A nitrogen-rich metamorphic fluid and coexisting minerals in slates from North Wales

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Abstract

Volatile species analysis of fluid inclusions in metamorphic quartz veins from the Llanbedr Formation, North Wales, show nitrogen to be an important component. Microthermometric and Laser Raman analysis indicates that the N_2 is resident in a generation of very N_2-rich inclusions and demonstrates the presence of both N_2-rich and aqueous fluids during metamorphism of the Llanbedr Formation. N_2-rich fluids do not appear to have been present in adjacent lithologies. Isotopic analysis of N_2 in fluid inclusions and in the slates indicates that the N_2 in the slates (thought to be present as NH_4^+ substituting for K^+ in muscovite and for Na^+ in albite) was probably originally derived from organic matter in the sediment and subsequently released to the fluid phase during metamorphism.

Mineral–fluid and fluid–phase equilibrium calculations show that the mineral assemblage in the slates could be in equilibrium with either N_2-rich or aqueous fluid depending on redox conditions. The N_2-rich and aqueous fluids in the veins could, therefore, have been trapped at different times under different conditions, though their coexistence as immiscible fluids is a possibility.

KEYWORDS: nitrogen-rich metamorphic fluid, coexisting minerals, slate, North Wales.

Introduction

THE occurrence of nitrogen in the metamorphic environment, both in fluids and as NH_4^+ in micas, has been noted previously, e.g. Stevenson (1962), Milovskiy and Volynets (1966), Bastoul (1983), Kreulen and Schuiling (1982), Casquet (1986). In this paper we describe a new occurrence of a very N_2-rich fluid in low grade metamorphic rocks and examine the fluid phase and mineral-fluid equilibria pertinent to this example.

Geology. The Llanbedr Formation is part of the Harlech Grits Group which forms the core of the Harlech Dome in North Wales (Matley and Wilson, 1943), Fig. 1. The formation is composed mainly of green, grey and purple, well cleaved mudstones (the slate lithology) with some siltstone and sandstone beds and is intruded by sills of microdiorite. All these rocks have undergone low grade metamorphism (Fettes *et al.*, 1985) with the development of a metamorphic mineral assemblage consisting of phengitic muscovite + chlorite + quartz ± albite ± epidote ± pyrite ± magnetite ± rutile. Kaolinite is present in some samples although it is not clear whether it is peak metamorphic, retrograde or both. Quartz veins are rare in the slate lithology but occur more commonly in sandstone and siltstone beds towards the top of the formation and in association with the microdiorite intrusions. The temperature of metamorphism, based on oxygen isotopic compositions of quartz, magnetite and chlorite in metamorphic veins in the Llanbedr slates (samples 1B and 2A of this study), is 425 ± 30 °C (details in Bottrell, 1986).

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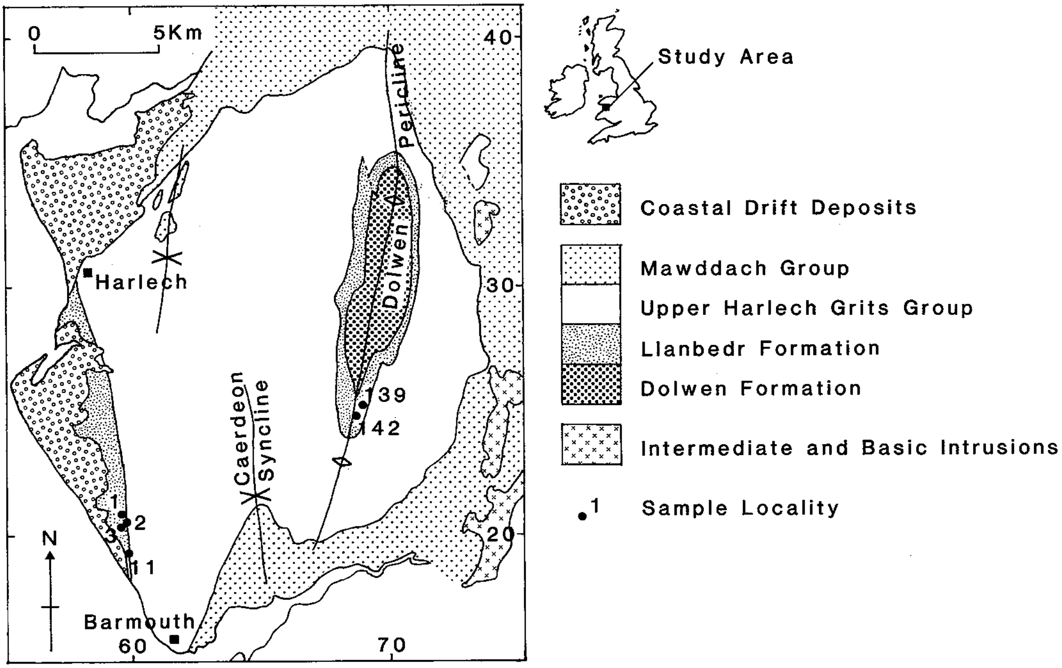

