

CH₄-rich inclusions from quartz veins in the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians – Discussion

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Kisch and van den Kerkhof (1991) presented an interesting study supporting our view that laser Raman microprobe (LRM) spectroscopy is a powerful tool for investigating fluid inclusions in the C-O-H-N system. We are not challenging the validity of either their microthermometric data or the geological interpretations drawn therefrom. However, we respectfully wish to point out some shortcomings in their analytical approach and interpretation of Raman spectra, which, in some circumstances, could lead to significant errors in the derivation of compositional and *P-V-T* information. In the context of this discussion, we also will comment on (1) which parameters can be determined or inferred from the Raman spectra of fluids, (2) the specific spectral data and analytical conditions necessary for such determinations, and (3) the potential errors involved in applying such data to geological systems. Moreover, to assist outside readers in the interpretation and evaluation of spectroscopic data, we also propose some guidelines for the documentation of Raman analyses.

DETERMINATION OF FLUID COMPOSITIONS

Quantitative compositional analysis from Raman spectroscopic data requires appropriate factors to convert the measured peak areas into relative molar concentrations. One commonly used methodology is the application of Raman scattering efficiencies determined for pure gas species at 1 atm; the results of such experiments have been summarized by Schrötter and Klöckner (1979). For greater accuracy, however, corrections also should be made for instrumental effects and for pressure- and composition-induced changes in the spectroscopic behavior, e.g., polarization properties, of the fluids. Our approach toward quantifying fluid compositions from Raman spectra has been an empirical calibration of the combined effects of the instrument function and the apparent Raman scattering efficiencies by means of the analysis of certified fluid mixtures of known, geologically relevant compositions at controlled pressures (Wopenka and Pasteris, 1987; Seitz et al., 1990, 1993; Chou et al., 1990;

Pasteris et al., 1990). This empirical approach has the added advantage of accounting for both the composition-dependent and pressure-dependent responses of the Raman bands in the specific kinds of fluids contained in inclusions (Pasteris et al., 1990; Seitz et al., 1993).

Kisch and van den Kerkhof (1991) chose the former, inherently less accurate, method: that of applying 1-atm values from the literature. Moreover, the Raman scattering efficiencies that they list (p. 235) were used incorrectly, considering their experimental conditions. As discussed by Dubessy et al. (1989), before the tabulated values of Schrötter and Klöckner (1979; presumably, the unattributed source of the values given in Kisch and van den Kerkhof, 1991) are applied to the spectra of fluids, they must first be corrected for the specific wavelength of the laser excitation used. Therefore, the Raman scattering efficiencies of CO₂ and CH₄ (relative to N₂) used by Kisch and van den Kerkhof, 1.21 and 8.9, respectively, should have been revised to 1.49 and 7.7 to account for the 514.532-nm laser line used. Accordingly, the CH₄ concentrations in their inclusions were underestimated. For example, analysis A7 in their Table 2, which is listed as 79.0 mol% CH₄ and 21.0 mol% CO₂, would be recalculated as 84 mol% CH₄ and 16 mol% CO₂. A difference of 5–6 mol% may seem inconsequential in the context of this study; however (1) the difference in inferred compositions increases with increasing CO₂ contents (of more concern in other studies); and (2) this difference affects the interpretation of trapping pressure (discussed below). Furthermore, the compilation of Schrötter and Klöckner (1979) contains several substantially different sets of Raman scattering efficiencies, only one of which was considered for recalculation by Dubessy et al. (1989). This situation, in addition to the factors discussed in the previous paragraph, convince us that instrument-specific empirical calibration on known gas mixtures is the superior analytical approach.

Readers also should be wary of any statements implying that absolute concentrations of species (e.g., number of moles or grams) can be determined directly from Ra-

man analyses. Such determinations require that mass balance (absolute concentration) be known for at least one Raman-active component. For example, Kisch and van den Kerkhof stated that “qualitative indications on the CH₄ content of the gas bubble can be obtained by the detection of Raman spectra at comparable conditions (inclusion size and depth, laser power, etc.)” (p. 235) and that “it can be assumed that the aqueous inclusions with highest CH₄ contents [our italics] were also saturated with methane . . .” (p. 236). Although the former statement itself is true, it does not reflect the difficulty in ensuring that the analyses are carried out at comparable conditions. Their latter statement may be a valid interpretation, but it implies that their Raman spectra could be used to infer, or confirm, absolute concentrations.

