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

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The paper of Kisch and van den Kerkhof (1991) gave rise to a discussion by Pasteris et al. (1993) about the accuracy of quantitative gas analysis by Raman microspectrometry. We feel that this discussion concerns not only our data, but many other Raman data published so far. The Raman data published in Kisch and van den Kerkhof (1991) have some shortcomings, as seen from the present state of knowledge. In this paper, we report some corrections of our earlier published Raman results, and we briefly discuss the possibilities of Raman analyses for geological applications. The recalculated gas compositions show only small deviations compared with the earlier values, and they do not change the interpretation of geological trapping conditions in Kisch and van den Kerkhof (1991).

The intensity of Raman light scattering is influenced by several optical and physical parameters, which cannot all be determined. In particular, the effects on Raman spectra of fluid pressure and of the polarity of different molecules in mixtures are incompletely quantified at present. That the composition itself influences the Raman signal further complicates the achievement of high accuracy in Raman analysis of fluids. Progress on accurate Raman microprobe calibration has been made for some binary systems (Chou et al., 1990). The continuing investigations by these authors and others are of great importance in obtaining more accurate quantitative analyses, particularly for the determination of physical properties from Raman spectra, such as the pressure in fluid inclusions. Accurate interpretations of Raman spectra are currently not possible, especially for fluid mixtures of more than two components. On the other hand, Raman gas analyses published so far appear to agree generally with microthermometry data, and in our opinion they are adequate for the interpretation of most geological materials.

WAVELENGTH CORRECTION OF RAMAN SPECTRA

Raman cross sections (σ), normalized to N_2, were given by Schrötter and Klöckner (1979) as 1.21 for the main peak of CO_2 ($2\nu_2 = 1388$ cm^{-1} at 1 atm) and 8.7, 9.1, and 9.3 for the CH$_4$ peak ($\nu_1 = 2917$ cm^{-1} at 1 atm). As we assumed the value of 9.3 is somewhat too high, we chose a mean value of 8.9 for our analyses. Dubessy et al. (1989) discussed the necessity of correcting relative Raman cross sections for specific wavelengths. The corresponding cross sections for CO_2 and CH$_4$ are then 1.5 and 7.7, respectively. Dubessy et al. (1989) chose 8.7 as the most reliable Raman cross section, resulting in 7.57 for the wavelength-corrected σ. These corrections were not applied to our data, and we admit that this should have been done. That would result in higher CH$_4$ contents. In the present samples, the lowest calculated CH$_4$ content is about 78 mol%, and corrections would be 6 mol% for this composition ($X_{CH_4} = 0.78$ would be 0.84). However, in our case the instrumental correction factor offsets the effect of wavelength correction, and CH$_4$ contents are not higher, but 0–5 mol% lower, than those published in Kisch and van den Kerkhof (1991).

THE INSTRUMENTAL CORRECTION FACTOR

Contrary to previously published statements (e.g., Burke, 1989), the comparison of Raman analyses of experimentally derived gas mixtures during the last three years has shown that an instrumental correction factor (f) should have been applied to the analyses made with the Microdil-28. The gas mixtures were produced by thermal decomposition of silver nitrate and ammonium nitrate with a surplus of graphite, as described in van den Kerkhof (1988); they contain CO_2-N_2 mixtures with 25 and 67 mol% N_2, respectively. Raman analyses of these mixtures have been carried out with the Dilor XY (CREGU, Nancy, France), the Ramanor U-1000 (I.G.D.L., Göttingen, Germany; BRGM, Orléans, France; Washington University, St. Louis, Missouri, U.S.A.; University of Windsor, Windsor, Ontario, Canada), and the MLR-1000, a noncommercial Raman probe (Potsdam, Germany, M. Ziemann) and resulted in compositions of 24–27 and 65–70 mol% providing reasonable agreement with the theoretical composition of the standard samples. However, measurements made by the Microdil-28 (Free University, Amsterdam, The Netherlands; Sofia University, Sofia, Bulgaria), also used for the present measurements, gave significantly higher apparent N_2 contents, namely 38–41 and 80–84 mol%, respectively. Detailed information can be given on request by the first author. From the present data we had to conclude that the instrumental factor for spectra of CO_2 must be significantly different from unity for the Microdil-28. Based on the results of the two standard CO_2-N_2 samples, the instrumental factor for CO_2 is calculated from the expression

