Final Report

Project Title: Experimental studies in the system H_2O - CH_4 - "petroleum" - salt using synthetic fluid inclusions

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The aim of this project was to determine phase equilibrium and PVT properties of fluids in the H_2O - CH_4 - "petroleum" - salt system using synthetic fluid inclusions. This information is critical to understanding the behavior of natural fluid inclusions trapped in hydrocarbon-bearing environments such as sedimentary basins, oil and gas fields, methane hydrate occurrences and Mississippi Valley type Pb-Zn deposits.

Completion of the project has been delayed significantly. During the first two years of the project very promising results were obtained. However, upon critical examination of these data, it was found that the results could not be duplicated, and new data obtained from the samples did not support earlier interpretations. Because the veracity of the data were in serious doubt, the PI decided to discard all the samples and data from this portion of the study and to begin the study anew. This resulted in considerable delay as, not only did the study have to be repeated, but it was necessary to find a graduate student with the appropriate skills to conduct the study.

In the Fall, 2000, Ms. Fang Lin entered the Department of Geosciences as a PhD candidate. Ms. Lin was interested in hydrocarbon systems and had the necessary background in geology and chemistry to undertake the experimental study of the H_2O - CH_4 - "petroleum" - salt system. Ms. Lin began her research on this project in the summer, 2001. The project consisted of two separate but related experimental and analytical studies. The first was to prepare synthetic fluid inclusions containing aqueous solution and liquid petroleum in order to study the behavior of petroleum-bearing inclusions during heating, and to develop a method of estimating the composition of oil inclusions based on thermodynamic modeling of the oil, using data from microthermometric and volumetric analysis of the inclusions. With this technique, the gas-to-oil volumetric ratio (GOR) of the inclusion at room temperature is obtained from confocal laser scanning microscopic (CLSM) imaging of the inclusions. Previous workers had noted that the combined microthermometric – CSLM – thermodynamic modeling technique produced very precise results for petroleum inclusions, but these workers were unable to assess the accuracy of the results because the composition of the oil in the inclusions studied was unknown. These workers suggested that the accuracy of the technique could best be tested using synthetic petroleum fluid inclusions of known composition and trapped at known P-T conditions.

To test this technique, Ms. Lin made numerous attempts to prepare synthetic petroleum fluid inclusions quartz. While some limited success was achieved, useful inclusions were never produced. When experiments to trap petroleum inclusions were conducted at temperatures above about 400°C, many inclusions were formed but microthermometric and UV-fluorescence studies indicated that the oils had "cracked" and changed composition as a result of the high temperatures. If lower temperatures (<200°C) were used in an attempt to avoid changes to the oil composition, fracture healing to produce fluid inclusions did not occur in a reasonable amount of time (up to a few months). After spending almost two years on this effort, the PI and Ms. Lin decided that the project should not be continued. A manuscript describing the results was prepared and submitted to Canadian Mineralogist.

Concurrent with the first study, Ms. Lin has been preparing synthetic fluid inclusions in the H_2O - CH_4 system to constrain phase relations and PVT properties in the vicinity of the critical point. In this study, it was relatively easy to prepare the inclusions using formation temperatures in the range 400° - 700°C, and Ms. Lin had assembled a large amount of experimental data in the period 2002-2004. Then, in 2004, two new laser Raman microprobes were acquired for the Fluids Research Laboratory. These new instruments had much lower detection limits than our earlier system, and analysis of the synthetic fluid inclusions being used for the H_2O - CH_4 study revealed that all samples formed at temperatures above 500°C contained significant amounts of carbon dioxide that was not detectable through microthermometry or with the older Raman microprobe. As a result, the large majority of the samples prepared earlier were discarded and a new batch of synthetic fluid inclusions was prepared at lower temperatures to avoid oxidation of methane to produce carbon dioxide. Using these samples, Ms. Lin has nearly completed her study of the H_2O - CH_4 system, and a manuscript will be submitted to Geochimica et Cosmochimica Acta in the Fall, 2005.

The final study being conducted in this project is the determination of methane hydrate phase equilibria using synthetic fluid inclusions combined with Raman spectroscopy. With this technique, the temperature of hydrate dissociation is obtained by observing the disappearance of the hydrate under the microscope, and the pressure at this temperature is determined from the shift in the position of the methane Raman peak with pressure. A summary of results for the pure H_2O - CH_4 system is presented in the figure below. A manuscript describing these results is in preparation and will be submitted to Science.

Future work will apply this same technique to determine hydrate stability in the presence of saline brines.

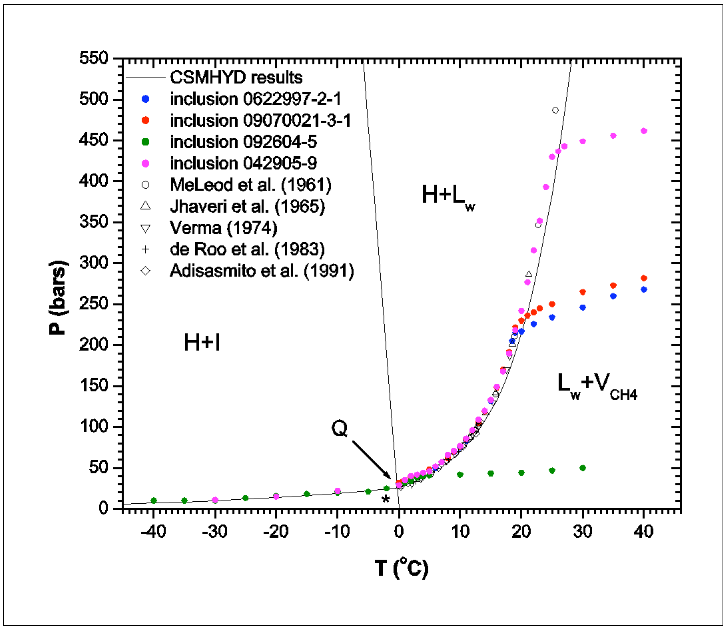

Figure 1. Stability limits for methane hydrate determined from Raman microprobe analysis of synthetic fluid inclusions containing H_2O-CH_4

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