FIG. 1. Geological sketch map of the Harlech Dome showing sample localities.

Sampling and analytical details

Samples were collected from the Llanbedr Formation in the centre and western parts of the Harlech Dome (Fig. 1). At each locality samples of quartz-vein and host-rock were collected (Table 1). Fluid inclusions were analysed microthermometrically in free-standing doubly-polished quartz chips using a Linkam temperature-programmable stage attached to a Leitz Ortholux microscope (Shepherd, 1981). Total inclusion fluid compositions were analysed at the BGS Geochemical Laboratories, London (courtesy of Dr T. J. Shepherd). Gases were released from the inclusions by thermal decrepitation under vacuum at 550 °C and abundances of the released gases measured by manometry and mass spectrometry as described in Shepherd and Waters (1984). Nitrogen for isotopic analysis was prepared from fluid inclusions by decrepitation over the range 200 to 800 °C and from micas by heating acid-washed powdered rock samples to 1200 °C. The gas was purified by cryogenic separation and analysed by static mass spectrometry; the error associated with the measurement is *c.* ±2‰.* Analysis of the vapour phase of a single N_2-rich inclusion was performed with a M.O.L.E. Raman microprobe (Dhamelincourt *et al.*, 1979; Dubessy *et al.*, 1983). XRF major element analyses of whole-rock samples were performed at the Department of Geology, Nottingham University, using the fused bead method of Norrish and Hutton (1969) as modified by Harvey *et al.* (1973).

Results and discussion

Fluid inclusion study. Petrographic examination of the quartz vein samples showed two distinct modes of occurrence of fluid inclusions: (i) isolated inclusions, or inclusions in small groups and (ii) inclusions in planar arrays on healed fractures.

It is assumed that the inclusions occurring in mode (i) were trapped earlier than those occurring in mode (ii), though the mode (i) inclusions are not of proven primary origin. Microthermometric analysis of fluid inclusions in vein quartzes from the Llanbedr Formation and associated intrusives showed the presence of two inclusion types: (*a*) two-phase (liquid + *c.* 10 vol. % vapour) at room

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* Since the nitrogen isotopic analyses were run it has been discovered that the errors on the sample analyses may be larger than the quoted figure of 2‰, which was derived from the reproducibility of analyses of isotopic standards. As it is not possible to determine the true magnitude of the error the isotopic data should be treated with caution.

Table 1. Locations and descriptions of samples.

