On ammonium in upper-amphibolite facies cordierite–orthoamphibole-bearing rocks from Rød, Bamble Sector, south Norway

DIEDERIK VISSER

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NH_4^+ values of 1100–3000 ppm and 250–458 ppm have been measured in biotites and whole rock samples respectively, from cordierite–orthoamphibole-bearing rocks at Rød, Bamble Sector, south Norway. The results indicate that given: (a) suitable (Mg, Fe, Al)-rich and (Ca, Na)-poor bulk compositions, (b) no high-grade (breakdown-)reactions involving biotite, (c) reducing conditions defined by graphite-bearing assemblages, and (d) an ammonium-rich protolith, significant amounts of ammonium in biotite can survive high-grade metamorphism. The high ammonium contents are considered supplementary evidence for a seuimentary origin of the cordierite–orthoamphibole-bearing rocks. The significant quantities of N_2 previously reported in quartz from this locality are thought to be genetically related to the retrogression of the ammonium-bearing biotites.

D. Visser, Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, PO Box 80.021, 3508 TA Utrecht, The Netherlands.

The presence of substantial amounts of ammonium in sedimentary, metamorphic and igneous rocks has been shown by the studies of, among others, Urano (1971), Honma & Itihara (1981) and Duit et al. (1986). The ammonium levels in igneous systems commonly range between 10 and 100 ppm for granitic rocks and much lower, between 1 and 12 ppm, for basic and ultrabasic rocks (Hall 1988a, b). Sedimentary rock types show variable ammonium levels due to the inheritance of nitrogen from organic matter. Shales (Urano 1971; Haendel et al. 1986) show high ammonium levels of several hundred ppm and occasionally over one thousand ppm, while levels in sandstones and cherts are in the 1 to 150 ppm range.

Ammonium concentrations in metamorphic rock types, in which ammonium may substitute isomorphously for potassium in minerals such as biotite, K-feldspar, plagioclase and muscovite, mainly depend on the sedimentary or igneous signature of the pre-metamorphic precursor. In principle, high ammonium levels may be used to indicate the sedimentary signature of the rock (Itihara & Honma 1979), while low levels alone are not enough to distinguish between a possible igneous or sedimentary origin of the rock. The primary ammonium content, however, can be modified due to the breakdown or formation of ammonium-bearing minerals during both prograde and retrograde regional or contact metamorphism (Duit et al. 1986; Cooper & Bradley 1990) and hydrothermal alteration processes (Cooper & Bradley 1990).

The occurrence of nitrogen in metamorphic fluids is reported by an increasing number of fluid inclusion studies. Breakdown or formation of ammonium-bearing minerals may involve N_2 (and NH_3?) as trace, minor or even dominant fluid species. In other words, the presence of these fluid species may serve as an exploration tool for ammonium-bearing minerals and rock types, as demonstrated by Duit et al. (1986), who investigated the nitrogen content of rock types in which nitrogen-rich fluid inclusions were described (Kreulen & Schuiling 1982).

Nitrogen-bearing fluids have been described by fluid inclusion studies in the high-grade metamorphic Bamble Sector, south Norway (Touret & Dietvorst 1983; Touret 1985; Touret 1987; Ploegsma 1989). Touret (1987) presented preliminary fluid inclusion data obtained from a cordierite–orthoamphibole-bearing sample indicating 'abundant CO_2 inclusions mixed with significant quantities of N_2 and some other unknown species (not CH_4), giving strange and yet unexplained microthermometric results' at excursion stop 2.3 of the NATO south Norway geological excursion in July 1984, near Rød in the central part of the Bamble Sector. The cordierite–orthoamphibole rocks occur within a unit consisting of metasediments (nodular gneisses, sillimanite–Garnet–biotite schists and quartzites) and garnet-bearing amphibolites of undetermined origin. Various explanations have been presented concerning the origin of cordierite–orthoamphibole-bearing rocks in the Bamble and genetically related Kongsberg Sectors. Jøsang (1966), Touret (1979) and Beeson (1988) suggested an evaporitic/metasedimentary origin, while metasomatic or hydrothermal alteration associated with metagabbros was suggested as the origin of these rocks by, among others, Bugge (1943), Starmer (1976) and Munz (1990). Morton et al. (1970) proposed a formation from hydrothermally altered basic volcanics. The nitrogen-rich fluid inclusions thus not only provided a good opportunity to test the presence of ammonium-rick rock types in

Table 1. Mineralogy and modal composition of specimens studied, Rød locality, Bamble Sector, south Norway.

