

Aleksandra GAWĘDA¹, Adam PIECZKA², Witold ŻABIŃSKI²

ORIGIN OF SOME CRYSTALLINE ROCKS FROM THE WESTERN TATRA MTS. IN THE LIGHT OF AMMONIUM IONS CONTENT

Abstract. The ammonium content in metamorphic and granitic rocks is considered to be an indicator of their origin (Hall et al. 1996). Increased contents of NH_4^+ ion in metasediments and their minerals (especially biotite) reflect the presence of nitrogen in their parent sedimentary rocks. Samples of metamorphic rocks, granitoids and pegmatites as well as their minerals from the Upper Kościeliska Valley and the western slopes of the Ornak Ridge were analysed for the NH_4^+ content. A significant variability in the ammonium content in the mentioned rocks has been interpreted in terms of their origin, but also of the influence of granite derived fluids.

An increased NH_4^+ ion content in some pegmatites and their minerals (Table 1) supports a thesis about their anatectic character (Gawęda 1995). The geochemical features of the pegmatites could be, consequently, inherited from a metasedimentary protolith. A decreased NH_4^+ ion content has been found in some parametamorphic gneisses, sampled in the vicinity of bigger granitoid bodies. This could be explained as a result of aggressive action of granite-derived fluids leaching primary constituents from the surrounding rocks. It has also been found that NH_4^+ ion content is positively correlated with the Th/Yb ratio in amphibolites. The authors suggest that the analyses for NH_4^+ ion, Th and REE may constitute a significant index of the contamination of primary magma by a crustal material.

Key-words: NH_4^+ ion, Tatra Mts., metamorphic rocks.

INTRODUCTION

For more than 30 years the ammonium content in some crystalline rocks and rock-forming minerals has been of great interest (Wlotzka 1961), which recently has considerably grown. The similarity of ionic radii and charge of NH_4^+ and K^+ results in the possibility of incorporating of ammonium ion in the alkali position of potassium-bearing minerals. Of special petrological importance is the substitution of ammonium for potassium in micas and feldspars, the highest NH_4^+ content being usually found in biotite. This

¹ Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland.

² Department of Mineralogy, Petrography and Geochemistry, University of Mining and Metallurgy, Mickiewiczza 30, 30-059 Kraków, Poland.

phenomenon may be suitable for discrimination between meta-igneous and meta-sedimentary rocks. Already in 1961 Wlotzka found that on the average paragneisses contain more NH_4^+ than orthogneisses. It was confirmed subsequently by numerous authors. The high ammonium content of biotites from metasediments is due to inheritance of nitrogen from organic matter contained in the original sediments. During diagenesis the organically bonded nitrogen may be converted into ammonium ion, first held within interlayer spaces of clay minerals and later within the crystal lattice of biotite formed during metamorphism (Honma, Itihara 1981; Itihara, Suwa 1985).

The enrichment of NH_4^+ in biotites of granitic rocks may be a result of partial melting of sedimentary materials enriched with organic matter or their assimilation by granitic magma (Itihara, Honma 1979). Neiva and Hall (1993) observed also a noticeable relationship between the mineralogy of the various granites and their ammonium content. Studying some Portuguese granites they found that varieties containing only muscovite are lower in ammonium than those containing both muscovite and biotite. The above mentioned authors cite most of earlier papers concerning the role of NH_4^+ ions in granites. The influence of secondary processes (greisenitization, albitization, influence of hydrothermal fluids) on the ammonium content in granitic rocks is a closely related problem (Hall 1993; Neiva, Hall 1993).

Generally speaking, the ammonium content in granites and some metamorphic rocks may be useful in discussing their origin and alteration processes. Many references to the problem are given recently by Visser (1992) and Hall et al. (1996).

Recent publication of Bruździńska et al. (1995) presents the first reconnaissance of the ammonium content in some Polish igneous and metamorphic rocks as well as some rock-forming minerals occurring in them. The aim of this paper is the use of NH_4^+ ion as one of the indicators of petrogenetic processes in the specific geological unit (Western Tatra Mts.).

