Applications of the Laser Raman Microprobe RAMANOR U-1000 to Hydrothermal Ore Deposits: Carlin as an Example

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Abstract
The laser Raman microprobe has been used effectively in the identification of polyatomic gases, complex ions, and daughter crystals in fluid inclusions in a variety of host rocks (e.g., Dhamelincourt et al., 1979a; Rosasco and Roedder, 1979). This is a generally nondestructive, in situ, semiquantitative analytical technique in which a monochromatic laser beam is focused into a sample. The spectrum resulting from the inelastically scattered radiation indicates the chemical speciation of the irradiated sample. Although laser Raman microprobe analysis is not very effective for brines composed of simple salts, the nonelectrolyte components of hydrothermal fluid inclusions can be readily analyzed. Raman spectroscopy also provides important information, on a microscale, for solid phases in the assemblage. Fluid inclusions in quartz and calcite from several samples of the disseminated gold deposit at Carlin, Nevada, were studied petrographically and analyzed by microthermometry and Raman spectroscopy. The laser Raman microprobe was used to scan for CO₂, CO, N₂, H₂S, and CH₄ ± H₂O. The semiquantitative microprobe analyses confirmed the presence of three-phase inclusions containing water and different amounts of CO₂, one-phase inclusions of high-density CH₄-dominated fluid, and very weak aqueous inclusions. Very minor H₂S was detected in a CO₂-H₂O inclusion and small amounts of CO₂ were detected in some of the CH₄-dominated inclusions. These gases may have affected ore deposition. In any event, their identification is necessary for correct estimations of pressure to be derived from homogenization temperatures of the fluid inclusions. The laser Raman microprobe provides more than compositional data. For instance, the exact spectral position and shape of the CH₄ peak indicate the internal pressure, even in inclusions too small (<3 μm) to be analyzed by microthermometry. The laser Raman microprobe was also used to help characterize the structure of the carbonaceous material in the jasperoid host rock at Carlin (disordered graphite, in part) and to distinguish between the TiO₂ polymorphs anatase and brookite (both present) in hydrothermal quartz deposits at Magnet Cove, Arkansas. The ability of the laser Raman microprobe to provide pinpoint analyses has many advantages over bulk extraction methods, which mix the volatiles from separate generations of fluids and may also produce chemical artifacts.

Introduction
In the early 1970s, two types of laser Raman microprobes were developed independently in France (e.g., Delhaye and Dhamelincourt, 1975; Dhamelincourt et al., 1979b) and in the United States at the National Bureau of Standards (e.g., Rosasco and Etz, 1977; Andersen and Muggli, 1981). Initially, only the French design was commercially available, however, recently a U. S.-based spectroscopy firm has begun to market its own Raman microanalysis system. For several years, the French research groups at Lille, associated with Paul Dhamelincourt, and at Nancy, under Jean Dubessy, have been using the MOLE, which is an earlier model of the RAMANOR U-1000. Both systems were manufactured by Instruments, SA (Jobin Yvon), but only the RAMANOR U-1000 is still marketed.

The laser Raman microprobe has been used effectively in the study of fluid inclusions to identify polyatomic gases in metamorphic and igneous rocks, complex ionic species in aqueous solutions, and daughter crystals in a variety of hosts (e.g., Rosasco et al., 1975; Dhamelincourt et al., 1979a; Etz, 1979; Rosasco and Roedder, 1979; Dubessy et al., 1982; Dubessy et al., 1983). Simple ionic species like Ca²⁺, Na⁺, K⁺, Cl⁻,
and their salts NaCl, KCl, and CaCl₂, however, are not appreciably Raman-active either in pure crystalline form or in aqueous solution. First appearances therefore might suggest that the laser Raman microscope is not very useful in the analysis of brine-filled fluid inclusions which typically are associated with certain types of hydrothermal ore deposits. There are, however, at least two different approaches to obtain important data on hydrothermal fluid inclusions by laser Raman microscope spectroscopy. First of all, there are some direct applications to brines. For instance, because the sulfate radical contains covalently bonded species and therefore is Raman-active, Rosasco and Roedder (1979) could measure the sulfate contents of inclusion fluids semiquantitatively. Also, hydrated solid phases (e.g., of NaCl, CaCl₂, and MgCl₂) that precipitate upon the controlled freezing of large brine-filled inclusions have been distinguished by careful, painstaking Raman spectroscopy (Dubessy et al., 1982). Second, as demonstrated in the present paper and in previous works (e.g., Beny et al., 1982; Guilhaumou et al., 1984; Touray and Guilhaumou, 1984; Ramboz et al., 1985), nonelectrolyte components of the fluid inclusions can be analyzed (in some cases, only) with the laser Raman microscope. Of special significance are the possible additional species dissolved in these aqueous fluids, which are readily identified by Raman spectroscopy but which remain unidentified and frequently undetected by microthermometry. Raman spectroscopy also provides important information—on a microscale—for solid phases in the hydrothermal assemblage. The results of a preliminary Raman study on the Carlin gold deposit demonstrate some of these findings and suggest additional applications of the laser Raman microscope.

**Analytical Technique**

**General**

The laser Raman microscope permits the spectroscopic analysis of solid, liquid, and gas phases as small as a few micrometers. In this technique of molecular spectroscopy, the sample is imaged through the high-power objective of an optical microscope. Raman scattering in the sample is induced by a monochromatic laser beam, which follows the same optical path as does white light in the reflection mode of the microscope. The Raman effect is the shift in frequency that monochromatic light (e.g., laser light) undergoes during inelastic scattering. Only the spectral distribution of the inelastically scattered light emitted by the sample (Raman scattering) is of analytical interest, since it is caused by component-specific molecular vibrational and rotational phenomena in the sample. The scattered light is transmitted through the microscope into a double monochromator, step scanned, and detected with a monochannel photon-counting system. The spectra are recorded in terms of the amount of displacement from the frequency of the exciting (laser) radiation.