Sample	DV 122	MA 780
Quartz %	27.8	8.2
Biotite	26.2	12.3
Garnet	32.6	42.6
Cordierite	8.0	14.0
Orthoamphibole	1.2	15.4
Tourmaline	–	0.2
Kornerupine	–	0.4
Graphite	0.2	0.5
Ilmenite	0.4	0.2
Rutile	1.2	2.0
Apatite	1.0	1.8
Dumortierite*	–	0.1
Chlorite*	0.8	0.7
Muscovite*/pinite*	0.6	1.6

* Secondary phases.

Table 2. Average biotite composition in samples DV 122 and MA 780.

	DV 122 ($n = 15$)	MA 780 ($n = 26$)
SiO_2	38.56	37.44
TiO_2	1.99	2.63
Al_2O_3	17.38	17.01
FeO	11.72	11.83
MnO	0.15	0.01
MgO	17.08	16.21
CaO	0.03	0.00
Na_2O	0.47	0.31
K_2O	7.04	7.80
BaO	n.a.	0.10
Cl	0.38	n.a.
Total	94.80	93.34

n.a. = not analysed.

high grade metamorphic terrains, thus may also be used to evaluate the possible origin of the cordierite–orthoamphibole-bearing rocks at this locality. For this purpose, ammonium contents of both biotite and whole rock of two cordierite–orthoamphibole-bearing samples from the Rød locality were investigated.

Samples

The locality investigated (5030–65096, map references are taken from the 1:50.000 map Tvedestrand, 1612 II) in this study is situated in the Søndeled–Sandnesfjord area, Bamble Sector, south Norway. The major structure and petrology of the rocks in this area have been described by Starmer (1976). The main geologic characteristics of the Proterozoic of the Bamble Sector have been summarized by Starmer (1985). Modal amounts and mineral associations in the selected samples are given in Table 1.

The samples studied are a quartz–biotite–garnet–cordierite ± orthoamphibole schist (DV 122) and a melanocratic quartz–garnet–orthoamphibole–biotite–cordierite–kornerupine rock (MA 780). Euhedral to subhedral brown biotite (Table 2) is the only major potassium-bearing phase in both samples; plagioclase and K-feldspar are absent. Together with euhedral orthoamphibole and H_2O-rich cordierite (0.17 wt% CO_2, 2.36 wt% H_2O and 0.04 wt% K_2O), biotite defines a very weak foliation in MA 780. An early generation of biotite is included in both orthoamphibole and cordierite. Garnet developed as large (max. 3 cm) anhedral to subhedral poikiloblasts overgrowing and consuming biotite, cordierite and orthoamphibole. Cordierite–quartz symplectites developed very irregularly between garnet and orthoamphibole. In MA 780 colourless kornerupine occurs as subparallel to irregular shaped aggregates intergrown with orthoamphibole. Accessory phases in both samples are rutile, apatite, ilmenite and graphite. Tourmaline occurs only in MA 780. Graphite usually occurs intimately intergrown with biotite and occasionally with garnet. Along narrow (up to 4 mm) retrograde zones or cracks, pinite, muscovite, chlorite and rarely pink dumortierite (Visser & Senior 1991) form after cordierite, garnet, biotite and orthoamphibole.

Garnet–biotite (Ferry & Spear 1978) and garnet–cordierite (Holdaway & Lee 1977) Fe–Mg exchange reactions indicate temperature ranges at 7 kbar of 770–805°C (MA 780, von Scheibler 1988) and 730–760°C (DV 122) for garnet cores and matrix biotites and 690–725°C (MA 780) and 655–700°C (DV 122) for garnet cores and matrix cordierites. Temperature estimates calculated from garnet–biotite rims and garnet–cordierite rims, assuming pressures of 4–5 kbar (Visser & Senior 1990), are 540–620°C, 530–590°C (MA 780) and 500–540°C, 520–550°C (DV 122) respectively.

Analytical procedures

Mica fractions of 125–250 μm were separated and purified by means of a Frantz magnetic separator, heavy liquids and handpicking. For wet chemical analysis the whole rock samples and mica fractions were dissolved in a concentrated HF/H_2SO_4 solution for 24 h at 80°C. The decomposed samples were subsequently neutralized with a saturated solution of boric acid. The ammonium was distilled with a Kjeldahl apparatus into a weak (0.05 N) H_2SO_4 solution. The ammonium was measured colourimetrically with a Perkin-Elmer type 550S spectrophotometer applying the Berthelot colouring reaction (Verdouw et al. 1978) at $\lambda = 660$ nm.