$$f = \frac{(1 - X^{*}_{N_2}) \cdot X_{N_2}}{(1 - X_{N_2}) \cdot X^{*}_{N_2}}$$

where X_{N_2} is the composition (in mole fractions) of the standard, and $X^{*}_{N_2}$ the actually measured composition. For the two standards, the instrumental factor was calculated as 0.48–0.54 (for $X_{N_2} = 0.25$) and 0.38–0.51 (for $X_{N_2} = 0.67$). For our purposes, we assumed $f = 0.5$ (in agreement with both standards), and the quantification factor is consequently $1.5*0.5 = 0.75$. Earlier Raman measurements should be accordingly corrected. The recalculated Raman analyses from Kisch and van den Kerkhof (1991) are presented in Table 1. Comparison of Raman data of natural CH_4-N_2 inclusions, measured with Ramanor U-1000 and Microdil-28, result in identical gas compositions. The composition of a high-pressure N_2-CH_4 standard mixture (supplied by G.B. Morgan and J.D. Pasteris, Washington University) can be reproduced within a 5% accuracy by both instruments. Therefore, a negligible additional intrumental factor (0.97 ± 0.07) may be assumed for CH_4, at least for pressures ≥ 100 bars.

RAMAN ANALYSIS OF AQUEOUS INCLUSIONS (H₂O-CH₄)

The quantitative analysis of H_2O-gas inclusions cannot be made from Raman spectra directly. We stated in our paper that CH_4 contents in aqueous inclusions are not exactly known, and there is no disagreement on that point. However, in their discussion Pasteris et al. referred to the uncontrolled factors that may influence the intensity of the Raman signal. We found that "some bubbles show high intensities for the CH_4 line, while others show only weak or no CH_4 signal." Although the quantitative determination of CH_4 contents is not possible, we concluded that most inclusions contain easily detectable amounts of CH_4, whereas others evidently are pure H_2O. We only could estimate maximum CH_4 contents for CH_4-saturated H_2O inclusions. Hanor (1980) reported methane solubility of 1–5 mol% in H_2O without salt between 200–300 °C at about 1 kbar. As proposed by Pasteris et al. (1993), the compositions can be potentially determined from gas pressure estimates by Raman spectra and phase volume proportions. However, given the problems discussed here, results are not (yet) highly accurate, especially for low gas pressures. We encourage the current investigations by Pasteris and coworkers, which may result in a refinement of the method.

We discussed two possible interpretations, namely the assumption of pure H_2O and the assumption of methane-saturated H_2O. In the latter case, gaseous and aqueous inclusions must have been formed from one $H_2O(\pm NaCl)$-CH_4-CO_2 fluid becoming immiscible at the trapping (homogenization) temperature. These temperatures best agree with formation temperatures obtained by other methods.