Micro-Raman spectroscopy generally is nondestructive, permits pinpoint analysis of crystalline and noncrystalline materials that are either unmounted or enclosed in a transparent nonfluorescing matrix, and can be used on normal polished thin sections as well as on unenclosed (loose) mineral grains or polished rock chips. Important geologic applications of the technique include the analysis of individual fluid and solid inclusions in minerals and the chemical-structural characterization of dissolved and solid phases (e.g., chemical speciation, degree of crystallinity, and distinguishing between polymorphs). Of particular concern in this project is the suitability of laser Raman microscope spectroscopy in the analysis of such species as CO₂, H₂O, CH₄, H₂S, SO₂, H₂, and N₂ in the gas and liquid phases of individual fluid inclusions.

**RAMANOR U-1000**

Figure 1 is a diagrammatic sketch of the RAMANOR U-1000 system. (Brand names are used here simply to identify the equipment used in our laboratory.) It differs somewhat from its predecessor, the MOLE, but the basic instrument design is very similar. The Raman-scattered radiation is collected within a cone (apical angle dependent upon numerical aperture of objective) whose axis lies at 180° to the incident beam. The same microscope objective is used to view the sample optically, to focus the laser beam into the sample, and to collect the scattered radiation for transmission to the double monochromator. Objectives with magnifications as high as 160× allow analysis of sample regions as small as 1 μm.

The RAMANOR U-1000 instrument at Washington University is operated by a dedicated Commander 964 computer (Columbia Data Products, Inc.) and uses a data management software package provided by Instruments SA for instrument control, data acquisition, and data manipulation such as counting, plotting, determining positions of peaks, and calculating peak areas.

The laser source is a 5-watt Ar⁺ Innova 90-5, manufactured by Coherent, Inc., of Palo Alto, California. For this study, the 514.5-nm green line provided the exciting radiation. The laser power is measured as the beam enters the microscope. The normal range of operation is 85 to 100 mW. The laser power actually impinging on the sample surface is about 10 percent of that entering the microscope.

The accompanying spectra (see below, Figs. 4–8) are plots of total counts vs. wave numbers (cm⁻¹), i.e., frequency-related units. The photon count rate of the inelastically scattered radiation is a function of both the sample and the instrumental conditions. Among
the latter are the exciting laser power, the alignment of the laser in the optical system, the optical properties of the objectives, the chosen slit width, and the electronic parameters of the detection system. The total number of recorded counts depends upon the count rate, the counting time (signal integration time per step of the monochromator during a scan), and the spacing of the steps (number of wave numbers between each step).

The spectral resolution, or width of the Raman peak at half height, is adjusted by changing the width of the slits of the monochromator. Narrower slits provide greater spectral resolution but decrease the count rate. Tests have been made on this individual unit for spectral reproducibility and resolution. For monochromator slit widths up to 520 μm, stepping intervals of 0.1 cm⁻¹, and 1-second counting intervals, the spectral reproducibility is ±0.1 cm⁻¹. For a typical analysis with the standard slit width of 500 μm, the spectral resolution is 4 to 5 cm⁻¹ over the range of interest (see below).

The focusing of the laser light into the sample and the size of the beam impinging on the sample are controlled primarily by the microscope objectives. Most of the following spectra were collected with a 160× Leitz objective (numerical aperture = 0.95) or an 80× Nachet objective (numerical aperture = 0.90). These focus the laser beam to about a 1-μm diameter. Fluid inclusions as small as 3 μm in diameter were analyzed successfully in the Carlin samples. The small size of the exciting beam also permits analysis of the individual phases in multiphase inclusions.

The detection limits of the RAMANOR U-1000 and our instrument in particular are not yet known, but tests are underway (J. D. Pasteris and B. Wopenka, unpub. analyses; Wopenka and Pasteris, 1986). Theoretical estimates of the detection limits of Raman microprobes in general are in the picogram (10⁻¹² g) range (Ett, 1979). As pointed out by Rosasco et al. (1975), the detection limit for a species in a fluid inclusion depends upon the scattering efficiency of the species itself, the counting time and stepping interval, the Raman and optical properties of the host, the geometry of the inclusion, spectral interference (e.g., overlapping Raman peaks, fluorescence) from other components, and the stability of the species under the impinging laser beam. For the analyses presented in this paper, "trace" means on the order of 1 to 2 mole percent, and "pure" means >98 mole percent.

Although the major scattering component in each Raman spectrum represents the sample within the minute focal volume of the objective, there are some matrix effects. With an 80× or 160× objective, spectral information from material 2 to 3 μm above and below the objective's focal plane is collected (Adar, 1981, and references therein). The characteristic Raman peaks of the two host minerals in this study, quartz and calcite, do not directly overlap those for the gases being analyzed. Therefore, it is believed that the RAMANOR U-1000 is operating at close to its highest level of sensitivity.