Even under comparable conditions of inclusion analysis, variations in the observed intensities of the CH₄ peak reflect only the differences in the number of methane molecules in the excitation volume of the laser. The latter is controlled by fluid density (or pressure) only to a first approximation. We emphasize that Raman spectroscopy is an optical technique. The light path of both the exciting laser beam and the Raman-scattered radiation are affected by the shapes of the upper inclusion matrix and H₂O-gas interfaces, as well as by the depth of the inclusion below the sample’s surface; these will vary among inclusions, and impose very strong controls on the intensity of Raman-scattered radiation that is available for detection. A meaningful comparison of Raman intensities thus requires that the same excitation volume be measured in all inclusions; this criterion cannot be met if the vapor bubbles in some inclusions are smaller than the excitation volume of the laser, or if differences in optical paths cause the excitation volume to differ among inclusions.

A more realistic means of inferring the CH₄ content of aqueous inclusions is to make use of existing calibrations relating the CH₄ band position to pressure (e.g., Fabre and Couty, 1986). Regardless of how strong or weak the CH₄ band is (given a sufficient signal to noise ratio), its calibrated position (see discussion below) will indicate the methane pressure in the bubble. Then, based on the measured sizes of both the vapor bubble and the entire inclusion, bulk H₂O-CH₄ compositions can be estimated from mass balance (with calculable uncertainties). In other words, Raman analysis can provide significantly more information (i.e., total bulk composition) than simply whether the aqueous fluid is methane-saturated at room temperature.

ESTIMATION OF INTERNAL PRESSURES IN INCLUSIONS

Kisch and van den Kerkhof (p. 235) reported that their Raman spectra of methane show various peak positions, which they interpreted as a reflection of differences in density. Unfortunately, they did not indicate whether the listed peak positions are simply raw data or have been corrected by means of a calibration lamp with an emis-

sion line at a wavelength near (i.e., within $\sim 100\text{ cm}^{-1}$ of, but preferably overlapping) that of the unknown. The specific position of the Raman band for a volatile species is a function of both pressure and bulk fluid composition. The relationship between peak position and pressure or density has been determined for several pure volatile species (e.g., May et al., 1959; Bertran, 1983; Fabre and Couty, 1986; Garrabos et al., 1989), and similar studies are also beginning to address various gas mixtures of geological interest, such as CH₄-N₂ (e.g., Chou et al., 1990; Seitz et al., 1993; Fabre and Oksengorn, 1992). It is uncertain if the peak positions reported in Kisch and van den Kerkhof (1991) reflect only differences in internal pressure of the inclusion fluids or incorporate deviations from pure CH₄ compositions or instrumental drift or both (e.g., because of temperature changes in the laboratory). Moreover, since actual peak positions were reported, they should have been referenced to the work of Fabre and Couty (1986), who calibrated the peak position of pure CH₄ up to 3 kbar of pressure. The reported value of 2919.5 cm^{-1} (presumably the listed value of 1919.5 is a typographic error) “for inclusions of lowest density” (p. 235) strongly suggests that the reported peak positions are not valid, not even within the reported uncertainty of 0.6 cm^{-1} . Our studies of pressure vs. band position show that the CH₄ band position, both in the pure phase and in binary mixtures with N₂, H₂, Ar, and CO₂, never shifts to a wavenumber position higher than 2916.8 cm^{-1} , which is the position of the pure phase at 1 atm (Pasteris et al., 1990; Seitz et al., 1993).