The characteristic absorption bands of the ammonium molecule occur at about 3250, 3060 and 2850 cm^{-1} for N–H stretching and at 1430 cm^{-1} for N–H–N bending. The peak intensity of the 1430 cm^{-1} bending vibration is proportional to the NH_4^+ concentration. Duit et al. (1986) calibrated the absorbances at 1430 cm^{-1} of micas against the concentrations of nitrogen liberated by heating under vacuum. Their calibration curves and KBr-disk preparation techniques were used in this study. Possible disturbance of the 1430 cm^{-1} vibration by carbonate vibrations was prevented by a weak acid treatment of the

Table 3. Ammonium concentration (ppm) in biotite and whole rock.

Sample no.	Kjeldahl analysis	Infrared absorption
DV 122 Biotite	1120 ($n = 2$)	1080 ($n = 1$)
MA 780 Biotite	3000 ($n = 4$)	3200 ($n = 3$)
DV 122 WR	250 ($n = 2$)	–
MA 780 WR	458 ($n = 5$)	–

n = number of analyses.

powdered samples before preparation. The infrared absorption spectra of the mica fractions were measured with a Perkin-Elmer 580 infrared spectrophotometer. The total ammonium contents of whole rock and separated biotites are given in Table 3.

Results and discussion

The Kjeldahl results are reproducible within 5–8% for whole rock and 7–10% for biotite. Correlation of the ammonium contents in biotite determined by Kjeldahl and infrared techniques is very good. The ammonium content of the biotites, 1080 in sample DV 122 and 3000 ppm in sample MA 780 are among the highest ever recorded. Itihara & Suwa (1985) recorded 1558 ppm NH_4^+ ($n = 1$) for biotite in tourmaline–muscovite–biotite schist from the Svecofennian Basement in Finland, and 1060–1940 ppm ($n = 16$) were reported in biotites from low to medium grade schists and quartz veins from Dôme de l'Agout, France (Duit et al. 1986). The ammonium concentration of biotite from sample MA 780 is comparable to the richest NH_4^+-bearing biotite found thus far (2000–5000 ppm by IR or 3000 ppm by wet chemical analysis; Darimont et al. 1988). The whole rock contents are 250 and 458 ppm NH_4^+ and are compatible with biotite as the only major ammonium-bearing phase. These high values and the presence of primary graphite, thought to have been derived from decomposed organic material, are compatible with a sedimentary rock precursor. A hydrothermal or metasomatic origin related to metagabbros can be precluded on the basis of the absence of metagabbros and the absence of any evidence of extensive metasomatic or hydrothermal activity at or near the outcrop. The sedimentary origin of the rocks is also supported by the REE geochemistry of MA 780. The REE pattern of MA 780 (Visser et al. in preparation) closely resembles that of North American and European Shale Composites (NASC and ES), with LREE enrichment ($(La/Yb)_N = 5.3$), flat HREE pattern and a distinct negative Eu-anomaly ($Eu/Eu^* = 0.57$). The presence of primary borosilicates indicates that the possible precursor shales, which may have consisted of a mixture of kaolinite/gibbsite, Fe oxides, Mg-rich chlorite, quartz and illite, originally contained a significant amount of boron.

As shown by the geothermometric and geobarometric results ammonium-rich biotite is able to survive P-T conditions of high-grade upper-amphibolite facies. This is in accordance with the experimental data of Bos (1990), who observed the decomposition of the ammonium–phlogopite endmember at conditions of 750°C and 850°C at 2 kbar, while intermediate compositions remained stable. The main factors explaining these high ammonium values in biotite are, apart from high initial amounts of ammonium, the Mg-, Fe-, Al-rich and Ca-, Na-poor bulk chemistry of the cordierite–orthoamphibole rocks, which produced biotite-bearing assemblages instead of other possible NH_4^+-(K^+)-bearing phases, and the absence of textural evidence for prograde breakdown reactions involving biotite that might have liberated NH_4^+ to the fluid system or other mineral phases. The presence of graphite in the samples, indicating a relatively low oxygen fugacity, fixes the fNH_3/fN_2 ratio of the coexisting fluid at a relatively elevated level. This will stabilize the ammonium component of the micas at higher grade conditions (Eugster & Munoz 1966).

The origin of the abundant N_2 in the fluid inclusions is thought to be related to the release of NH_4^+ upon low grade oxidation and retrogradation of the ammonium-bearing biotite along the narrow alteration zones. High-grade entrapment of N_2 along with CO_2 is considered unlikely as CO_2-rich fluids are incompatible with the presence of H_2O-rich cordierite.

Low grade release of ammonium is in agreement with the N_2 isochores presented by Touret & Dietvorst (1983) and the low densities encountered in all other N_2 fluid inclusions observed so far in the Bamble Sector (Touret 1985; Ploegsma 1989).

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