Once it has been established that the mineral and gas peaks do not overlap, it is usually unnecessary to run a "blank" (spectrum of host only) for each analysis...
in order to subtract the effect of the host from that of the inclusion spectrum. However, when analyzing for \( \text{N}_2 \), interference from the spectrum for air (between the sample surface and the objective) must be subtracted from the spectrum for the inclusion. After \( \text{N}_2 \) has been analyzed in the inclusion, the sample is shifted slightly laterally and under the same analysis conditions, only the mineral host is irradiated to the same depth as the inclusion. The \( \text{N}_2 \) peak that arises in the latter case, due to air, is subtracted from the \( \text{N}_2 \) peak for the inclusion.

The laser beam has very little heating effect on transparent fluid inclusions in transparent hosts as proved by the fact that it does not even cause two-phase \( \text{CO}_2 \) inclusions to homogenize. (Pure \( \text{CO}_2 \) should homogenize at no more than 31.1°C.)

**Carlin Samples**

**Sample descriptions**

The Carlin mine (Fig. 2) is the type locality for sediment-hosted disseminated gold deposits. This type of deposit presently accounts for the largest proportion of gold production in the United States. Located in the Lynn mining district, at the south end of the Tuscaraora Mountains, Carlin is one of at least nine sediment-hosted gold deposits that lie in a northwesttrending belt over 60 km in length in north-central Nevada (Fig. 2). Previous geologic and geochemical studies (e.g., Rye et al., 1974; Dickson et al., 1979; Radtke et al., 1980) have shown that Carlin-type gold deposits are formed by hydrothermal fluids of dominantly meteoric origin at temperatures of 175° to 200°C, that gold is accompanied by As, Sb, Hg, and other elements, and that carbonaceous argillaceous limestones are favorable hosts. However, many unanswered questions remain concerning the geochemical controls on the transport and deposition of the gold and accompanying trace elements.

Previous studies of fluid inclusions from Carlin (Radtke et al., 1980; Nash, 1972) reveal the presence of rare, three-phase, \( \text{CO}_2 - \text{H}_2\text{O} \) fluid inclusions in some samples. As discussed by Kuehn and Bodnar (1984), in addition to low-salinity aqueous inclusions, volatile-rich inclusions containing \( \text{CO}_2 \) or \( \text{CH}_4 \) are abundant in certain vein minerals at Carlin. Relative ages of the various inclusion types and their relationship to gold deposition are presently being investigated (C. A. Kuehn, in prep.). These high bulk density, volatile-rich inclusions require high trapping pressures and suggest that the rocks hosting the Carlin deposit experienced pressures on the order of 1 kb at some time.

Small amounts of \( \text{CO}_2 \) or \( \text{CH}_4 \) cannot be detected easily using standard heating-freezing techniques (Roedder, 1984). However, even small amounts of dissolved gases can significantly affect the pressure estimations derived from combining homogenization temperatures with information on boiling point curves. Knowledge of the exact speciation of C-O-H-(S) fluids furthermore aids in determining the prevailing \( f_{\text{O}_2} \) and \( f_{\text{H}_2\text{O}} \) during trapping of the fluid inclusions.

In this preliminary Raman study, samples were examined petrographically and subsequently analyzed by microthermometry and laser Raman spectroscopy. In each case, a doubly polished, unmounted rock chip of approximately 75 µm thickness was used (see Tables 1, 2, and Fig. 3). Five compositionally distinct types of inclusions were observed and analyzed with the laser Raman microprobe (see Fig. 3 and Table 1). At 25°C, these appear as: three-phase inclusions of \( \text{H}_2\text{O}(l) \), \( \text{CO}_2(g) \) and \( \text{CO}_2(g) \), in which \( \text{CO}_2 \) is dominant (type A); the same type of three-phase inclusions, except that liquid \( \text{H}_2\text{O} \) is dominant (type B); minute, dark, one-phase or empty inclusions (type C); and minute two- and one-phase inclusions (types D and E). The phases in type A and type B inclusions initially were identified optically and confirmed by microthermometry. However, the minute inclusions of types C, D, and E as well as minor dissolved species in types A and B are not readily amenable to standard microthermometric methods. The difference between type D (aqueous) and type E (\( \text{CH}_4 \)-dominated) was revealed by the laser Raman microprobe, although some of these inclusions are large enough for microthermometry.

![Fig. 2. Index map showing outline of pre-Tertiary rocks of Carlin district in north-central Nevada.](image-url)
FIG. 3. A. Three-phase inclusion of type A (H₂O, CO₂, CO₂·H₂O) in which CO₂ is dominant. Area 1 of quartz sample C83-36-A. Both scale bars = 10 μm. B. Three-phase inclusion of type B, in which H₂O is dominant. Area 2 of quartz sample C83-36-A. Both scale bars = 10 μm. C. Larger one-phase and smaller two-phase inclusions of H₂O (type D). Area 4 in quartz sample C83-36-A. Scale bar = 20 μm. D. Minute fluid inclusions of type E and opaque irregular solid inclusions of carbonaceous matter in fine-grained jasperoid of C81-03E. Scale bar = 20 μm. E. Euhedral quartz grain (Q) in a coarsely crystalline calcite (Cc) vein in sample C81-001. The calcite is filled with fine-grained opaque material. Analysis areas 1 to 4 are circled. Scale bar = 200 μm. F. Fluid inclusion-lined fractures in area 1 of sample C81-001 (see E). Many of the inclusions are high density CH₄ of type E. Scale bar = 20 μm.
A = CO₂-rich, large, three-phase inclusion with CO₂, CO₃, and H₂O; B = H₂O-rich, large, three-phase inclusion with CO₂, CO₃, and H₂O; C = two- and one-phase inclusions with only CO₂; D = two- and one-phase inclusions with only H₂O; E = minute (two- and one-phase inclusions) with CH₄ (liquid-rich) — the two-phase inclusions probably also contain H₂O; ND = not detected

Sample C83-36-A comes from a quartz-calcite vein in the Carlin East pit (mine coordinates: 6300' level, 24,075 N, 20,450 E). This vein is in mineralized, unoxidized Devonian Popovich Formation near the South Bounding fault. All the inclusions examined are in highly fractured quartz filled with abundant, commonly minute (<10 μm), fluid inclusions. Examples of types A, B, C, and D were analyzed.

