In deep clastic reservoirs with significant amounts of calcite cement the calcite becomes thermodynamically unstable and eventually breaks down thermally to give carbon dioxide that dilutes the methane and makes gas composition uneconomic. The details of the thermal decomposition of calcite depend on rock mineralogy, so that it is not possible to specify an exact depth or temperature where this reaction becomes important. Equilibrium iron-bearing systems become more reducing with depth and hematite decreases while magnetite increases. This reduction is balanced by the oxidation of methane to carbon dioxide and hydrogen. In addition the oxidation of methane by water goes on at the same time. Sulfur-bearing systems lead to the formation of hydrogen sulfide, but the increasing number of phases considered, and the large number of possible interactions, make it difficult to identify specific reactions. In general as the concentration of iron-bearing phases increases sulfur is likely to be combined in pyrite or pyrrhotite and less hydrogen sulfide is generated. Thermodynamic modeling can be a useful tool for predicting gas composition in the deep, undrilled subsurface, but it cannot be applied at shallow depths where gases have not reached thermodynamic equilibrium.

4. GEOLOGICAL STUDIES

Over the past several years a wide variety of samples has been analyzed in order to understand the capabilities and limitations of the analytical system. Many of these studies have been carried out in collaboration with other researchers who have been able to provide well-characterized samples with supporting geological information. Results from some of the more important, recently completed studies are briefly summarized, and data from other supporting studies also outlined. These illustrate the analytical capabilities of the DMS system.

(1) Arkoma Basin, Oklahoma and Arkansas:

The Arkoma basin of southeastern Oklahoma and west-central Arkansas provides an example of a basin that is now at drillable depth but has been deeply buried and/or subjected to high temperatures in the past (Hathon and Houseknecht, 1987; Wylie, 1988). The Arkoma basin is one of the most prolific gas producing basins in the U.S., with production from 25 zones ranging in age from the late Cambrian Arbuckle dolomite to early Desmoinesian clastics. Recent studies suggest that beneath the Ouachita frontal zone the depth of the Arbuckle is approximately 40,000 ft (12,192 m). Arbuckle cores and cuttings have been obtained from the Wilburton, Red Oak, and Bonanza Fields and all show the presence of well-developed calcite cements containing fluid inclusions. Materials were available from the Western Coal and Mining Company Well, 36-7N-32W (Bonanza Field); 2 Orr Unit "A" Well, 8-6N-22E and the 2 Roy Redd "C" Unit, 4-6N-23E (Red Oak Field); and the Williams 3A Well, Anadarko Petroleum Co., 23-T5N-R18E (Wilburton Field) (Tabibian, 1993). Recently the Danville USA A#1 was drilled to 20,661 ft (6,297 m) as a deep Arbuckle test in the central Arkansas part of the Arkoma Basin. Unfortunately only side wall cores were taken, and examination of these showed no suitable fracture-filling cements or overgrowths.

High surface vitrinite reflectance (R_o) values of $>3\%$ (Houseknecht and Matthews, 1985) suggest either deep burial or high paleogeothermal gradients for the rocks that are now at drillable depths. The present gradient is only about $1.8^\circ\text{F}/100\text{ ft}$ ($33^\circ\text{C}/\text{km}$). Gas production is associated with some of the highest R_o values in the world, and both the Wilburton and Red Oak Fields produce from the Spiro at R_o of approximately 3.0% , while values will be much higher for the Hunton and Arbuckle. The association of pyrobitumen with the gas in the Arbuckle, Hunton, Cromwell and Spiro Formations suggests that it is the product of thermal cracking of oil, and the heavy carbon isotope value (-32‰) for gas associated with an R_o of 3.7% supports this (Stahl et al, 1981).