GEOLOGICAL SETTING

Metamorphic complex of the Polish Western Tatra Mts. represents envelope rocks of the Variscan granodioritic pluton. The complex suffered poly-stage metamorphism in Paleozoic time, documented by the P-T paths, typical of upper amphibolite facies conditions. Near the granitic intrusion the high-temperature conditions (andalusite zone) could be traced (Gawęda, Kozłowski 1996). The protoliths of the metamorphic rocks under consideration are thought to be sedimentary, pelitic-psamitic series injected by MORB-type basalts (Gawęda et al. 1996). At present these rocks are gneisses, migmatites, mica schists and amphibolites.

In the metamorphic envelope veins and nests of pegmatites could be found. They are considered as partial melts conserving the primary, metasedimentary geochemical features (Gawęda 1995).

MATERIALS AND METHODS

Samples of the metamorphic and magmatic rocks as well as the pegmatites and their chosen minerals from the Upper Kościeliska Valley and Ornak were taken from several points with the growing distance from the granite body (Fig. 1). Their petrographical/mineralogical description is given in the Table 1.

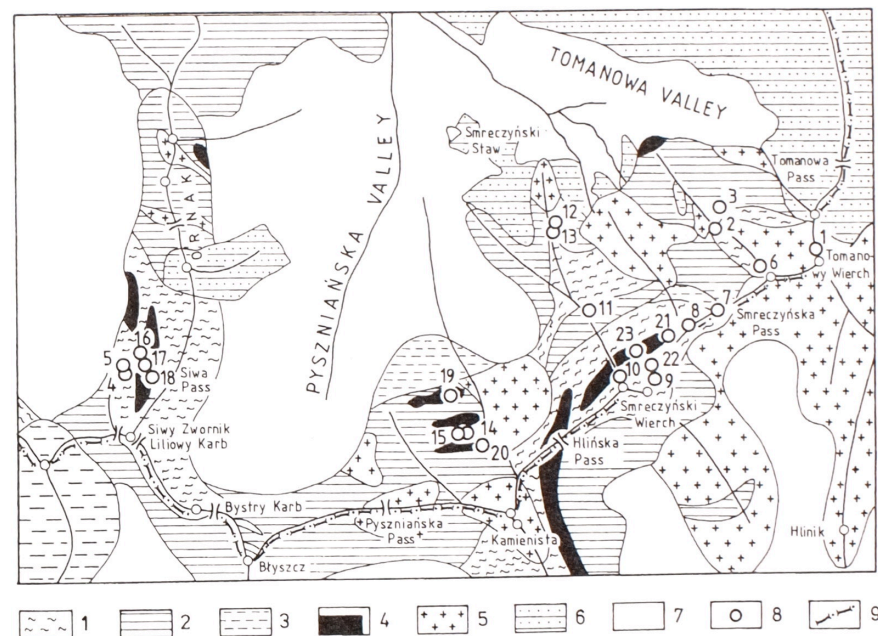


Fig. 1. Simplified geological map of the Upper Kościeliska Valley and Ornak Zone with sampling points

1 — migmatites, 2 — gneisses, 3 — mica schists, 4 — amphibolites, 5 — granites, 6 — sedimentary cover, 7 — Quaternary deposits, 8 — sampling points, 9 — Polish-Slovak border

Fixed ammoniacal nitrogen contents of rocks are obtained as the difference between total and soluble ammoniacal nitrogen, which were measured separately.

For the determination of the total ammonium content the powdered samples were decomposed using hydrofluoric and sulphuric acids. After evaporation the residue was dissolved in distilled water and transferred to distillation apparatus, KOH being added to distillation flask. Distilled ammonium was collected in the diluted H_2SO_4 solution and determined colorimetrically using Nessler's reagent (cf. Urano 1971).

For determination of soluble ammonium content 1 g of powdered sample, prepared as a suspension in water, was transferred to a distillation flask containing 40% solution of KOH. The following procedure was the same as in the case of the total ammonium content. The results are presented in the Table 1.