Sample C81-03E is from the 6340' level in the East pit at Carlin (mine coordinates 24,050 N, 20,550 E). The polished chip consists predominantly of dark silicified limestone ("jasperoid") with numerous inclusions of fine-grained pyrite as well as carbonaceous and other opaque phases but without distinguishable fluid inclusions. The jasperoid is crosscut by veins of a later stage, inclusion-free, vug-filling quartz. There are also irregular patches of an early stage of cloudy quartz, which contains a myriad of minute inclusions commonly aligned in trails. The inclusions which were analyzed are one-phase or empty inclusions (type D) and high density, one-phase liquid or two-phase inclusions (type E) (see Fig. 3).

Sample C81-001 was collected from the oxide ore stockpile. The location of the sample is unknown, but it was probably mined from about the 6250' level of the main pit (C. Ekberg, pers. commun., 1981). The sample consists of silicified limestone of the Roberts Mountain Formation crosscut by coarsely crystalline calcite veins. Within the widest (~0.5 cm) calcite vein are small, typically euhedral (hexagonal) quartz crystals. Both the calcite and quartz contain small one- and two-phase inclusions (types D and E, Table 1 and Fig. 3) and release gases during crushing tests.

Raman and microthermometric analyses

In most cases, each inclusion was scanned for CO₂, CO, N₂, H₂S, and CH₄. The spectral regions scanned for the five species are 1,250–1,400, 2,120–2,170, 2,300–2,360, 2,590–2,640, and 2,995–2,930 cm⁻¹, respectively. In some of the CH₄-rich inclusions, H₂ also was analyzed for (4,120–4,180 cm⁻¹). In some of the CO₂-rich inclusions, SO₂ also was analyzed for (1,120–1,180 cm⁻¹). The monochromator was stepped at frequency intervals of 0.3 cm⁻¹ and time intervals of 10 seconds. Slower scans were done for H₂O in some inclusions (3,100–3,600 cm⁻¹). Because of the weak Raman signal for H₂O, it was not scanned for routinely. The weak Raman response of H₂O and the fact that a separate H₂O phase would line the walls of an inclusion mean that significant amounts of H₂O could go undetected in these minute inclusions.

### Table 1. Distribution of Fluid Inclusion Types

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>C83-36-A</td>
<td>Present</td>
<td>Present</td>
<td>Present</td>
<td>Present</td>
<td>Present</td>
</tr>
<tr>
<td>C81-03E</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Possible</td>
<td>Present</td>
</tr>
<tr>
<td>C81-001</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Present</td>
<td>Present</td>
</tr>
</tbody>
</table>

### Table 2. Composition of Fluid Inclusions

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Inclusion type¹</th>
<th>Inclusion no.</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂O</th>
<th>H₂S</th>
<th>H₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C83-36-A: Quartz</td>
<td>Area 1</td>
<td>A</td>
<td>1</td>
<td>A</td>
<td>ND</td>
<td>A</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Area 2</td>
<td>B</td>
<td>1</td>
<td>A</td>
<td>ND</td>
<td>A</td>
<td>TR</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Area 3</td>
<td>C</td>
<td>1</td>
<td>A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Area 4</td>
<td>D</td>
<td>1–4</td>
<td>ND</td>
<td>ND</td>
<td>A</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

| C81-03E: Jasperoid | Area 1 | E | 1, 2 | ND | A | NA | ND | ND |
| Area 2 | D² | 4–6 | ND | ND | A | NA | TR | TR |

| C81-001: Mineral | Area 1 Qtz | E | 1, 2 | ~8² | ~92² | ND | ND | ND |
| Area 2 Qtz | D | 1 | ND | ND | A | NA | NA | NA |
| Area 3 CC | E | 1, 4, 5 | ~11² | ~89² | NA-ND | ND | ND | TR |
| Area 4 Qtz | E | 1, 2, 3 | ~10² | >90² | NA | ND | ND | ND |

¹ See Table 1 for definition of inclusion types
² In mole percent

Abbreviations: A = abundant; NA = not analyzed for; ND = not detected; TR = trace (<2 mole %); CC = calcite; Qtz = quartz
The results of the laser Raman microprobe analyses are summarized in Table 2.

The spectra in Figures 4 to 8 are actual data plots, not redrawn. They were taken with the 514.5-nm green line of the argon laser, with a spectral resolution of 4 to 5 cm\(^{-1}\), unless otherwise stated. The peak positions were determined from the peak center at half height, as corrected by calibration against Ar and Hg.