Data from deep profiles in the areas of the Wilburton, Red Oak, and Bonanza Fields have been combined with literature data for present formation thicknesses, probable erosional losses, lithology, present geothermal gradients, and vitrinite reflectance values, to reconstruct burial and thermal histories. The *BasinMod* program (Platte River Associates) was used, and the calculated vitrinite reflectance values for different models were compared with actual values in an iterative procedure to establish the most likely burial and thermal histories. When a present day geothermal gradient is combined with a higher temperature initial rifting event, a Mesozoic rifting overprint of the Mississippi embayment (Houseknecht and Mathews, 1985), and a 6000 ft (1830 m) erosional loss, there is good prediction of the observed shallow high maturities. The temperature interpolated at any time can be combined with rock mineralogy and used to calculate equilibrium gas composition with the thermodynamics

program described above. Then, the composition of the gases in the inclusions in fracture-filling cements can be analyzed and compared with the calculated compositions. In doing the thermodynamic calculations, pressure-corrected fluid inclusion homogenization temperatures (= trapping temperatures) were used as input temperatures.

Figure 9 shows a typical burial history reconstruction for the Wilburton area, and includes the timing of cement formation based on fluid inclusion filling temperatures. Using temperatures derived from this thermal history, together with reservoir mineralogy, the equilibrium gas composition can be calculated thermodynamically. Predicted gas composition in the Wilburton (west) side of the basin is much more methane-rich than the gas composition predicted for the Bonanza area (east) (Figure 10). When fluid inclusions in fracture-filling cements are analyzed their compositions are in general agreement with the calculated values (Tabibian, 1993; Barker, 1994; Tabibian and Barker, 1995). Selected mass spectra for individual inclusions are shown in Figure 11. Heating-freezing stage examination of inclusions in the Arbuckle reservoir of the Bonanza field shows the presence not only of two-phase (L/V) primary and secondary inclusions, but also the presence of inclusions containing a very dark residue, presumably graphitic. Mass spectrometric analysis shows the presence of methane in these inclusions, and this is thought to be formed (together with the graphitic residue) by the thermal cracking of trapped crude oil. Barker (1990) showed that this cracking process generates very high pressures and we have noticed that inclusions of this type are associated with fractures and so have presumably leaked.

The thermodynamic program has been used to evaluate the effect of anhydrite on gas composition. When 1.0 or 5.0 percent anhydrite are added to the system methane concentration is decreased and hydrogen sulfide becomes prominent. Figure 11 shows that hydrogen sulfide is detected in some fluid inclusions (Tabibian, 1993; Tabibian and Barker, 1995).

(2) Inclusions in Overgrowths:

In the summer of 1989 Dr. Peter Eadington of CSIRO, Australia, visited the University of Tulsa and used our DMS system to try and develop techniques for analyzing inclusions in quartz overgrowths. These have considerable potential for defining conditions of temperature, pressure, and composition during the evolution of petroleum reservoir sandstones, including the critically important process of porosity reduction. Unfortunately, most inclusions in overgrowths were very small and close to the analytical limits, but information on methane content that is needed for interpreting

ARKOMA, WILBURTON

W-23WI-F, 23-5N-18E

Figure 9 : Depth - geologic age reconstruction for the Wilburton area of the Arkoma Basin using *BasinMod* (Platte River Associates). The cementation window shown on the burial history is based on the range of fluid inclusion homogenization temperatures obtained from two-phase aqueous inclusions in saddle dolomites.

Figure 10a : Variation of calculated equilibrium gas composition with depth for initially trapped crude oil using conditions from Bonanza Field. Left : Calculated volume percents. Right : Calculated number of moles.

Figure 10b : Variation of calculated equilibrium gas composition with depth for initially trapped crude oil using conditions from Wilburton Field. Left : Calculated volume percents. Right : Calculated number of moles.

W-34-13591 (92061101)

Burst: 32
Spectrum: 21955
Temperature: 301 C.
Max peak ht: 136
Size: 4221016

W-34-13562 (92052504)

Burst: 1
Spectrum: 9754
Temperature: 298 C.
Max peak ht: 43
Size: 1536

Figure 11a : Selected methane-rich, CO₂-poor inclusions from Wilburton Field.

