N_2-CO_2-CH_4-H_2O metamorphic fluids in microdiamond-bearing lithologies from the Western Gneiss Region in Norway

RUNE B. LARSEN, ERNST A. J. BURKE, LARISSA F. DOBRZHINETSKAYA, ELIZABETH A. EIDE & BRIAN A. STURT

Rune B. Larsen, Elizabeth A. Eide & Brian A. Sturt, Geological Survey of Norway, P.O.Box 3006-Lade, N-7002 Trondheim, Norway.
Ernst A. J. Burke, Vrije Universiteit, De Boelelaan 1085, NL-1085 HV Amsterdam, Netherlands.
Larissa F. Dobrzhinetskaya, University of California Riverside, Institute of Geophysics & Planetary Physics, Riverside, California 92521-0412, U. S. A.

Introduction

Previous studies of volatiles in metamorphic lithologies from the Western Gneiss Region (WGR) in Norway document that eclogite- and granulite-facies metamorphism is associated with mixtures of CO_2, N_2 and H_2O fluids (e.g. Andersen et al. 1993). Our study of microdiamond-bearing granulites from the island of Fjørtoft supports this conclusion but also documents a strongly reducing volatile regime, with CH_4 as a significant constituent, during parts of the metamorphic history.

Results

Microthermometry and Raman analysis (see Burke & Lustenhouwer) (1987)) were conducted on fluid inclusions in garnet-kyanite granulite and in eclogite lenses enclosed in a garnet-clinopyroxene granulite. Microdiamonds occur in both granulite types (Dobrzhinetskya et al. in review).

Garnet-kyanite granulite/rock

This granulite is characterised by porphyroblastic, coarse-grained, almandine-rich garnet, coarse-grained kyanite, medium- to coarse-grained lepidoblastic phlogopite and graphite, and a matrix dominated by medium- to fine-grained, predominantly granoblastic quartz, plagioclase and rutile with minor iron oxides, zircon and sulphides.

CO_2-N_2 fluids in garnet core

These inclusions are primary and form negative crystal imprints and vary in size from 2 to 5 μm. Calcite daughter crystals were commonly detected during Raman analyses of these inclusions. The average composition is 78 mole % CO_2 and 22 mole % N_2.

CO_2-N_2-CH_4 fluids in garnet rims and quartz

Inclusions of this type carry trace amounts of CH_4 and occur in garnet rims as primary or pseudo-secondary species, or as primary inclusions in matrix quartz. They form negative crystal imprints and vary in size from 2 to 5 μm. The average composition is 62 mole % CO_2, 36 mole % N_2 and 2 mole % CH_4. Daughter minerals of magnesian calcite ((Ca, Mg)CO_3) were commonly detected in these fluids.

N_2-CH_4-H_2O fluids in quartz and garnet

Fluids with this composition have not previously been reported from the WGR. They occur in primary and secondary subhedral inclusions in quartz and secondary inclusions in garnet, and measure from 5 to 20 μm. The inclusions contain mixtures of N_2 and CH_4, and in some cases immiscible H_2O. The proportions of H_2O vary from ≤10, to approximately 60 vol. %. An average composition of 66 mole % CH_4 and 34 mole % N_2 characterises these fluids. The density for the entire N_2-CH_4-H_2O system is presently unknown because the mole-fraction of H_2O remains to be determined.

Extension gashes in eclogites

Both garnet-kyanite and garnet-clinopyroxene granulites contain lenses of eclogite varying in size from a few metres to several hundred metres. Fluid inclusion studies were conducted on quartz in extension gashes in two eclogite lenses enclosed by the garnet-clinopyroxene granulites. The extension gashes intersect the 2 to 5 metre wide eclogite lenses in an en echelon pattern and rapidly dissipate upon entering the enclosing garnet-clinopyroxene granulite. They are dominated by granoblastic, medium- to coarse-grained quartz, locally with a few percent euhedral, medium- to coarse-grained plagioclase crystals. Inclusion fluids represent the fluid regime both from the eclogites and the garnet-clinopyroxene granulite since the extension gashes transgress both lithologies.

CO_2 fluids in quartz

Two populations of CO_2 fluids occur as primary fluid inclusions in quartz. They are 4 to 7 μm in diameter and display negative crystal imprints.

One population, with an average liquid homogenisation at -22.0°C, has the highest density of any CO_2 fluid so far recorded in the Western Gneiss Region (pers. comm. Tom Andersen, 1994).