Sample	Grid Ref.	Description
1A	SH 605205	5cm. thick Qv in sltst. bed in green slate.
1B	SH 605205	15cm. thick bleb of vein qz in green slate.
1C	SH 605205	Green coloured slate hosting 1A and 1B.
1D	SH 605205	Grey slate, 20m. higher than 1C.
2A	SH 605206	10cm. thick bleb of vein qz in grey slate.
2B	SH 605206	Grey coloured slate.
3A	SH 604205	Green coloured slate.
3B	SH 604205	Altered microdiorite.
3C,3D	SH 604205	Qv from contact of 3A and 3B.
11A	SH 603191	5cm. thick Qv in 25cm. thick sst. bed.
11B	SH 603191	Sst. hosting 11A.
11C	SH 603191	Green slate below 11B.
139A	SH 693251	1cm. thick pre-folding Qv in green slate
142A	SH 692250	5cm. thick Qv in microdiorite
142B	SH 692250	Altered microdiorite

sltst. = siltstone sst. = sandstone Qv = quartz vein

qz = quartz

temperature, aqueous inclusions and (*b*) dark single-phase (i.e. low refractive index, ?vapour) inclusions.

Type (*a*) were present in all the samples studied while type (*b*) were only observed in samples 1B and 2A. Type (*a*) occurred as isolated inclusions and also in arrays and were up to 10 μm in diameter, while type (*b*) were present only as isolated inclusions and were smaller, of 4 to 5 μm maximum diameter. Detailed microthermometric analysis was carried out on sample 1B. Type (*a*) inclusions gave final ice melting temperatures between −2 and −5 °C and homogenisation temperatures in the range 150 to 210 °C. Type (*b*) inclusions appeared to remain single phase down to the lowest operating temperatures of the stage used (*c.* −180 °C) and were therefore thought to contain nitrogen. The type (*b*) inclusions in sample 2A exhibited similar behaviour.

Laser Raman microprobe analysis was used to identify the contents of the vapour phase of a single, 5 μm diameter, type (*b*) inclusion and gave a composition of 76 mol. % N_2 and 24 mol. % CO_2. Under the operating conditions used it is possible that up to 0·5 mol. % CH_4 could also be present. The relatively low signal intensity obtained from the inclusion during analysis requires a very low density for the fluid in the inclusion, suggesting that the analysed inclusion had leaked since entrapment. As no other type (*b*) inclusions were large enough for laser Raman analysis, no further data could be obtained. Touret (1982) presents a phase diagram for the system N_2-CO_2 at low temperatures which, for the composition determined by Raman analysis, shows phase changes at *c.* −70 °C (CO_2 solid + vapour to vapour) and −147 °C (CO_2 solid + N_2 liquid + vapour to CO_2 solid + vapour), neither of which is observed in the type (*b*) inclusions. This is probably due to the volumes of solid and liquid phases formed being too small to be observed microscopically in such small, low-density inclusions. For example, a thin (0.5 μm) film of condensed nitrogen on the walls of a 5 μm diameter inclusion could easily remain invisible and yet would account for over 30% of the inclusion volume; thus in a low-density inclusion of this size, the liquid nitrogen phase might never be observed. In addition, it is also possible that there is a film of liquid (water) on the walls of the type (*b*) inclusions which is also too thin to be observed and hence the total inclusion composition could be quite water-rich. As the density of the vapour phase is not known it is not possible to calculate the bulk inclusion composition that a thin film of water would produce.

Table 2 presents analyses of the proportions of six volatile species in the total bulk inclusion fluid in seven quartz-vein samples. The highest nitrogen contents of the bulk fluids (samples 1B/2 and 2A) are *c.* 55 mol. %, but since water is also contributed to these analyses from the aqueous type (*a*) inclusions, the maximum H_2O content of the type (*b*) inclusions must be appreciably less than *c*. 45 mol. %. The proportion of CO_2 to N_2 in the bulk analyses is lower than that in the Raman analysis. This might indicate that there is a range of CO_2/N_2 ratios in the type (*b*) inclusions, with many being less CO_2-rich than that analysed by Laser Raman. The levels of CH_4 in the bulk analyses are consistent with its non-detection in the N_2-rich fluid by Laser Raman. It is impossible to constrain the compositions of the type (*b*) inclusions further by the data acquired, but the presence of a generation of inclusions containing more than 55 mol. % N_2, some CO_2 and possibly some H_2O and CH_4 has been demonstrated.