THE POSITION OF RAMAN BANDS

The position of the Raman band (in cm⁻¹) of CH_4 and other gases is lowered with increasing fluid pressure (< 1 kbar) and with additional components in the fluid. An extensive discussion of the interpretation of Raman data could not be given in our paper on a regional study. We reported Raman peak positions for CH_4, CO_2, and N_2, which are lower than for gases at 1 atm. The peak position of CH_4 is known to be the most sensitive to pressure and has been studied by May et al. (1959), Fabre and Couty (1986), and Chou et al. (1990), and as a part of fluid-inclusion studies by Dhamelincourt et al. (1979) and van den Kerkhof (1987, 1988). For the present CH_4-CO_2 inclusions (with highest $X_{CO_2} = 0.28$), those that are purest in CH_4 have the lowest molar volumes: methane-rich inclusions of 41 cm³/mol contain only 4–5 mol% CO_2 and traces of N_2 and H_2S. The internal pressure of the highest density and highest pressure inclusions is 1.0 kbar at room temperature, as determined by microthermometry and reference to the Peng-Robinson equation of state. In our 1991 paper we stated by mistake that the maximum pressure is 0.5 kbar. For these inclusions, we found the lowest Raman line positions at 2913.5–2914.1 $\pm$ 0.6 cm⁻¹. Pasteris et al. (1993) correctly point to the fact that Raman line positions shift to lower values in the presence of additional components, and thus conclusions on the pressure of fluid mixtures cannot be drawn from Raman spectra of pure fluids. However, there are no indications that 4–5 mol% of CO_2 causes drastic shifts of Raman peaks in CH_4.

The peak position of low-density pure CH_4 inclusions ($V \sim 300$ cm³/mol, $P \sim 65$ bar at room temperature) was measured at 2919. 5 cm⁻¹, i.e., higher than the maximum peak position given in the literature: Pasteris et al. (1990) reported 2916.8 cm⁻¹, Fabre and Couty (1986) 2916.7 cm⁻¹. Our deviation must be due to calibration problems in this part of the Raman spectrum. The Raman probe was calibrated for peak positions of some crystalline phases (calcite at 1086 cm⁻¹, diamond at 1332 cm⁻¹). In this way, Raman lines of CO_2 (around 1388 and 1285 cm⁻¹) could be measured accurately, but a deviation for the CH_4 line (2–3 cm⁻¹) is still possible because of the absence of appropriate reference peak positions. The reproducibility of peak positions is much better and normally falls within the instrumental resolution of 0.6 cm⁻¹ for the CH_4 range of the Raman spectrum. We did not find evidence for a strong temperature dependence of peak positions nor for a significant instrumental drift in a day's time span. Therefore, we assume that the relative values of the CH_4 Raman line can be correctly determined without accurate calibration; the measured peak position at 1.0 kbar is 2913.5–2914.1 cm⁻¹, i.e., a shift of about 6 cm⁻¹ compared with an inclusion of ~65 bars, consistent with the findings of Fabre and Couty (1986).

Other evidence for the higher pressure character of Raman CH_4 spectra is the broadening of the peak, reported by May et al. (1959) and by others. Comparing the Raman spectra of the lowest and highest density inclusions from the Appalachian samples, we find a width at half height of 3.5 cm⁻¹ for $V = \sim 300$ and 6.5 for $V = 41$ cm³/mol (the slit width of the instrument was set at 200 μm).

TABLE 1. Microthermometry data and corrected Raman results for fluid inclusions from the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians

			Ths	Thm	m/s	Tm/s	Th	L/C/V
Ap80-28I	C10	H1			—	—	−96.3	V
Ap80-28I	B15	H1			—	—	−94.7	V
Ap80-28I	C9	H1			—	—	−82	C
Ap79-7B	A1	H1/H2?				?	−86.6	L
Ap79-5C	A6	H1/H2?				?	−81.4	L
Ap79-7B	A2	H2			m	−90.7	−77.5	L/C
Ap80-28I	A1	H2			m	−77.4	−70.8	L
Ap80-28I	B1	H2			m	−76.9	−70.8	L
Ap80-51	A7	H2			m	−72.8	−67.1	L
Ap80-28I	C1	H2			m	−76.9	−70.6	L
Ap79-7B	A4	S2	−124		s	−95.8		L
Ap79-7B	A3	S2	−124		s	−95.8		L
Ap79-5C	A4	S2	−108		s	−89.3		L
Ap79-5C	A1	S2	−108		s	−89.3		L
Ap80-56F	A5	S2	−88.1	−85	s	−79.1		L
Ap80-56F	A1	S2	−88.4	−85	s	−78.4		L
Ap80-56F	A3	S2	−90.4	−87	s	−78.4		L
Ap80-26	A1	S2	−84.1	−81	s	−76.4		L
Ap80-51	A1	S2	−77.2	−74	s	−73.5		L
Ap80-51	A4	S2	−82.4	−78	s	−73.9		L