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**Fig. 4.** Raman spectra of all three phases of the type B fluid inclusion in sample C83-36-A shown in Figure 3B. 160X objective. For A, B: C: single scan, 10 sec/point, points spaced by 0.3 cm\(^{-1}\). A, B: 1,284 and 1,388 cm\(^{-1}\) peaks for CO\(_2\) in central, vapor phase. C: 1,387 cm\(^{-1}\) peak for CO\(_2\) in inner liquid phase in intermediate rim. D: Ten added scans of outer liquid phase, each with 10 sec/point and points spaced by 2 cm\(^{-1}\). The broad spectral feature is from the stretching mode of H\(_2\)O. The small narrow peaks have not been identified. They are extremely weak features that were also found in inclusions known to be pure H\(_2\)O in clean, natural quartz. Reference numbers are: A, 36A2-A.DA1, J27; B, 36A2-A.DA2, J27; C, 36A2-C.DAT, J27; D, 36A-2H.CA2, J10.
emission lamps. Thus, the peak labels (correct) may differ slightly from the nominal labels on the x-axis. Other spectral specifications are given in the figure captions.

The microthermometry stage used is a U.S.G.S.-type, gas-flow system (Werre et al., 1979; Woods et al., 1981) as modified by Pasteris (1983). It was calibrated using pure H$_2$O and CO$_2$ fluid inclusion standards.

In the quartz matrix of sample C83-36-A, analyses were made on about eight different inclusions in four areas of the chip. The first area (Fig. 3A) contains a 15-$\mu$m, three-phase, CO$_2$-rich inclusion (type A). Among the five species analyzed for in the CO$_2$ liquid and vapor phases, only CO$_2$ gave a strong Raman signal. The individual vapor bubble was difficult to analyze because it was almost constantly in motion. Microthermometry of this inclusion showed initial melting of the CO$_2$ phase at $-56.5 \pm 0.3^\circ$C and final melting at $-56.4 \pm 0.3^\circ$C. The H$_2$O solid melted at $-3.3^\circ$C and CO$_2$-H$_2$O clathrate at $+7.3^\circ$C (both very difficult to see). CO$_2$ homogenized to the liquid at $26.4^\circ \pm 0.3^\circ$C. To avoid decrepitation of the inclusion, total homogenization was not attempted. Similar inclusions in a matching chip totally homogenized at $\geq 200^\circ$C. Some decrepitated before total homogenization.

The second area (Fig. 3B) investigated in C83-36-A had a 20-$\mu$m, H$_2$O-rich, three-phase inclusion (type B). Laser Raman microprobe analysis showed that the vapor bubble was almost pure CO$_2$ (Fig. 4A and B), perhaps with a trace of H$_2$S. Only CO$_2$, however, was detected in the liquid CO$_2$ phase (Fig. 4C), which forms a thin annular ring around the vapor bubble (Fig. 3B) and therefore was difficult to analyze. Scans on the abundant liquid water phase showed the presence of only H$_2$O (Fig. 4D) and minor dissolved CO$_2$ (not shown). Microthermometry of this inclusion showed initial melting of the CO$_2$ phase at $-57.0^\circ$C and final melting at $-56.6 \pm 0.3^\circ$C. The H$_2$O solid melted between about $-8^\circ$ and $-6^\circ$C, and clathrate melted at $+9^\circ$ to $+10^\circ$C (both phase changes difficult to see). Homogenization of the CO$_2$ phases to the liquid occurred at $30.0^\circ \pm 0.3^\circ$C. Total homogenization was to the H$_2$O liquid phase at T > $200^\circ$C.

Area 3 in the quartz has small one-phase and two-phase inclusions (type C) in which only CO$_2$ was detected by the laser Raman microprobe. Area 4 (Fig. 3C), near the opposite edge of the chip, has numerous inclusions which appear empty. They were analyzed...
for CH$_4$ and CO$_2$, but none was detected. Some very
minute (few micrometers) two-phase inclusions with
moving vapor bubbles gave a signal for H$_2$O but
showed no CO$_2$ or CH$_4$ (type D).

In the C81-03E jasperoid, six fluid and two solid
inclusions were analyzed. The fluid inclusions are
minute (3–6 μm), one-phase inclusions in cloudy
quartz. Most of them appear empty at room tem-
perature. Two such inclusions showed only CH$_4$, but no
CO$_2$, CO, N$_2$, H$_2$S, or H$_2$ (type E). Graphite was not
detected in them (see below). A third inclusion
showed a strong CH$_4$ peak, very minor H$_2$S, and perhaps
very minor N$_2$ (appears slightly above N$_2$ back-
ground levels for air). CO$_2$ was not found in the three
inclusions. Several other minute (3–4 μm) inclusions
with the same appearance have no detectable gases.
They may contain H$_2$O or be empty. H$_2$O was not
analyzed for in the C81-03E inclusions because of
their small size. Their size and poor optics also hinder
microthermometry.

In the immediately adjacent jasperoid of sample
C81-03E, scans were made of two very dark, fuzzy
opaque inclusions that appeared to be aggregates of
grains on the order of 3 μm (Fig. 3D). Both spectra
(Fig. 5) indicate partially disordered graphitic matter
(see below). Fluid inclusions were not observed in
the dark jasperoid.

In sample C81-001, 11 inclusions were analyzed
in a veinlet containing euhedral quartz grains enclosed
in calcite (Fig. 3E and F). The quartz has numerous
internal fractures, some of which are lined with
opaque material. Two type E fluid inclusions, which
occur along a narrow fracture, showed very strong
peaks for CH$_4$ (area 1, Figs. 3E and F, 6A, and 7).
Addition of multiple scans of inclusion 2 produced a
CO$_2$ peak (Fig. 7) barely sufficient for semiquantifi-
cation: ~8 mole percent CO$_2$ and 92 mole percent
CH$_4$ (see below). CH$_4$, however, clearly is the dom-
inant species in these inclusions.