Table 2. Volatile species analyses of total inclusion fluids, as mole percent

Sample	H_2O	N_2	CO_2	CH_4	H_2	Ar
1A	89.60	8.40	1.85	0.08	0.07	0.00
1B/1	47.75	49.87	2.18	0.05	0.14	0.01
1B/2	42.06	55.36	2.25	0.11	0.21	0.01
2A	44.23	54.58	1.02	0.06	0.10	0.01
3D	77.27	21.61	1.00	0.08	0.03	0.00
11A	81.09	17.64	1.05	0.18	0.03	0.00
139A	96.10	1.52	2.18	0.12	0.07	0.00
142A	93.83	4.01	1.78	0.20	0.18	0.00

The occurrence of the nitrogen-rich fluid. The bulk fluid inclusion analyses in Table 2 show very high levels of N_2 (50 to 55 mol. %) in samples 1B and 2A; these are both post-cleavage metamorphic quartz veins in the slate lithology. Samples 1A, 11A and 3D are also rich in N_2 (8 to 21 mol. %) and are from thin sandstones in the slate (1A, 11A) and from the faulted contact of slate and an intrusion (3D). Sample 139A is an earlier, pre-folding vein in the same lithology and contains far less N_2 (1.5 mol. %) while sample 142A from within a microdiorite sill contains 4 mol. % N_2. There is then an association between the high N_2 levels and the slate lithology. The low N_2 levels in the early vein 139A and the apparently early trapping of the N_2-rich inclusions in samples 1B and 2A suggest that the N_2-rich fluid was present close to the peak of the metamorphism of the slates. More widely, veins in contrasting lithologies (sandstones, siltstones and shales) in adjacent formations never contain N_2 levels comparable with those found in the Llanbedr Formation. Bottrell (1986) reports 18 bulk inclusion analyses from other formations. The majority of these give < 1 mol. % N_2, the highest being 2.5 mol. %.

Isotopic study. Isotopic measurements were made on two nitrogen samples from inclusion fluids and on two nitrogen samples from slates. During pyrolysis of the acid-washed slate samples all nitrogen species are converted to N_2 for measurement and analysis, and the original speciation of the nitrogen is unknown. We assume that the nitrogen released was originally present as NH_4^+ substituted for K^+ in the muscovite in the rock (e.g. Vedder, 1965; Yamamoto and Nakahira, 1966; Shigorova *et al.*, 1982) and for Na^+ in albite (Barker, 1964), there being no other mineral present which could accommodate significant nitrogen. The nitrogen release profile from the slate (Fig. 2) shows a bimodal pattern which is interpreted as due to release from muscovite in the range 500 to *c*. 900 °C and from albite above *c*. 900 °C. This implies that *c*. 20% of the ammonium in the rock is resident in albite.

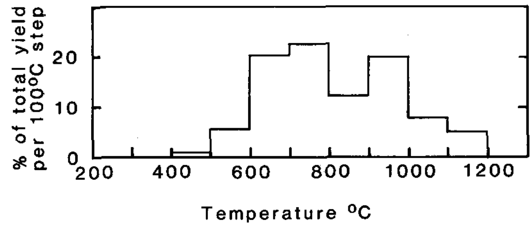

FIG. 2. Nitrogen release profile during pyrolysis of slate sample 1D.

The results are presented in Table 3; the two slate samples are from adjacent outcrops and give similar values, the difference between them being less than the analytical uncertainty. The most likely source of the nitrogen in the slates is organic matter in the original sediment. This would have a nitrogen composition in the range 0 to $9‰_{AIR}$ and there is a small fractionation ($+1‰$) on fixing of the organic nitrogen into the sediment (Peters *et al.*, 1978). Thus the nitrogen compositions in the slates (3.9 and $5.2‰_{AIR}$) are consistent with an original organic source. During diagenesis the nitrogen released by the breakdown of the organic material may become incorporated into clays and micas as ammonium and thus enter the metamorphic cycle. Subsequently nitrogen may be released to the fluid phase as a result of increasing temperature (see discussion in Hallam and Eugster, 1976, and Dubessy and Ramboz, 1986). It is also possible that nitrogen could be released to the fluid phase from

Table 3. Nitrogen isotopic measurements on inclusion fluids and whole-rock samples.