Note: Ths = partial homogenization; Thm = metastable homogenization; m/s denotes melting (m) or "sublimation (s)—here, melting without vapor; Th = homogenization to liquid (L), critical (C), or vapor (V). All temperatures in degrees Celsius. Raman quantification factors (new) are 7.57 (CH_4), 1.5*0.5 = 0.75 (CO_2), 1 (N_2) and 6.37 (H_2S). The Raman lines at 2576–2582 cm⁻¹ were earlier attributed to ionic HS⁻, but are now interpreted as H_2S dissolved in liquid methane mixture. Molar volumes were calculated according to (A) Angus et al. (1976) for CH_4 data, (KK) Kisch and van den Kerkhof

APPLICATION OF DATA: CALCULATION OF TRAPPING PRESSURE AND TEMPERATURE

The trapping conditions of fluid inclusions are normally estimated from molar volumes, fluid compositions, and equations of state for the appropriate system. Isochores present the extrapolations from the homogenization points to higher pressure-temperature conditions. The determination of the molar volume of fluid inclusions is essential for the interpretation of trapping conditions; the fluid composition is a much less sensitive parameter. Pasteris et al. (1993) point to the need of highest accuracy of molar volume determination, particularly important in the case of extrapolation to very high temperatures and pressures (i.e., granulite-facies or eclogite-facies conditions), where most equations of state are likely to be increasingly more inaccurate. However, we disagree with Pasteris et al. (1993) that "a small inaccuracy in the compositional analysis . . . could ramify into significant inaccuracies in the slopes of the calculated isochores. . . . and could imply completely erroneous trapping conditions." Differences in composition (within ~10 mol%), but at constant molar volume, have only a little effect on the position of the isochore. The determination of the molar volume from microthermometry and composition, and not the composition itself, is the important factor. In our case extrapolations do not exceed 300 °C. However, that does not alter the fact that the highest possible accuracy is desirable.

Molar volumes are estimated from phase diagrams presenting composition, molar volumes, and phase transition temperatures (XVT diagrams). The data used can be either microthermometry data only (partial or total homogenization temperatures and melting temperatures) or homogenization temperatures and compositions, obtained by Raman analysis. In our case we used only microthermometric data, which were interpreted by means of the diagram of Herskowitz and Kisch (1984), which is valid for molar volumes <65 cm³/mol and $X_{CH_4} > 0.4$ in the system CO_2-CH_4 (Table 2 in Kisch and van den Kerkhof, 1991). As an internal check, Raman results have been compared with compositions obtained from microthermometry data and the same phase diagram (Fig. 1). Except for two inclusions, discrepancies do not exceed 5 mol% for the corrected Raman results, which in our opinion is acceptable. Considering CO_2-CH_4 inclusions from other studies and the full compositional range, the fit of Raman and microthermometry data was found to be within 10 mol% (van den Kerkhof, 1988, Fig. 4.13), even when Raman data are not corrected for the recently calculated quantification factors. Before the recent availability of suitable standards, this was a reason for us to accept the quantification factors, although not highly accurate, as reliable. The accuracy of molar volumes calculated from phase transitions mainly depends on the accuracy of partial homogenization temperatures (in the range between −125 and −70 °C). These temperatures were measured within 1 °C accuracy and correspond to 0.3–0.6 cm³/mol, i.e., a better than 1 cm³/mol accuracy of the molar volume. The error caused by temperature inaccuracies are assumed to be less than the error inherent in the inaccuracy of the applied phase diagram. The VX diagram for the system CO_2-CH_4, like those for many other systems, is based on a limited number of experi-