The spectral region around the broad CH$_4$ peak in
inclusion 2 was scanned numerous times at increasing
spectral resolution down to 1 cm$^{-1}$ in order to deter-
mine if higher hydrocarbons were present in addition
to CH$_4$ (e.g., ethane, propane). This test was not con-
exclusive, but if higher hydrocarbons do occur in that inclusion, they must be present in very minor amounts. The inclusion was also scanned for H$_2$O, with negative results.

It was very difficult to do microthermometry on the inclusions in area 1. Although inclusion 2 is about $\sim 4$ μm in diameter, its high relief (causing it to be internally dark) prevented observation of phase changes. It appeared to freeze at about $-170^\circ$C. A very irregular 8-μm, one-phase inclusion nearby was analyzed. It has a Raman spectrum very similar to that of inclusion 2, although not as strong. During rapid cooling, a bubble formed at $-86^\circ$C. There appeared to be two freezing events, at $-118^\circ$C and $-186^\circ$C. Upon heating, some phase (presumably CH$_4$ rich) melted at $-178^\circ$C $\pm 4^\circ$C. Between about $-104^\circ$C and $-102^\circ$C, movement of the bubble was detected, which could have resulted from the melting of a solid phase. The bubble disappeared by about $-84^\circ$C (total homogenization to the liquid). No definite phase changes were observed above this temperature, but some subtle changes were detected between $-70^\circ$C and $-60^\circ$C.

In area 2 (Fig. 3E), a few tens of micrometers away from inclusion 2, are small, two-phase inclusions, which do not appear to be associated with fractures. Analysis of one of them showed no CO$_2$ and CH$_4$ but a strong signal for H$_2$O (type D). On the opposite side of the euhedral quartz grain in area 4 (Fig. 3E) are more one-phase minute (2–6 μm) inclusions of type E, three of which were analyzed. CH$_4$ is the dominant species; about 5 to 10 mole percent CO$_2$ was also detected.

Microthermometry was not very successful in area 4. In two inclusions, some phase changes could be observed. In one inclusion, rapid cooling produced a bubble at $\sim -105^\circ$C. Freezing events apparently occurred at $\sim -110^\circ$C and $-182^\circ$C. Upon slow heating, the bubble began to move at $\sim -109^\circ$C (potentially in response to a melting event) and disappeared at $\sim -100^\circ$C (total homogenization to the liquid). Similarly, during slow heating of a second inclusion, the bubble began moving at $\sim -112^\circ$C and disappeared by $\sim -103^\circ$C.

In the vein calcite (area 3) immediately adjacent to the quartz grain above, five inclusions were analyzed for the standard five gas species. All the inclusions are one-phase and 5 μm or less in diameter. CH$_4$ is again the dominant species detected (Fig. 6B). Inclusion 1 has a strong CH$_4$ and possibly a minor N$_2$ peak. Inclusions 2 and 3 had no detectable gases and are presumed empty or aqueous. Inclusions 4 and 5
show higher relief than 2 and 3 and are indeed filled, both having strong CH$_4$ peaks. Addition of multiple scans from an individual CH$_4$-rich inclusion produced a CO$_2$ peak barely sufficient for semiquantification: $\sim$11 mole percent CO$_2$ and 89 mole percent CH$_4$. The accuracy of the determination makes this composition indistinguishable from that for the inclusions in area 1 of the quartz sample, discussed above. Inclusion 5 was also scanned four times to detect H$_2$O bending and stretching modes. Even when the spectra were added together, however, no spectral features were found for H$_2$O. The optics were so poor and the inclusions so small that microthermometric data could not be collected from the calcite.

Discussion of Raman and microthermometric analyses

Presently our ability to estimate proportions of species in a multicomponent fluid inclusion is based on theoretical calculations (Plazek, 1934; Dhameleoncourt et al., 1979a; Wopenka and Pasteris, 1986) that yield an accuracy of no better than $\pm$ several mole percent (Wopenka and Pasteris, 1986). In practice, one makes several simplifying assumptions and uses the areas of the Raman peaks and the scattering cross sections (a measure of the scattering efficiency of a particular vibrational mode) for those species to calculate their relative molar proportions. For the semiquantitative analyses presented above, the scattering cross sections used for CH$_4$ and CO$_2$ are 9.1 and 1.2, respectively (Schroit and Klöckner, 1979). The low scattering efficiency of CO$_2$ compared to CH$_4$ and the weakness of the recorded CO$_2$ peaks suggest uncertainties of at least $\pm$5 mole percent in the semiquantitative analyses.

There are also limitations on the ability both to obtain and to interpret microthermometry data. For instance, melting temperatures different from those of pure CO$_2$ (56.6°C) and pure CH$_4$ (-184°C) indicate the presence of more than one component, but usually not which one(s) or how many. The more chemically complex the system, the more phases that are required to yield an unambiguous compositional analysis. Usually enough phases do not form or at least are not visible to determine an invariant point in the system of interest. For the CO$_2$-CH$_4$ system considered above, both the melting and homogenization temperatures of individual inclusions must be determined accurately (Burruss, 1981). The temperatures recorded for phase changes above -100°C are probably only accurate to $\pm$0.2°C to 0.3°C. Furthermore, due to the limited amount of available experimental data (see e.g., Burruss, 1981), microthermometric interpretation is much more accurate for the CO$_2$-rich than for the CH$_4$-rich part of this system. Lastly, the minute size of many inclusions, such as those from Carlin, makes observation of phase changes difficult or impossible in a microthermometry stage. Obviously, a combination of microthermometric and laser Raman microprobe analyses on a given inclusion would yield more data than either technique alone (e.g., Dhameleoncourt et al., 1979a; Pasteris et al., 1985). In many inclusions, however, the small size and/or poor optics make only laser Raman microprobe analysis possible.