Inclusion fluids

Sample	$\delta^{15}N$
1B	-1.5
2A	-6.9

Whole-rock samples

Sample	$\delta^{15}N$	N_2 yield (ppm)
1C	+5.2	168
1D	+3.9	129

Nitrogen isotopic compositions are in per mil relative to air

breakdown during metamorphism of organic matter which had survived diagenesis. As the proportion of nitrogen to carbon in organic material and kerogen is small (Tissot and Welte, 1978), the latter process would also generate larger amounts of CH_4, which are not found in the Llanbedr Formation veins, so direct release of nitrogen into the fluid is discounted.

The two inclusion samples have a large difference between them but are from separate veins. The nitrogen in the slates is enriched in ^{15}N relative to both of the fluid-inclusion nitrogen samples. The two slate samples were collected from close to the quartz-vein samples and the differences in the fluid and slate nitrogen compositions are approximately 6‰ and 11.5‰. Equilibrium fractionations between ammonium and both NH_3 and N_2 at temperatures of interest are given by Haendel *et al.* (1986); at 425 °C their fractionations are 8.6‰ for NH_3 and 2.9‰ for N_2. Our measured values at *c.* 425 °C are, respectively, between the experimental values for NH_3 and N_2 and above the higher value (NH_3). The large difference in mineral and fluid nitrogen compositions for sample 2A could represent an original equilibrium fractionation between mineral ammonium and fluid NH_3 at a lower temperature of *c.* 360 °C with subsequent complete oxidation of NH_3 to N_2. In the case of sample 1B the measured mineral-fluid isotopic difference would represent an equilibrium fractionation between ammonium and NH_3 at over 600 °C, an impossibly high temperature for these rocks. However, it is possible that, in this case, the N_2 in the fluid has partially re-equilibrated with the mineral ammonium.

Fluid-mineral and fluid phase equilibria

The purpose of this section is to estimate the composition of the fluid phase which would be in chemical equilibrium with the rock during metamorphism using available mineral-fluid and fluid phase equilibrium data. The results of these calculations are then used to make observations on the origin and nature of the N_2-rich fluid. Throughout this section all calculations have been performed for 425 °C and 2 kbar pressure. The temperature is the estimate of Bottrell (1986) for the formation of the quartz-vein samples 1B and 2A from the oxygen isotopic composition of quartz, magnetite and chlorite. 2 kbar is the pressure at which Hallam and Eugster (1976) give experimental data for equilibria between NH_4 minerals and fluid. Hallam and Eugster (1976) stress the provisional nature of the data from their experiments so the treatment below can only be considered semi-quantitative. Isochores for the aqueous [type (*a*)] inclusions in sample 1B give entrapment pressures in the range 3.1 to 3.5 kbar at this formation temperature; hence the entrapment pressures of the N_2-rich inclusions may well be above the 2 kbar used in the calculations, but this difference will not affect the overall conclusions.

Calculations. From the data of Hallam and Eugster (1976):

$$6NH_4AlSi_3O_8 \cdot 0.5H_2O = 2NH_4Al_3Si_3O_{10}(OH)_2 + 12SiO_2 + 4NH_{3(g)} + 3H_2O_{(g)} \quad (1)$$

$$\log K_1 = 37935/T - 56.65.$$

For sample 1C the total nitrogen yield is known (Table 3) and the rock contains 3.63 wt.% K_2O and 0.92 wt. % Na_2O by XRF analysis. Assuming all the K and Na to be resident in mica and albite and taking the NH_4 distribution derived in Fig. 2 then the mole fraction of ammonium mica is 0.013 and of ammonium feldspar is 0.016. Assuming ideal mixing small amounts of ammonium silicates in the alkali hosts and a quartz activity of unity gives:

$$4 \log f_{NH_3} + 3 \log f_{H_2O} = -9.7 \quad (2)$$

where f_i is the fugacity of component i.