In their reply to this discussion, van den Kerkhof and Kisch (1993) explain the method of their calibration. Two remaining points of concern are (1) the significance of reporting peak positions as $\pm 0.6\text{ cm}^{-1}$, in light of their recognized uncertainty of $\pm 3\text{ cm}^{-1}$ in the accuracy of this measurement, and (2) whether the reported peak positions are useful even for the determination of relative peak positions, for the purpose of inferring differences in pressure among inclusions. We would like to point out that for Raman spectrometers the functional relation between measured and true band positions is known to be frequency dependent and nonlinear and, moreover, dependent on ambient temperature. Thus, advantage can be taken of the pressure sensitivity of the peak position for methane and other gases only by reference to a calibration lamp (e.g., Ar emission lamp) at reasonable intervals during the analytical session. Also of importance is the fact that the positions of Raman bands in most published examinations of pressure sensitivity (e.g., Fabre and Couty, 1986) are corrected to in-vacuo values. For bands near CH₄, in-vacuo values are about 0.8 cm^{-1} lower than those measured in air, and thus failure to account for this difference can lead to pressure inaccuracies of up to ~ 200 bars.

APPLICATION OF THE DATA

One principal goal of fluid inclusion analysis is an estimation of the trapping conditions of the fluid. With a

bulk composition and density (or molar volume) of a fluid, an appropriate equation of state can be used to derive the P - T trajectory of the appropriate isochore. Together with another independent piece of information (either the pressure or temperature of entrapment), the isochore permits estimation of trapping conditions. Consideration of the leverage of an inappropriately chosen isochore makes it clear that accuracy is required in all parts of this procedure, especially if the trapping conditions were at high pressure and temperature.

It is not clear from Kisch and van den Kerkhof's (1991) article exactly how the values for molar volumes were calculated or how the Raman and microthermometric data were integrated in the analytical interpretation of their inclusions. (Clarification of these points was only provided in the reply to this discussion: van den Kerkhof and Kisch, 1993.) The combination of microthermometry and Raman microprobe spectroscopy is, in principle, a powerful tool for the unique determination of composition and density in an inclusion, provided that internal consistency is maintained within the data. In other studies, the fluid compositions determined by Raman analysis have been combined with microthermometric observation of homogenization temperatures to determine fluid isochores (e.g., Dubessy et al., 1989), an approach that van den Kerkhof and Kisch (1993) regard as acceptable. However, the combination of a single homogenization temperature with several compositions, like those resulting from the application of different Raman quantification factors, will produce different isochores. [Example, by application of Kisch and van den Kerkhof's (1991) Fig. 5: A homogenization temperature of -90°C coupled with two compositions, 50 mol% CH₄ and 44 mol% CH₄ (for CH₄-CO₂ mixtures), yields molar volumes of 44 and 41 cm³/mole.] Of concern in geologic modeling is the fact that, although the use of an incorrect quantification factor might produce only a small inaccuracy in the compositional analysis, the analysis could ramify into significant inaccuracies in the slopes of the calculated isochores. Depending upon how far those isochores are projected in P - T space, they obviously could imply completely erroneous trapping conditions. [In the above pair of examples, application of Holloway's (1981) MRK-based isochore calculations, by means of Brown's (1989) Flincor program, produces isochores that deviate by 800 bars at 300 $^{\circ}\text{C}$ (within the valid temperature range of the program, i.e., $>100^{\circ}\text{C}$.)] The above example provides a clear indication of why the highest achievable level of accuracy is needed in the determination of fluid composition. We have not evaluated how the necessary changes in scattering efficiencies discussed above would affect the ultimate geological interpretation presented by Kisch and van den Kerkhof (1991) for their analyzed inclusions. We infer that their results may not be in great error, because the isochoric projections used were only on the order of a couple of hundred degrees Celsius and because the fluid compositions are nearly pure CH₄.

CONCLUDING REMARKS

There is no question about the validity and usefulness of applying Raman microsampling spectroscopy to fluid inclusions. Indeed, a major point of our discussion is that well-calibrated Raman spectra, collected under carefully chosen analytical conditions, can provide a greater variety of more accurate data than is typically utilized by most fluid-inclusion researchers.

In most studies deriving quantitative results from Raman spectra, the discussion of spectroscopic methods includes a list of only such information as the instrument manufacturer and model, wavelength of the laser excitation, laser power at the sample, spectral resolution, type of detector, counting times for analyses, and spectral regions analyzed. To provide a measure of analytical consensus and to help interested researchers evaluate and interpret Raman data, we suggest that the following kinds of information also be documented: (1) the values and sources (i.e., empirically derived factors or a combination of Raman scattering and instrumental efficiencies) of quantification factors used for converting Raman band areas into relative concentrations; (2) estimated uncertainties (relative mol%) in compositional analyses, and the detection limits for the species of interest (note that detection limits are valid only in terms of partial pressures, and not absolute contents or relative mol%); (3) the method for determining band positions (e.g., midpoint at half height) and uncertainties in band positions, together with the lamp source and reference wavelengths (calculated in-vacuo positions) used to correct the observed positions; and (4) how corrections were made on N₂ analyses to account for possible interference from atmospheric N₂.