WCM#1-9,510

Burst: 27
Spectrum: 53461
Temperature: 423 C.
Max peak ht: 388
Size: 8768

WCM#1-9,960

Burst: 224
Spectrum: 77021
Temperature: 439 C.
Max peak ht: 82
Size: 2468

Figure 11b : Selected methane-poor, CO₂-rich inclusions from Bonanza Field.
Note that WCM#1-9,510 has considerable hydrogen sulfide.

phase relationships observed microscopically was obtained (Eadington, Barker, and Underwood, 1990 and 1991).

(3) Raven Creek and Reel Field, Wyoming:

Overgrowths are important in petroleum reservoir rocks because their fluid inclusions sample the fluids present at various times during reservoir development and filling. They have the potential for providing important information about migration pathways. We have tried to build on our previous experience with fluid inclusions in overgrowths ((2), above) and have examined fluid inclusions in carbonate cements in the "B" sand of the Upper Minnelusa Formation in the vicinity of Raven Creek and Reel Fields, Powder River Basin, Wyoming (Underwood, 1993). The Permian (Wolfcampian) Upper Minnelusa Formation consists of sandstone, carbonate (predominantly dolomite) and anhydrite formed by a combination of eolian and marine sedimentation. Sandstones of the Upper Minnelusa Formation were deposited as coastal dune complexes and shoreline sands in a sabkha environment much like the modern Persian Gulf. Deposition occurred during falling sea level and was terminated by a rise in sea level. Each cycle is composed of a shoaling upward sequence of subtidal carbonates overlain by eolian sandstones. The "B" sand of the Raven Creek Field area was formed during the second of three major cycles.

A suite of 25 cores was selected from the USGS Core Research Laboratory (Table 2). Thin sections were prepared and described for all samples used for fluid inclusion analyses because a clear understanding of the sequence of diagenetic events and their relative timing, especially in relation to cement formation, is essential for an accurate interpretation of fluid inclusion data. These studies showed five major diagenetic events:

- (a) precipitation of poikilotopic anhydrite in dune sands (some reworked)
- (b) fine-grained carbonate replacements, particularly of feldspars
- (c) dissolution of anhydrite cement forming secondary porosity, in some cases accompanied by delayed compaction of the framework
- (d) formation of authigenic clays, perhaps derived from the decomposition of detrital illite and feldspar
- (e) precipitation of rhombic dolomite in pores during petroleum migration.

TABLE 2

CORE SAMPLE MATERIAL USED IN THE STUDY
OF RAVEN CREEK AND REEL FIELD, WYOMING

Wells with samples and thin sections.

SMP: X = fluid inclusion samples from this well

TS: X = thin sections from this well

Operator	Well Name	SEC	TWP	RNG	SMP	TS
Mobil Oil Corp	12-6-G Government F	06	48N	68W	X	X
Mobil Oil Corp	F-12-2-P Krause	02	48N	69W	X	
Mobil Oil Corp	F-21-2-P Krause	02	48N	69W	X	X
Mobil Oil Corp	F-23-2-P Krause	02	48N	69W	X	X
Mobil Oil Corp	F-32-3-P Krause	03	48N	69W	X	X
Mobil Oil Corp	F-41-3-P Krause	03	48N	69W	X	X
Mobil Oil Corp	33-11 Unit Williams	11	48N	69W	X	X
Mobil Oil Corp	F-12-11-P Krause	11	48N	69W		X
Southland Royalty	2-19 Opha White Fed	19	48N	69W	X	
McCulloch Oil	1-31 Bishop	31	48N	69W	X	X
McCulloch Oil	1-31 Pickrell	31	48N	69W	X	X
Ashland Oil Inc	1 Neuenschwander Govt	01	48N	70W	X	X
Mobil Oil Corp	F-22-31-P Krause	31	49N	68W	X	
Sinclair O&G	2 Moran	07	49N	69W	X	
Mobil Oil Corp	F-34-16 State	16	49N	69W	X	X
Grace-Ford O&G	1 Reel	21	49N	69W	X	X
Mobil Oil Corp	F-14-21 V R Reel	21	49N	69W	X	X
Mobil Oil Corp	F-34X-21-P Reel	21	49N	69W	X	X
True Oil	1 Russel	25	49N	69W	X	X
Mobil Oil Corp	14-34-P Krause	34	49N	69W	X	X
Mobil Oil Corp	F-34-34-P Krause	34	49N	69W	X	X
Mobil Oil Corp	F-41-34 State	34	49N	69W		X
Prenalta Corp	14-1 Government	14	49N	70W	X	X

Cores received from the USGS core laboratory in Denver, CO.