The nitrogen in the fluid phase is present as N_2 rather than NH_3 (NH_3 was below the detection limit of the Raman probe) so in order to relate the fugacity ratio calculated above to the N_2-rich fluid, consideration must be given to the equilibria involving N_2 and NH_3 in the fluid phase. This is most conveniently done via the reaction:

$$N_2 + 3H_2O = 2NH_3 + 1.5O_2 \quad (3)$$

for which the log equilibrium constant

$$\log K_3 = 2 \log f_{NH_3} + 1.5 \log f_{O_2} - \log f_{N_2} - 3 \log f_{H_2O} \quad (4)$$

can be calculated from data in the JANAF thermochemical tables (Stull and Prophet, 1971; the calculations are presented in detail in Bottrell, 1986). Log K_3 is -50.5 at the conditions of interest. By combining equations (3) and (4) to eliminate f_{NH_3} we have:

$$9 \log f_{H_2O} + 2 \log f_{N_2} = 91.3 + 3 \log f_{O_2}. \quad (5)$$

From which, using the relationships

$$P(i) = f_i / \gamma_i, \quad (6)$$

where the fugacity coefficients (γ_i) are 2.73 for N_2 and 0.25 for H_2O, taken from the data of Ryzhenko and Volkov (1971), and

$$X(i) = P(i)/P_{tot}, \quad (7)$$

(where $X(i)$ is the mole fraction of i) we have, for an N_2-H_2O fluid

$$\log[X(N_2)/X(H_2O)] = 45.7 + 1.5 \log f_{O_2} - 5.5 \log f_{H_2O} - 0.5 \log[\gamma(N_2)/\gamma(H_2O)]. \quad (8)$$

The only constraint on the parameter f_{H_2O} is the presence of muscovite in the mineral assemblage, as the minimum f_{H_2O} required to stabilise muscovite relative to an anhydrous assemblage can be calculated from the data of Chatterjee and Johannes (1974), who, for the reaction

$$\text{quartz} + \text{muscovite} = \text{sanidine} + \text{andalusite} + H_2O \quad (9)$$

give:

$$\log f_{H_2O} = 8.337 - 4682/T + 0.0163(P-1)/T. \quad (10)$$

This gives a minimum value of log f_{H_2O} of 1.73. There is an additional constraint that:

$$P(N_2) + P(H_2O) = P_{total} = 2000 \text{ bars}. \quad (11)$$

These constraints on fluid composition are represented diagrammatically in Fig. 3, together with the following independent estimates of oxygen fugacities:

(i) The slates contain pyrite and magnetite, so the oxygen fugacity must also be constrained between the hematite–magnetite and pyrrhotine–pyrite–magnetite buffers. Using the data summarised by Frost (1985), log f_{O_2} at each buffer was calculated as -21.2 and -24.4 respectively.

(ii) The ratio of the minor components of the fluid, CO_2/CH_4, may be used to constrain its oxygen fugacity via the equilibrium

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (12)$$

for which log K can be calculated from data in Ohmoto and Kerrick (1977). The CO_2/CH_4 mole ratio used was a mean for samples 1B and 2A (Table 2) of 27 and is assumed to be that of the N_2-rich fluid. Fugacity coefficients for these species were taken from Ryzhenko and Volkov (1971).