TABLE 1

List of examined samples

No. on the map	Sample No.	Petrographic/mineral characteristic	NH ₄ ⁺ [ppm]
1	2	3	4
1.	2/I	perthitic microcline (Or ₈₁ Ab ₁₉); $\Delta r = 0.975$ pegmatite from alkali-feldspar granite	32
2.	5/III	pegmatite: Kfs + Ab + Q + Ms; A/CNK = 1.246; K ₂ O = 2.59% wt.	31
3.	TM	paragneiss: I. Pl (An ₂₄) + Q + Bt + Kfs + Ms + Ap II. Chl + Sc + Q A/CNK = 1.961; K ₂ O = 4.40% wt.	66
4.	SK2	perthitic microcline (Or ₇₂ Ab ₂₇ An ₁); $\Delta = 1.00$; pegmatite from plagioclase-biotite gneiss	100
5.	P/Or	pegmatite: Kfs + Ab + Q + Ms; from plagioclase-biotite gneiss; A/CNK = 1.323; K ₂ O = 3.92% wt.	95
6.	GN3	paragneiss: I. Pl (An ₂₀₋₂₅) + Bt + Q + Grt + Kfs + Ap II. Chl + Sc A/CNK = 1.165; K ₂ O = 3.89% wt.	28
7.	15M	mezosome of migmatite: Bt(fm = 0.604) + Pl(An ₂₂) + Q + Ap + Sil A/CNK = 1.453; K ₂ O = 2.62% wt.	44
8.	GN4	paragneiss: Pl(An ₃₀) + Bt + Q + Ap A/CNK = 1.243; K ₂ O = 2.22% wt.	45
9.	GN2	paragneiss: I. Pl (An ₂₀₋₂₅) + Bt + Q + Grt + Kfs + Ap II. Chl + Sc A/CNK = 1.165; K ₂ O = 3.89% wt.	75
10.	GN1	paragneiss: I. Pl (An ₂₃) + Bt + Q + Grt + Kfs II. Chl + CC A/CNK = 1.125; K ₂ O = 2.7% wt.	112
11.	Bi/S	biotite from pegmatite (fm = 0.592; TiO ₂ = 2.93% wt.) K ₂ O = 6.72	280
12.	10/VIII/P	pegmatite from the paragneiss: Kfs + Ab + Ms; A/CNK = 0.987; K ₂ O = 6.34% wt.	46
13.	10/VIII/G	paragneiss: I. Pl (An ₃₀) + Q + Bt + Kfs + Ap II. Sc + Chl + Q	118
14.	GnBnl	granitic vein: Pl(An ₁₆) + Kfs + Q + Bt + Ap	80
15.	GnBn	paragneiss: I. Pl (An ₂₅) + Q + Bt + Ms + Kfs + Ap II. Chl + Ab + Q	228
16.	A9	orthoamphibolite: I. Hbl + Pl(An ₃₅) + Q + Ilm II. Ab + Ep + Chl A/CNK = 0.570; K ₂ O = 0.6% wt.	72
17.	A10	orthoamphibolite: I. Hbl + Pl(An ₃₄) + Q + Ilm II. Ab + Ep + Chl A/CNK = 0.626; K ₂ O = 1.16% wt.	25

cd. table 1

1	2	3	4
18.	A13	orthoamphibolite: I. Hbl + Pl(An ₃₆) + Q + Ilm II. Chl + Sc + Ab + Q	50
19.	BN1	orthoamphibolite: I. Hbl + Pl(An ₅₄) + Q ₁ + Mt + Ap II. Bt + Ab + Q ₂ A/CNK = 0.872; K ₂ O = 1.91% wt.	53
20.	BN3	orthoamphibolite: I. Hbl + Pl(An ₅₀) + Q + Ilm ± Mt + Ap A/CNK = 0.775; K ₂ O = 1.09% wt.	23
21.	A4	paraamphibolite: I. Ed/Pgs + Pl(An ₄₃) + Q ₁ + Sph ₁ + Ilm II. Sph ₂ + Ep + Q + Ab A/CNK = 0.606; K ₂ O = 1.60% wt.	30
22.	A2	orthoamphibolite: I. Hbl/Fe-Hbl + Pl(An ₃₅) + Q + Ilm + Ap II. Act + Ab + Q ₂ A/CNK = 0.725; K ₂ O = 1.81% wt.	45
23.	A5	orthoamphibolite: I. Hbl + Pl ₁ l(An ₄₀) + Q ₁ + Ilm + Ap II. Bt + Grt(Alm ₇₁) + Pl ₂ (An ₄₀) III. Chl + Q ₂ A/CNK = 0.827; K ₂ O = 0.28% wt.	16