Operator	Well Name	SEC	TWP	RNG
Mobil Oil Corp.	12-2 F P Krause	02	48N	69W
Southland Royalty	2-19 Opha White Federal	19	48N	69W
Mobil Oil Corp	F 22-31 P Krause	31	49N	68W
Sinclair Oil & Gas	2 Moran	07	49N	69W
Southport Expl.	1-23 Driskell Estate	23	48N	67W
Southport Expl.	1-34 Walkingstick	34	48N	67W
McCulloch Oil	1X-12 Robbins	12	48N	72W
Davis Oil Company	1 RT Federal	19	50N	68W
Davis Oil Company	1 State Huckaby	21	50N	70W
Home Petroleum	12 N. Timber Creek Unit	31	50N	70W
McCulloch Oil	1-8 Bishop	08	47N	69W

Two distinct episodes of dolomite cementation can be seen in thin sections, one early, perhaps syndiagenetic, and the other late, coeval with petroleum migration (see also Markert and Al-Shaieb (1984)). At least one petroleum-bearing fluid inclusion was identified in thin section.

Individual crystals of carbonate cement are usually less than 0.05 mm across, so most inclusions are small. Some samples have only minor amounts of cement and in many samples no fluid inclusions are present. The limited number of fluid inclusions analyzed showed dominant water with lesser amounts of methane, carbon dioxide, and, occasionally, minor amounts of hydrogen sulfide. When samples contain large numbers of very small inclusions monitoring curves can provide useful compositional information. However, interpretation is complicated by the thermal breakdown of carbonates (e.g., dolomite), hydrated minerals (e.g., gypsum), and organic matter (e.g., oil). Figure 12 shows 3 monitoring runs from the more than 65 analyses made. When the data are plotted for the study area they show that in the vicinity of the fields methane and ethane are high, while updip methane remains prominent but there is no C₂. In contrast, samples outside the presumed southwest-northeast migration pathway have low or very low methane contents (Figure 13).

(4) Bald Eagle Formation, Pennsylvania:

A suite of samples from crack-seal veins in the Bald Eagle Formation, central Pennsylvania, the underlying Reedsville shale, and the overlying Juniata Formation were analyzed in cooperation with A. Lacazette (Texaco) (Table 3). Mass spectrometric analysis of individual fluid inclusions, together with microthermometry, were used to study compositional changes in the fluids that moved through the section. The lower portion of the Bald Eagle has been altered to a green color, with the color boundary varying as much as 200 m above the Reedsville, but having no stratigraphic significance. The color change was probably caused by the passage of reducing fluids derived from the Reedsville Formation which led to reactions such as:

Quartz from the organic-rich, black, marine Reedsville shale contained high concentrations of methane with variable amounts of water and only traces of higher hydrocarbons (Figure 14). In the overlying Bald Eagle formation inclusions in the calcite and quartz contained water with variable but minor quantities of methane, while the quartz from the Juniata breccia itself had inclusions with water but no methane. This suggests that reducing, methane-rich fluid was available from the Reedsville shale

Figure 12a : Monitoring curve for water and methane (top) and carbon dioxide and carbon monoxide (bottom) for the Mobil F34x-21 Krause well. (From Underwood, 1993.)

Figure 12b : Monitoring curves for water and methane for the Mobil F12-6-G Government well (top), and the McCulloch 1-31 Bishop well (bottom). (From Underwood, 1993.)

R68W

R69W

T49N

T48N

Figure 13 : Migration pathways in the vicinity of Raven Creek and Reel Fields, Powder River Basin. Migration is generally from the deep southwest part of the basin to the northeast.