N_2-CH_4-H_2O fluids in quartz
These fluids are similar to those described previously. However, the content of CH_4, at an average of 19 mole %, is somewhat lower compared to the inclusions in garnet-kyanite gneiss.

H_2O-$CaCl_2$ fluids in quartz
This is an unusual type of saline aqueous fluid characterised by $CaCl_2$ rather than NaCl that is the norm in the WGR (Andersen et al. 1993). The fluids are confined to inclusions in secondary intergranular trails and measure from 5 to more than 25 μm in diameter. The presence of $CaCl_2$ is strongly supported by the low initial melting of ice observed at -55.6 ± 4.7°C which is fairly close to the eutectic minimum in the H_2O-$CaCl_2$ binary system (≈ -50°C). However, the deviation from the eutectic minimum and the occasional presence of the daughter mineral nahcolite ($NaHCO_3$) indicate that NaCl and CO_2 are present in trace amounts in the H_2O-$CaCl_2$ liquid.

Final melting of ice at -14.3°C is equivalent to 17.9 wt. % of dissolved $CaCl_2$ in these inclusions. Total homogenisation at 89°C emphasises an extremely high density at the time of trapping of these fluids.

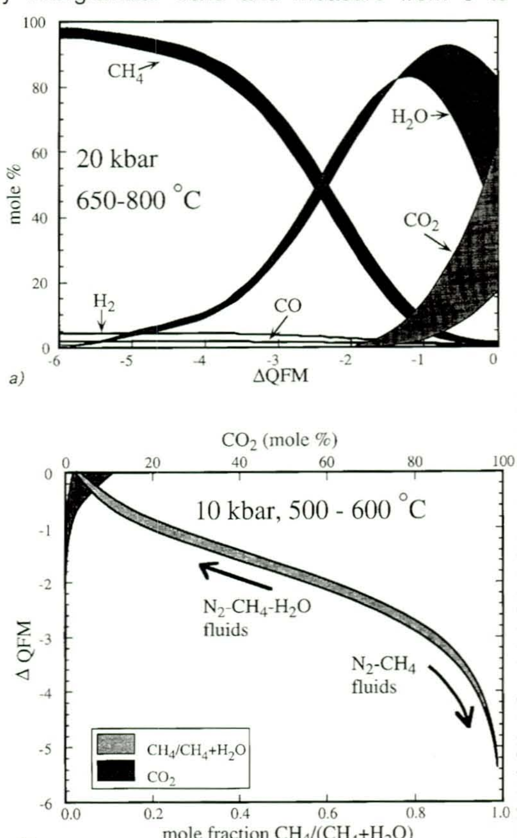

Fig. 1. Theoretical modelling of the dominant volatile constituents in a graphite buffered C-O-H solution that has equilibrated to the p, T conditions estimated for the Fjørtoft granulites. *Figure 1A*: Total speciation of a C-O-H fluid at the p and T when CO_2-N_2 fluids dominated the fluid regime. *Figure 1B*: Proportions of CH_4, H_2O and CO_2 under the p and T when N_2-CH_4 (±H_2O) volatiles characterised the fluid regime. See text for discussion and additional comments.

Discussion and conclusions

Primary fluid inclusions with CO_2-N_2 mixtures occur in the cores of garnets and as such, were formed before the primary CO_2-N_2-CH_4 fluids enclosed in the garnet rims. The CO_2-N_2-CH_4 fluids are older than the N_2-CH_4 and the N_2-CH_4-H_2O inclusions that occur in secondary trails intersecting garnet or in primary inclusions in matrix quartz post-dating garnet. The relative chronology between N_2-CH_4 and N_2-CH_4-H_2O fluids is somewhat ambiguous because both types of fluids may occur as secondary inclusions in different parts of the same healed crack. However, some quartz grains carry primary N_2-CH_4 inclusions and secondary N_2-CH_4-H_2O inclusions within the same crystal. These relationships indicate a continuum from anhydrous types to inclusions with progressively higher proportions of H_2O together with N_2 and CH_4.

The two generations of primary CO_2 inclusions occur in quartz grains intersected by secondary N_2-CH_4 (±H_2O) and, as such, predate these fluids. Their relative chronology compared to the CO_2-N_2 (±CH_4) fluids cannot be deduced from the textural relations.

The H_2O-$CaCl_2$ fluids are clearly later than the CO_2-N_2 (±CH_4) and the CO_2 inclusions because they are only confined to secondary trails in quartz. Their relative chronology compared to N_2-CH_4 (±H_2O) could not be unravelled from the textural relations.