Explanation of symbols: Ab — albite, Act — actinolite, Ap — apatite, Bt — biotite, CC — calcite, Chl — chlorite, Ed/Pgs — edenite/pargasite, Ep — epidote, Grt — garnet, Hbl — hornblende, Ilm — ilmenite, Kfs — K-feldspar, Ms — muscovite, Mt — magnetite, Pl — plagioclase, Q — quartz, Sc — sericite, Sil — sillimanite, Sph — sphene, A/CNK — $\text{Al}_2\text{O}_3/\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, fm — $\text{Fe}/(\text{Fe} + \text{Mg})$ (p.f.u.), Δ — triclinitity of K-feldspar, Or_x/Ab_y — K-feldspar/albite content in alkali feldspar, An_x — anorthite content in plagioclase, Alm_x — almandine content in garnet.

DISCUSSION

The crystalline rocks in question and their mineral separates have revealed the high variability of the ammonium ion content. This may result from either their origin or the action of post-magmatic aggressive fluids in the immediate vicinity of the Tatra Mts. granite. The studied samples were collected at various distances from this granite. The most proximal specimens, taken from the zones affected by the granite where parageneses typical of high temperatures were found (Kozłowski 1996, Gawęda and Kozłowski 1996), have shown the low concentrations of NH₄⁺ ion (25—75 ppm, Table 1) both in whole-rock samples and in minerals separated from them. There is also correlation between the ammonium and potassium ions. Considering that the NH₄⁺ ion substitutes the K⁺ ion in crystalline structure, the origin of the two components may be different. The low amount of ammonium ion in gneisses and migmatites of sedimentary origin (Burda 1995) may be explained, most probably, by exchange of rock components (mainly alkalies and ammonium ion substituting them) with granite-derived fluids.

Samples collected from the areas in which the conditions of the pre-intrusion metamorphism were preserved and the chemical action of the emplaced granite was insignificant contain elevated amounts of NH₄⁺ (95—280 ppm). It should be

emphasized that higher amounts of this component occur in some pegmatites (samples no. 4, 5 and 11), both in whole-rock samples and in minerals separated from them (biotites — 280 ppm, also in feldspars). These pegmatites resulted, most probably, from partial melting of metamorphic rocks and, consequently, could inherit numerous features of a metasedimentary protolith (Gawęda 1995). A small increase of ammonium ion (80 ppm) in a minor granitoid vein intersecting a paragneiss (228 ppm) may be explained as a result of contamination of primary igneous melt.

Similar explanation seems to be probable in the case of amphibolites. Despite their unquestionable orthometamorphic nature, local increases of NH_4^+ have been noted. Continental tholeiites, formed during extension of a weakened continental crust and contaminated to various degree by crustal material, were the protolith of the amphibolites in question (Gawęda et al. 1996). This contamination resulted in the observed difference in the NH_4^+ content.

The ammonium contents in amphibolites is quite variable (16–72 ppm). Except the sample A4 (Table 1) which is a paraamphibolite, the other are of unquestionable magmatic origin. They are considered as continental tholeiites or their tuffs, characterized by 'MORB-like' chemistry, modified by crustal contamination. Primary basalts were probably emplaced in an extensional basin, floored by attenuated continental crust (Gawęda et al. 1996).

Taking into account the Th content and Th/Yb ratio, the degree of crustal contamination was different in analysed samples. It is worth to emphasize, that the lowest NH_4^+ content was noted in the sample A5 (Table 1) representing a primary intrusive dolerite showing rather small degree of contamination (Gawęda and Kozłowski 1996). The observed correlation between NH_4^+ content and Th/Yb ratio (Fig. 2) suggests that noticeable differences in ammonium ion content in amphibolites in question could be a result of their contamination by crustal material.