TABLE 3. Samples from Central Pennsylvania

ROCK (vertical section)	SAMPLE NO.	MINERAL	DEPTH	NO. OF ANAL.	GASES IN INCLUSIONS
JUNIATA FM (Breccia)	WB	QTZ	OUTCROP	2	water dominated
BALD EAGLE FM (Fractures)	CA1	QTZ CAL	OUTCROP	3	water with variable methane
	CA4		OUTCROP	5	
	AE1		4042 m	3	
	AE2		4042 m	3	
	AE3		4042 m	3	
	AE4		4042 m	2	
REEDSVILLE FM (Shale)	LD	QTZ	OUTCROP	1	methane

Figure 14 : Analysis of fluid inclusions in 2 samples of quartz from the Reedsville Shale, central Pennsylvania. Top left shows 56 methane-rich inclusions, while the bottom left ternary diagram shows a methane-water mixing line defined by 406 individual inclusions. The summary mass spectrum (top right) is obtained by summing all of the 406 individual spectra. It shows traces of ethane but is dominated by methane.
 (From Underwood et al, 1994.)

at the time tectonism produced the horizontal fractures as conduits in the Bald Eagle formation. Interestingly it has been suggested that tectonism also led to brecciation of the Juniata formation, but no methane was incorporated into fluid inclusions there. Heating/cooling stage examination of quartz from the Reedsville shale shows coexisting gas and brine inclusions (Sullivan et al, 1996).

Analysis of gases in individual fluid inclusions in quartz and calcites that filled fractures shortly after fracturing show a systematic compositional trend of decreasing methane from the Reedsville shale up through the Bald Eagle sandstone and into the Juniata sandstone. Fluid inclusion compositions in quartz from the Reedsville shale range from methane-rich with minor water, to water-rich with minor methane. There are no higher hydrocarbons or hydrogen sulfide. In contrast, the two-phase inclusions in the Juniata are exclusively water-rich. Quartz and calcite from the intermediate Bald Eagle have water-rich inclusions with minor methane, but also contain considerable amounts of carbon dioxide as expected from Equation 2 (Figure 15). Little methane appears to have reached the Juniata sandstone even though fractures with green, halos (reduced) are observed. The accumulated data support the concept that lithostatically-pressured, methane-rich fracturing fluids from the organic-rich Reedsville shale fractured and reduced the overlying Bald Eagle sandstone before pressures returned to hydrostatic as the fractures intersected the meteoric groundwater system. Fluid inclusions in the Juniata tend to be less saline and poorer in methane than the fluids in the underlying Bald Eagle and Reedsville. An alternative way of summarizing the data is shown by the 3-D plot of Figure 15 which compares the water, carbon dioxide, and methane contents of inclusion populations in inclusions in quartz samples from the Bald Eagle, Reedsville, and Juniata. In Figure 16 composition (expressed as water/methane ratio) for inclusions in a quartz sample from the Reedsville Shale is plotted against size (given as water response) and burst sequence. Since the inclusion ruptures are produced by rising temperature, burst sequence is also the direction of increasing temperature. This plot shows that for this particular sample inclusion size covers a limited range and that gas composition does not show marked changes from inclusions that ruptured at low temperatures to those that ruptured at high temperatures, and there is only a slight increase in the water/methane ratio.

Figure 16 presents a histogram of the water contents of 2400 individual fluid inclusions in a quartz from the Reedsville Shale. The cutoff value is software selectable. Microscopic examination shows that the largest inclusions are no more than about 15 μm in longest dimension, but most appear to be close to 5 μm . This suggests that inclusions greater than a few microns in longest dimension are being analyzed in this case.

Reedsville/Bald Eagle/Juniata

Figure 15: Comparison of the compositions of gases in fluid inclusions for the Bald Eagle, Reedsville, and Juniata Formations.

Reedsville-LD (4/30/96)

Figure 16: Variation of gas composition with inclusion size (H_2O) and burst temperature (given as Burst Sequence) for inclusions in a quartz sample from the Reedsville Shale.