In conclusion, textural relations document a continuous evolution from: (1) N_2-CO_2 fluids during the growth of the garnet core through (2) N_2-CO_2-CH_4 fluids during the crystallisation of the garnet rim to fluid mixtures of (3) N_2-CH_4 and, finally, to (4) N_2-CH_4-H_2O, both coexisting with the matrix.

It is apparent from this chronology that the main difference from (1) to (4) is the continuous addition of hydrogen to mixtures of N_2 and CO_2. Depending on the oxygen fugacity of the system, the hydrogen component can be one or more of the volatile components H_2, CH_4 and H_2O.

According to the equilibrium,

(i) $CO_2 + 2H_2O = CH_4 + 2O_2$

with the equilibrium constant,

$K = fCH_4(fO_2)^2/fCO_2(fH_2O)^2$

it is apparent that the ratio between CH_4 and H_2O is a function of fO_2, p, T, K and fCO_2. However, the presence of graphite and diamond in both garnet-kyanite and garnet-clinopyroxene granulites indicates that the fluids were buffered by elemental carbon. Consequently, the ratio between CH_4 and H_2O is solely a function of p, T, fO_2 and K for various key equilibria including (i), as demonstrated in previous studies of the C-O-H system (e.g., French 1966).

Microprobe analyses of coexisting phases in the garnet-clinopyroxene and the garnet-kyanite granulites indicate that high-grade metamorphism, which probably concurs with the formation of garnet cores, occurred at $p \geq 17\text{-}21$ kbar and T between 650° and 800 °C. The matrix, in contrast, re-equilibrated during retrograde metamorphism at $p \geq 10\text{-}11$ kbar and T between 500° and 600 °C. These conditions correspond to the p and T when the CO_2-N_2 and the N_2-CH_4 ($\pm H_2O$), respectively, dominated the volatiles. Figs. 1a and 1b show the properties of a graphite-buffered C-O-H fluid calculated as a function of the oxygen fugacity under the estimated p-T conditions. Fluid speciation calculated according to the thermodynamic computer application 'GEOFLUID' (Larsen 1993) show that CH_4, H_2O and CO_2 comprise more than 98 mole % of the C-O-H volatiles under the high-grade conditions prevailing in the granulites and extension gashes (Fig. 1a).

Modelling also shows that the CO_2-N_2 fluids existed under hydrogen-free conditions, since H_2O and CH_4 would have been present in substantial amounts together with graphite, CO_2 and N_2 under the relevant p-T-fO_2 conditions (Fig. 1a). As a consequence, it is not possible to estimate the fO_2 at which the garnet cores crystallised, but we conclude that hydrogen-fixing volatiles (H_2, H_2O and CH_4) were absent at this stage. This absence was due to the fact that hydrogen was fixed in hydrous minerals, was absorbed by anatectic silicate melts or, simply, was not present at the metamorphic stage when garnet cores formed.

Fig. 1b indicates that the fO_2 must have been quite low when hydrogen (e.g. as H_2O) was introduced during crystallisation of the gneiss matrix. Upon introduction, hydrogen was immediately fixed by CH_4. Fixation of almost all hydrogen in CH_4 could only have been accomplished if the fO_2 was more than 3 log units lower than the quartz-magnetite-fayalite buffer (Fig. 1b). The higher proportions of H_2O contained in the subsequent fluids indicate that the fO_2 fluid-mineral assemblage increased as re-crystallisation of the matrix proceeded during retrograde conditions.

It is still unclear whether the fluid regime had any impact on the diamond genesis. Nonetheless, the present study demonstrates that the microdiamond-bearing granulites on Fjørtoft island were exposed to a complex variety of C-H-N-O fluids. Several studies document that diamonds in kimberlitic rocks as well as in eclogites and high pressure gneisses formed in a volatile-rich environment characterised by various C-H-N-O species (e.g. Haggerty 1986, Guthrie et al. 1991). The role of volatiles in diamond genesis is vigorously debated but some studies suggest that diamond inherits the carbon component as well as trace amounts of nitrogen from co-existing CO_2-N_2 fluids (e.g. Boyd et al. 1992).

What seems to be clear from the studies of fluids in the granulites from Fjørtoft island is that microdiamond may have co-existed with graphite-buffered N_2-CH_4-CO_2-H_2O fluids in a strongly reducing environment that, indeed, provided the components necessary for the crystallisation of diamond.

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