TABLE 1—Continued

Raman analysis (old)				Raman analysis (new)				Microtherm.		
CH$_4$	CO$_2$	N$_2$	H$_2$S	CH$_4$	CO$_2$	N$_2$	H$_2$S	CH$_4$	V	
100.0	n.d.	n.d.	n.d.	100.0	n.d.	n.d.	n.d.	100	303	(A)
100.0	n.d.	n.d.		100.0	n.d.	n.d.		100	281	(A)
99.5	n.d.	n.d.	0.5	99.6	n.d.	n.d.	0.4		99	(A)
96.2	3.0	0.8		95.3	4.1	0.7			62	(KK)
94.5	4.3	1.2		93.2	5.8	1.0			72	(KK)
95.9	3.6	n.d.	0.5	94.7	4.9	n.d.	0.4	95	79	(KK)
89.7	9.5	n.d.	0.7	86.8	12.7	n.d.	0.6	88	72	(KK)
89.3	10.7	n.d.	n.d.	85.8	14.2	n.d.	n.d.	87	70	(KK)
79.0	21.0	n.d.		73.3	26.7	n.d.		82	64	(KK)
77.7	22.3	n.d.	n.d.	71.7	28.3	n.d.	n.d.	87	69	(KK)
96.3	2.9	n.d.	0.8	95.3	4.0	n.d.	0.7	94	41	(HK)
95.4	3.8	0.8		94.3	5.1	0.7		94	41	(HK)
92.9	5.8	1.3		91.1	7.8	1.1		92	46	(HK)
92.0	6.5	0.7	0.8	90.0	8.7	0.6	0.7	92	46	(HK)
92.6*	7.4*			90.1*	9.9*			86	56	(HK)
91.9	8.9	n.d.		89.2	10.8	n.d.		85	56	(HK)
86.1	13.9			81.8	18.2			85	54	(HK)
85.1	14.9	n.d.		80.6	19.4			84	58	(HK)
85.1	14.9	n.d.	n.d.	80.6	19.4	n.d.	n.d.	82	62	(HK)
84.7	15.3	n.d.		80.1	19.9	n.d.		81	59	(HK)

(1991) for H-type inclusions, and (HK) Herskowitz and Kisch (1984) for S-type inclusions. Dashes = temperatures could not be measured; n.d. = not detected. Raman analyses (old) are taken from Kisch and van den Kerkhof (1991); new calculations are corrected for wavelength and instrumental factors.
* Formation of graphite during analysis.

mental data, mostly outside the range of interest for fluid inclusion studies. It can be deduced from Figure 6 (Kisch and van den Kerkhof, 1991) that for Th between −77 and −110 °C and between ~0.5 and 1.5 kbar, 1° difference in Th corresponds to a difference of 27–43 bars at 200 °C and a difference of 35–57 bars at 300 °C, according to the Peng-Robinson equation. Even in the case of determination of volumes from combined partial homogenization temperatures and Raman analyses, errors are also small: the maximum error in molar volume due to the 5 mol% uncertainty in fluid composition (at a given partial homogenization temperature) was estimated from the diagram of Herskowitz and Kisch (1984) to be ~0.7 cm³/ mol (for ~40-cm³/mol inclusions with X_{CH_4} ~ 0.9) and ~1.9 cm³/mol (for 60-cm³/mol inclusions with X_{CH_4} = 0.8). These ranges cover most gas inclusion data from the Pennsylvania Appalachians described in our paper.

CONCLUSION

Most criticisms by Pasteris et al. (1993) are justified from the analytical point of view. The corrected results of Raman analyses are presented in this paper. However, because of low CO_2 contents in our samples from the Appalachian Mountains, the geological implications of the corrections are only minor. Although we are aware of the problems and inaccuracies inherent in the quantitative Raman analysis of gas mixtures and fluid-inclusion studies in general, we hold to our statement that the present study of fluid inclusions presents accurate data on metamorphic pressure. Pressure estimates by other methods in our case were even more inaccurate and more sensitive to the temperature.