Quartz from the Reedsville Shale was also used in a preliminary attempt to obtain carbon isotope ratios from methane-bearing inclusions. The 16 amu response has a contribution from water (as O^+), but this diminishes towards zero as the water content decreases. In Figure 17 extrapolating to zero for $18/16_{CH_4}$ gives a 17/16 ratio for the carbon in the methane. The expected number should be close to 0.01. Clearly, the scatter on the data points and the long extrapolation make this number unreliable. Further refinements will hopefully improve the values obtained.

(5) Other Studies:

(a) Smackover Formation: Because of their wide range of compositions, selected calcites recovered from the Smackover Formation (Gulf Coast) at depths of roughly 20,000 ft (6100 m) have been analyzed repeatedly in developing analytical techniques (Barker and Sullivan, 1987). Figure 3 showed 100-second traces for 18 amu (water) and 34 amu (H_2S) across bursting inclusions. Mass spectra for individual inclusions show the presence of variable amounts of methane, water, hydrogen sulfide and carbon dioxide. Relative amounts vary somewhat within individual samples and there are major differences with sample depth in the wells. Barker and Smith (1986) used the $H_2^{34}S/H_2^{36}S/H_2O$ ternary diagram, (i.e., 36/34/18) to show that it may be possible to estimate isotopic ratios for sulfur in these inclusions.

(b) Ghost Rocks Melange: Quartz samples now at the surface in the Ghost Rock melange, Kodiak, Alaska were provided by Dr. P. Vrolijk. They appear to have crystallized at approximately 90,000 ft (27,450 m), and some of these samples are extremely methane-rich with individual inclusions that contain no water (Figure 19). Intermediate methane-water compositions lead to mixing lines on ternary diagrams (Barker and Sullivan, 1989). The subducting plate causes rapid burial and produces very low geothermal gradients, and so although these samples crystallized at great depth the oil window, and presumably gas survival, is pushed very deep. Samples analyzed from subduction complexes in the Olympic Peninsula, Washington, (samples from P. Snively) and Barbados (samples from R. Torini) contain only traces of methane, if any. None of the subducted samples contained sulfur gases.

(c) Salt: Evaporites have been suggested as potential sites for nuclear waste storage. We have analyzed gases in inclusions in both domal and bedded salts from the Gulf Coast (10 samples) and the Palo Duro basin, Texas, (7 samples) respectively (Patton, 1989). Gas compositions are generally similar with water dominating. However, no higher hydrocarbons were observed in domal salts whereas they were seen occasionally in bedded salts. Five of the 17 samples contained appreciable methane.

Figure 17: Histogram showing water contents of 2400 inclusions from a quartz in the Reedsville Fm.

Figure 18: (see text for discussion)

K3-05B QTZ-CAL

Burst: 26

Spectrum: 29720

Size: 632

Figure 19: (top) Mass spectrum of gas from a very methane-rich fluid inclusion in a quartz crystal from the Ghost Rocks melange, Kodiak, Alaska. (bottom) Methane-water mixing line on a 14 amu - 15 amu - 18 amu ternary diagram. Data are shown for 24 individual fluid inclusions from the same quartz crystal as the inclusion shown above.

(d) Pressure Compartment Seals: Gases in individual fluid inclusions in silica and calcite cements from pressure seals from the Gulf Weaver well in the Anadarko Basin were analyzed mass spectrometrically (Underwood and Barker, 1992). Samples came from the 11,099 ft to 11,609 ft (3385 - 3541 m) depth range and included silica cements from the First Bromide, the Second Bromide, and Tulip Creek, and carbonate and silica cements from the McLish. Several of the cements had no detectable fluid inclusions, but others showed a large number of water-rich bursts. None of the inclusions contained methane, so that if the seals are formed by hydrocarbon-derived carbonates oxidation appears to be complete. Most inclusions contained a few percent carbon dioxide, but other gases (such as higher hydrocarbons, H₂S, N₂) were absent.

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