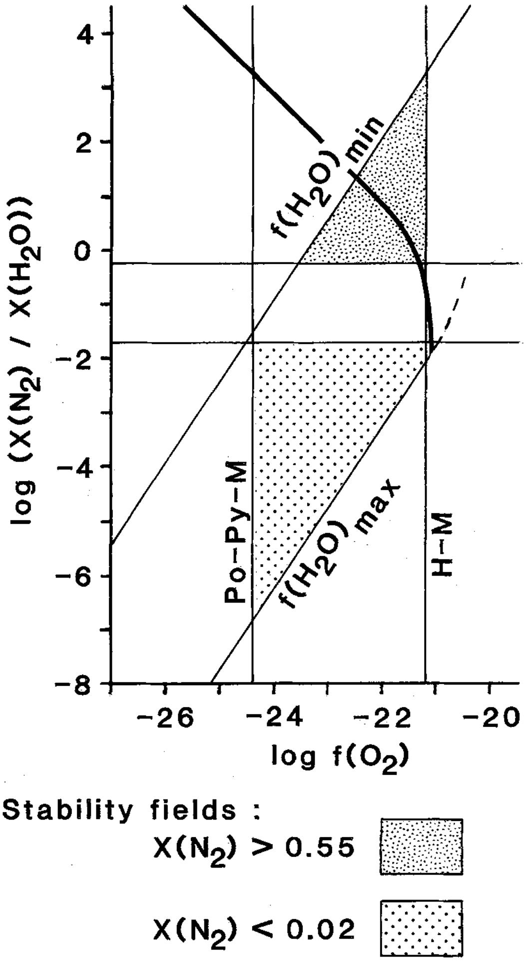

FIG. 3. Constraints on fluid composition in the system N_2-H_2O at 425 °C and 2 kbar. The curve $f_{H_2O\,min}$. corresponds to the minimum water fugacity calculated for a muscovite-bearing assemblage from equation 10. $f_{H_2O\,max}$. corresponds to the maximum possible water fugacity (equation 11). The limiting fluid compositions are $X(N_2) = 0.55$ from gas analysis data and $X(N_2) = 0.02$, an assumed maximum for the water-rich fluid inclusions. The heavy curve gives oxygen fugacities calculated from CO_2/CH_4 ratio using equation 12.

Discussion. The constraints on fluid composition portrayed in Fig. 3 show clearly that both an N_2-rich fluid (with $X(N_2) > 0.55$) and a water-rich fluid (with $X(N_2) < 0.02$) could coexist in equilibrium with the ammonium-bearing silicate assemblage in the slates. Furthermore, for the range of possible compositions, the oxygen fugacities calculated for the N_2-rich fluid are consistent with those given by the limiting mineral buffers (Fig. 3).

Thus the two fluids observed in inclusions may both represent compositions in equilibrium with the slates trapped at different times, as the ammonium-bearing silicates provide only a broad constraint on the $X(N_2)/X(H_2O)$ ratio of a coexisting fluid.

A possibility also exists that the two fluids coexisted immiscibly. Japas and Franck (1985) have demonstrated immiscibility in the N_2–H_2O system at temperatures up to 385 °C at 2 kbar and the presence of dissolved salts will extend the field of fluid immiscibility. The microthermometric data on the N_2-rich inclusions are insufficient to satisfy rigorous criteria to prove the immiscible coexistence of N_2-rich and H_2O-rich fluids.

Conclusions

Fluid inclusion evidence shows the presence of both nitrogen-rich (> 55 mol. % N_2) and aqueous fluid inclusions in metamorphic quartz-veins in the Llanbedr Formation. These imply the presence of a nitrogen-rich fluid during the metamorphism of the slates in this formation. Isotopic studies are compatible with the hypothesis that the nitrogen was derived from organic material in the sediment via incorporation of ammonium ion into clays and micas during diagenesis and subsequent release to the fluid phase during metamorphism. Thermochemical calculations indicate that the rock could be in equilibrium with either a water-rich or a nitrogen-rich fluid during metamorphism dependent on the prevailing conditions. The quality of microthermometric data for the N_2-rich inclusions is severely limited by their small size and low density and are inadequate to satisfy rigorous criteria for immiscibility with aqueous inclusions. Hence it is impossible to distinguish whether the nitrogen-rich and aqueous fluids observed in inclusions were present at different times or coexisted as immiscible fluids.