The Raman analyses as published in Kisch and van den Kerkhof (1991) were not used for the calculation of molar volumes but were carried out in order to characterize the fluid system and as an internal check for the validity of the phase diagram of Herskowitz and Kisch (1984). In our opinion the recorded isochores were con-
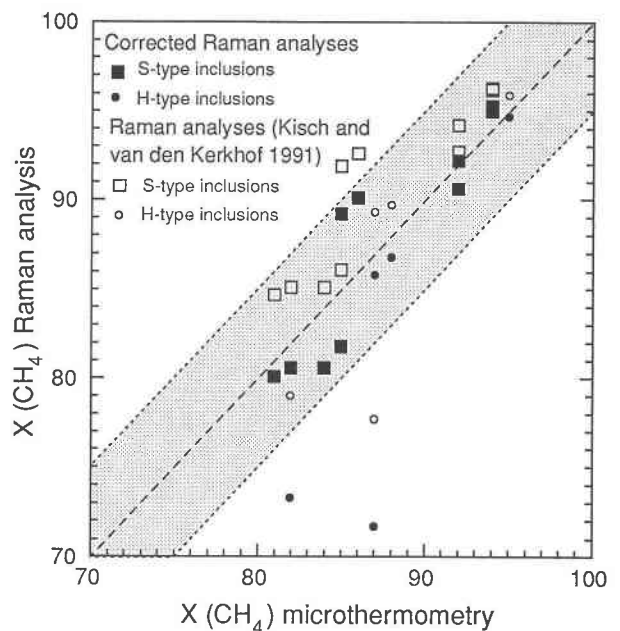

Fig. 1. Correlation between fluid compositions obtained by microthermometry and Raman analysis (corrected and noncorrected values).

structed from the most accurate molar volume determinations possible with the present state of knowledge of the system CO_2-CH_4. In spite of the several restrictions of the method, Raman analysis has unique advantages and gives acceptable compositions for nonaqueous inclusions. Higher accuracies might be possible but are not essential for geological interpretation.

REFERENCES CITED

Angus, S., Armstrong, B., and de Reuck, K.M. (1976) Carbon dioxide. In I.U.P.A.C. International thermodynamic tables of the fluid state, vol. 5. Pergamon, Oxford, England.

Burke, E.A.J. (1989) Quantitative laser Raman microspectrometry on fluid inclusions: An appraisal of five years of experience in Amsterdam. Contributions of Georaman-89: Applications of Raman spectrometry to the earth sciences, Toulouse, May 1989, p. 5.

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.

Dhamelincourt, P., Bény, J.M., Dubessy, J., and Poty, B. (1979) Analyse d'inclusions fluides à la microsonde MOLE à effet Raman. Bulletin de Minéralogie, 102, 600–610.

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'Académie des Sciences de Paris, 303, Série II, 1305–1308 (in French).

Hanor, J.S. (1980) Dissolved methane in sedimentary brines: Potential effect on the PVT properties of fluid inclusions. Economic Geology, 75, 603–617.

Herskowitz, M., and Kisch, H.J. (1984) An algorithm for finding composition, molar volume and isochores of CO_2-CH_4 fluid inclusions from T_h and T_{fm} (for $T_h < T_{fm}$). Geochimica et Cosmochimica Acta, 48, 1581–1587.

Kisch, H.J., and van den Kerkhof, A.M. (1991) CH_4-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 H_2 and CH_4 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.

Pasteris, J.D., Seitz, J.C., Morgan, G.B., and Wopenka, B. (1993) CH_4-rich inclusions from quartz veins in the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians—Discussion. American Mineralogist, 78, 216–219.

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, Berlin.

van den Kerkhof, A.M. (1987) The fluid evolution of the Harmsarvet ore deposit, central Sweden. Geologiska Föreningens i Stockholm Förhandlingar, 109, 1–12.

——(1988) The system CO_2-CH_4-N_2 in fluid inclusions: Theoretical modelling and geological applications, 206 p. Ph.D. thesis, Free University, Amsterdam.