REFERENCES CITED

- Bertran, J.F. (1983) Study of Fermi doublet ν_1 - $2\nu_2$ in the Raman spectra of CO₂ in different phases. *Spectrochimica Acta*, 39A, 119-121.
- Brown, P.E. (1989) FLINCOR: A microcomputer program for the reduction and investigation of fluid-inclusion data. *American Mineralogist*, 74, 1390-1393.
- Chou, I-M., Pasteris, J.D., and Seitz, J.C. (1990) High-density volatiles in the system C-O-H-N for the calibration of a laser Raman microprobe. *Geochimica et Cosmochimica Acta*, 54, 535-543.
- Dubessy, J., Poty, B., and Ramboz, C. (1989) Advances in C-O-H-N-S fluid geochemistry based on micro-Raman spectrometric analysis of fluid inclusions. *European Journal of Mineralogy*, 1, 517-534.
- Fabre, D., and Couty, D. (1986) Investigations on the density effects in the Raman spectrum of methane up to 3000 bars. Application to the determination of pressure in fluid inclusions trapped in minerals. *Comptes Rendus de l'Academie des Sciences de Paris*, 303, Série II, 1305-1308 (in French).
- Fabre, D., and Oksengorn, B. (1992) Pressure and density dependence of the CH₄ and N₂ Raman lines in an equimolar CH₄-N₂ gas mixture. *Applied Spectroscopy*, 46, 468-471.
- Garrabos, Y., Echargui, M.A., and Marsault-Herail, F. (1989) Comparison between the density effects on the levels of the Raman spectra of the Fermi resonance doublet of the ¹²C¹⁶O₂ and ¹³C¹⁶O₂ molecules. *Journal of Chemical Physics*, 91, 5869-5881.
- Holloway, J.R. (1981) Compositions and volumes of supercritical fluids in the earth's crust. In L.S. Hollister and M.L. Crawford, Eds., *Short*

- course in fluid inclusions: Applications to petrology, p. 13–38. Mineralogical Association of Canada.
- Kisch, H.J., and van den Kerkhof, A.M. (1991) CH₄-rich inclusions from quartz veins in the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians. *American Mineralogist*, 76, 230–240.
- May, A.D., Stryland, J.C., and Welsh, H.L. (1959) Raman spectra of H₂ and CH₄ at high pressures. *Journal of Chemical Physics*, 30, 1099–1100.
- Pasteris, J.D., Seitz, J.C., Wopenka, B., and Chou, I-M. (1990) Recent advances in the analysis and interpretation of C-O-H-N fluids by application of laser Raman microspectroscopy. In J.R. Michael and P. Ingram, Eds., *Microbeam analysis—1990*, p. 228–234. San Francisco Press, San Francisco.
- Schrötter, H.W., and Klöckner, H.W. (1979) Raman scattering cross-sections in gases and liquids. In A. Weber, Ed., *Raman spectroscopy of gases and liquids*, p. 123–166. Springer-Verlag, New York.
- Seitz, J.C., Pasteris, J.D., and Chou, I-M. (1990) Raman spectroscopy of CH₄-N₂ fluids with applications to the quantitative analysis of fluid inclusions. In *Program and Abstracts of PACROFI III*, Toronto, 3, 80.
- (1993) Raman spectroscopic characterization of gas mixtures I. Quantitative composition and density determination of CH₄, N₂, and their mixtures. *American Journal of Science*, in press.
- van den Kerkhof, A.M., and Kisch, H.J. (1993) CH₄-rich inclusions from quartz veins in the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians—Reply. *American Mineralogist*, 78, 220–224.
- Wopenka, B., and Pasteris, J.D. (1987) Raman intensities and detection limits of geochemically relevant gas mixtures for a laser Raman microprobe. *Analytical Chemistry*, 59, 2165–2170.

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