In summary, combined petrographic, microthermometric, and laser Raman microprobe analysis has revealed at least five chemically distinct types of fluid inclusions in these samples from Carlin, as described in Tables 1 and 2. More than one compositional type exists in each small sample. The timing of the fluids and their significance in the deposition of the Carlin ores can be interpreted best in the context of a detailed paragenetic study, which is currently underway (C. A. Kuehn, in prep.). This initial study and the microthermometry work by Kuehn and Bodnar (1984) suggest that Carlin potentially has been exposed to at least three chemically distinct fluids in its history.

Significance of and Further Application of Raman Spectroscopy to Hydrothermal Deposits

Volatiles

Certainly the identification, in individual inclusions, of one or more nonaqueous volatiles at Carlin is a contribution that could be provided by few other analytical techniques (perhaps by the laser microprobe: Kotra and Gibson, 1982; Sommer et al., 1985; or the new Fourier transform infrared microprobes). Although visual observations, microthermometry, and
use of a crushing stage in some cases indicate the presence of other volatiles in hydrothermal fluid inclusions, the species frequently are present in very minor amounts. There is also the possibility of multiple species, which complicates their identification. On the other hand, bulk extraction and analysis techniques such as decrepitation-heating followed by gas chromatography and mass spectrometry suffer from at least two problems: fluids from all the generations of inclusions are mixed, and artifacts may be produced from the handling procedures, especially where organic materials are present (Aleksandrova et al., 1980; Cheilletz et al., 1984). The latter is of particular concern in deposits hosted by organic-bearing sedimentary rocks.

Dissolved CO₂ was detected in the coexisting liquid H₂O in a three-phase inclusion in C83-36-A. Unlike many other analytical techniques, Raman analysis not only identifies a species but also provides information on its chemical environment. For instance, the position of the Raman peak for CO₂ in the liquid CO₂ phase of the above inclusion is 1,387 cm⁻¹ (Fig. 4C), whereas the peak for the coexisting CO₂ dissolved in H₂O is 1,385 cm⁻¹ (not shown). This effect has been documented in experiments by Davis and Oliver (1972).

Not only compositional but also density information is desired and can be obtained from many fluid inclusions. In microthermometry, the homogenization temperature of a fluid inclusion of known composition indicates the density of the bulk inclusion. Given the P-V-T data on this particular chemical system, one can extrapolate that equal-density line (isochore) upward in P-T space. Given the exact composition of an inclusion, independent knowledge of either pressure or temperature of trapping defines the other variable. This has been the major means of using fluid inclusion data to help constrain the pressure of formation of the host rock. However, among the assumptions of such an approach are: (1) the inclusion is large enough and optically clear enough for accurate determination of both a melting and homogenization temperature to be determined, (2) these temperatures unambiguously indicate the exact bulk composition of the fluid, and (3) the isochores appropriate to this compositional system are well known. The above three assumptions are not totally satisfied for the minute CH₄-dominated inclusions studied at Carlin; however, some estimates of the inclusion densities still may be made.

The sensitivity of bond configuration to the pressure on or density of a phase has been documented in the Raman spectra of gaseous CH₄ (May et al., 1959), CO₂ (Bertran, 1983), and N₂. This effect has been previously noted in the spectra of natural fluid inclusions (Rosasco et al., 1975; Dhamelincourt et al., 1979a). The results from several inclusions from Carlin suggest how the pressure sensitivity of the Raman peaks of some gas species may be a further aid in the interpretation of fluid inclusions.

As shown by May et al. (1959), the Raman spectrum of CH₄ in the fluid state depends on pressure. The wave number of the Raman peak for the symmetric C-H stretching mode decreases as pressure increases; it is approximately 2,917 cm⁻¹ at 1 bar pressure and 298 K. Using the same operating conditions and the same instrumental calibration for spectral positioning, reproducible analyses (over two days of repeated analysis) on the three samples from Carlin showed that almost all the quartz grains containing methane inclusions have peaks at about 2,910 cm⁻¹, whereas inclusions in calcite are at about 2,912 cm⁻¹ (see Fig. 6A and B). This pertains even for directly adjacent (few hundred micrometers separation) calcite and quartz grains in C81-001. This suggests a high internal pressure, on the order of 450 bars, in the quartz (May et al., 1959; Din, 1961). Obviously, there are major uncertainties in the calculation. Although the Ramanor’s monochromator was calibrated against an argon emission lamp in the spectral region of 2,920 cm⁻¹, only ±1 cm⁻¹ precision is claimed for the position of the CH₄ peak. There are uncertainties in the density vs. peak position of May et al. (1959) and in the P-V-T data of Din (1961) for CH₄. Furthermore, our Raman analyses show that minor amounts of CO₂ are present in the CH₄-dominated inclusions in both the calcite and quartz of sample C81-001. Because both sets of inclusions have approximately the same composition, however, differences in their peak positions should be reliable and significant.

These differences indicate that the internal pressures in the methane-rich inclusions in quartz and calcite differ by about 240 bars (cf. May et al., 1959). One could postulate that the two minerals trapped their inclusions at different times, perhaps separated by an uplift, an erosional event, or a tectonically induced drop in fluid pressure. However, the euhedral quartz grains under study are completely enclosed in the coarse-grained calcite vein. The two mineral phases appear approximately contemporaneous.