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References

Barker, D. S. (1964) *Am. Mineral.* **49,** 581–5.

Bastoul, A. (1983) Ph.D. thesis, INPL Nancy.

Bottrell, S. H. (1986) Ph.D. thesis, University of East Anglia.

Casquet, C. (1986) *J. Metamorphic Geol.* **4,** 117–30.

Chatterjee, N. D., and Johannes, W. (1974) *Contrib. Mineral. Petrol.* **48,** 89–114.

Dhamelincourt, P., Beny, J. M., Dubessy, J., and Poty, B. (1979) *Bull. Mineral.* **107,** 155–68.

Dubessy, J., and Ramboz, C. (1986) Extended abstracts, **WRI-5,** 171–4, Reykjavik.

——Geisler, D., Kosztolany, C., and Vernet, M. (1983) *Geochim. Cosmochim. Acta,* **47,** 1–10.

Fettes, D. J., Long, C. B., Bevins, R. E., Max, M. D., Oliver, G. J. H., Primmer, T. J., Thomas, L. J., and Yardley, B. W. D. (1985) In Harris, A. L. (ed.) *Memoir No. 9.* The Geological Society, 41–53.

Frost, B. R. (1985) *J. Petrol.* **26,** 31–63.

Haendel, D., Mühle, K., Nitzsche, H.-M., Stiehl, G., and Wand, U. (1986) *Geochim. Cosmochim. Acta,* **50,** 749–58.

Hallam, M., and Eugster, H. P. (1976) *Contrib. Mineral. Petrol.* **57,** 227–44.

Harvey, P. K., Taylor, D. M., Hendry, R., and Bancroft, F. (1973) *X-ray Spectrometry,* **2,** 33–44.

Japas, M. L., and Franck, E. U. (1985) *Ber. Bunsenges. Phys. Chem.* **89,** 793–800.

Kreulen, R., and Schuiling, R. D. (1982) *Geochim. Cosmochim. Acta,* **46,** 193–203.

Matley, C. A., and Wilson, T. S. (1943) *Q.J. Geol. Soc. London,* **102,** 1–35.

Milovskiy, A. V., and Volynets, V. F. (1966) *Geochem. Internat.* **3,** 752–8.

Norrish, K., and Hutton, J. T. (1969) *Geochim. Cosmochim. Acta,* **33,** 431–53.

Ohmoto, H., and Kerrick, D. (1977) *Am. J. Sci.* **277,** 1013–44.

Peters, K. E., Sweeney, R. E., and Kaplan, I. R. (1978) *Limnol. Oceanogr.* **23,** 598–604.

Ryzhenko, B. N., and Volkov, V. P. (1971) *Geochem. Internat.* **8,** 468–81.

Shepherd, T. J. (1981) *Econ. Geol.* **75,** 1244–7.

——and Waters, P. (1984) *Mineral. Deposita,* **19,** 304–14.

Shigorova, T. A., Kotov, N. V., Kotel'nikova, Ye. N., Schmakin, B. N., and Frank-Kamenetskiy, Va. (1982) *Geochem. Internat.* **18,** 76–82.

Stevenson, F. J. (1962) *Geochim. Cosmochim. Acta,* **26,** 797–809.

Stull, D. R., and Prophet, H. (1971) *U.S. Dept. Commerce, Nat. Bur. Stds.* **37.**

Tissot, B. P., and Welte, D. W. (1978) *Petroleum formation and occurrence. A new approach to oil and gas exploration.* Springer-Verlag.

Touret, J. (1982) *Chem. Geol.* **37,** 49–58.

Vedder, W. (1965) *Geochim. Cosmochim. Acta,* **29,** 221–8.

Yamamoto, T., and Nakahira, M. (1966) *Am. Mineral.* **51,** 1775–8.

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