If we assume that the quartz and calcite formed at the same time and under the same P-T conditions, then the present difference in internal pressure could reflect their different factors of isothermal compressibility and thermal expansion. The calculation of the change in external pressure (from P bars to 1 bar) that would produce the observed differential in internal pressure is a potential geobarometer. However, even assuming extreme conditions of formation at Carlin of 200° to 400°C and 1 to 2 kb pressure, an internal pressure difference in coexisting calcite and quartz of at most 20 bars can be accounted for in this way (data from Clark, 1966). It therefore seems likely that the methane inclusions in calcite may have stretched or may have leaked some of their fluid (cf. Bodnar
and Bethke, 1984; Pecher and Boullier, 1984). This also demonstrates the potential problems of using data from inclusions with high bulk density and high internal pressure that are contained in weak minerals such as calcite. It also is clear that without the use of a very high magnification objective (e.g., 160×) in conjunction with a laser Raman microprobe, it might be almost impossible either to identify CH₄ (and other volatiles) or to estimate the density of the fluid. Certainly, for the 3- to 5-µm, one-phase inclusions like the ones under discussion, it is difficult in many cases to determine accurate freezing and homogenization temperatures with the optics of a heating-freezing stage.

Because the laser Raman microprobe is a generally nondestructive technique, other analyses subsequently can be done on the same samples. In addition, as Dubessy et al. (1982) demonstrated, the laser Raman microprobe can be used in conjunction with a heating-freezing stage. This permits Raman analysis of individual solid, liquid, and gas phases produced during cooling of an inclusion. In many cases, the Raman spectral features are sharper at very low temperatures. Most of the Carlin inclusions studied are too small to permit analysis of individual frozen phases.

Solid inclusions

The laser Raman microprobe can also be used to characterize solids. Because the solid state of a substance is a stronger Raman scatterer than the liquid or gaseous state, in general, smaller amounts of solids than of other states should be detectable. Although the laser Raman microprobe can never replace the electron microprobe in the chemical characterization of mineral phases, Raman spectroscopy does have two advantages—the ability to distinguish between compositionally identical polymorphs and to analyze minute inclusions that are not exposed at the surface of a rock chip.

The discrimination of polymorphs is frequently difficult even using X-ray diffraction analysis. That the minor diffraction peaks of one phase may coincide closely with the major peaks of its polymorph is particularly troublesome. Thus, the presence of a significant amount (e.g., 10%) of one phase may be masked by its more abundant polymorph. The TiO₂ polymorphs brookite, rutile, and anatase are one such example. The different bonding modes of the polymorphs make them readily distinguishable by Raman spectroscopy.

A study of the hydrothermal quartz-TiO₂ deposits of Magnet Cove, Arkansas, convinced Viscio (1981) that more than one TiO₂ phase was present in his samples. Color differences and sector zoning in TiO₂ grains were recognizable by transmitted light microscopy of doubly polished thin sections and indicated that two polymorphs might be present. Because of the coincidence of peaks, X-ray diffraction analysis could not show conclusively whether some anatase was present with the abundant brookite in the euhedral, tetragonal crystals commonly regarded as classic specimens of brookite from Magnet Cove. However, pinpoint analysis with the RAMANOR U-1000 (by F. Adar, J. Pasteris, and B. Wopenka) rapidly revealed that both brookite (peak at ~155 cm⁻¹) and anatase (peak at ~146 cm⁻¹) are present (Fig. 8).

Another useful application of the laser Raman microprobe's ability to distinguish among different structural (i.e., bonding) types is its sensitivity to the degree of crystallinity of a substance. Even amorphous materials such as glasses can be characterized by Raman spectroscopy (e.g., Mysen et al., 1982; McMillan, 1984). Raman spectra are also very sensitive to the degree of crystallinity or range of structural order in carbonaceous materials (e.g., Tulinstra and Koenig, 1970; Beny-Bassez et al., 1981; Lespade et al., 1982; Rouzaud et al., 1983). The nature of the abundant carbonaceous matter in some Carlin-type ores has been the subject of a number of previous investigations (e.g., Radtke and Scheiner, 1970; Nelson et al., 1982). Bulk-rock analyses are not always satisfactory due to possible changes produced in the material during extraction and the problems of interpreting the often complex spectra derived from various analytical techniques (e.g., Aleksandrova et al., 1980). In addition, there may be more than one type of carbonaceous material, perhaps even as distinct particles, and some of the carbon is not extractable. Laser Raman microprobe analysis provides an alternative analytical approach to this problem.

Lespade et al. (1982) produced a series of spectra relating the degree of crystallinity/order (in terms of crystallite size) and the spectral features for graphitic material (see also previous references for carbon). These spectra can be compared to those derived from individual dark fuzzy inclusions in the jasperoid sample C81-03E (Fig. 5). The inclusions can be characterized as disordered graphitic material, because the broad spectral feature at approximately 1,200 to 1,450 cm⁻¹ is still present. As ordering increases, the latter feature becomes increasingly subdued and the peak at about 1,600 cm⁻¹ becomes sharper. The crystallite size of the carbonaceous material analyzed in this study appears to be about 70 Å according to the data of Lespade et al. (1982).

The ability of the laser Raman microprobe to characterize the crystallinity of carbon could be very important in tracing the thermal history of a rock and/or the specific organic precursors of the present carbonaceous material. For the Carlin samples it would be useful, for instance, to do comparative Raman spectroscopy on the solid carbonaceous material in the correlative unsilicified limestone far removed.