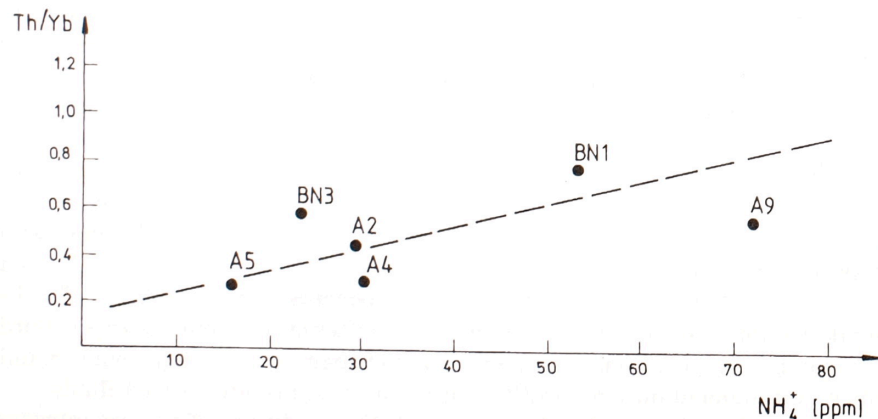


Fig. 2. Th/Yb versus NH_4^+ plot of amphibolites from the Polish Western Tatra Mts.

CONCLUSIONS

1. The ammonium ion content may be applied as an indicator of the origin of metamorphic rocks providing that no chemical changes caused by genetically alien solutions (fluids?) have been found.

2. The suggestion that an elevated NH_4^+ ion content is inherited by rocks formed by partial melting of a protolith of sedimentary origin has been confirmed.

3. The ammonium ion content may be considered as convenient geochemical index of the contamination of igneous rocks with a crustal material but further researches in these field are needed.

Acknowledgements. This study was supported by the Academy of Mining and Metallurgy in Cracow, Project No. 10.140.376. The field research and major elements analyses were carried out thanks the support of the Polish KBN grant 6P 20100107.

REFERENCES

- BRUŹDZIŃSKA A., OLKIEWICZ S., PIECZKA A., ŻABIŃSKI W., 1995: Ammonium content in micas and feldspars from some Polish crystalline rocks — preliminary report. *Miner. Polon.* 26, 2, 55–59.
- BURDA J., 1995: Migmatyty górnej części Doliny Kościeliskiej w Tatrach Zachodnich. Ph.D. thesis (unpubl.) Arch. of the University of Silesia, Sosnowiec.
- GAWĘDA A., 1995: Geochemistry and Rb/Sr isochron age of pegmatites from the Western Tatra Mts. (S-Poland). *Geol. Carpathica* 46, 2, 95–99.
- GAWĘDA A., KOZŁOWSKI K., 1996: Pressure-temperature-time evolution of metamorphic complex in the Polish part of the Western Tatra Mts. *PTMin. Pr. Spec.* 7, 20–22.
- GAWĘDA A., WINCHESTER J., KOZŁOWSKI K., NAREBSKI W., 1996: Geochemistry and paleotectonic setting of the amphibolites from the Western Tatra Mts. *PTMin. Pr. Spec.* 7, 54–56.
- HALL A., 1993: The influence of secondary alteration on the ammonium content in granites, exemplified by the Rosses complex of Donegal. *Miner. Mag.* 54, 455–461.
- HALL A., PEREIRA M.D., BEA F., 1996: The abundance of ammonium in the granites of central Spain, and the behaviour of the ammonium ion during anatexis and fractional crystallization. *Miner. Petrol.* 65, 105–123.
- HONMA H., ITIHARA Y., 1981: Distribution of ammonium in minerals of metamorphic and granitic rocks. *Geoch. Cosm. Acta* 45, 983–988.
- ITIHARA Y., HONMA H., 1979: Ammonium in biotite from metamorphic and granitic rocks in Japan. *Geoch. Cosm. Acta* 43, 505–509.
- ITIHARA Y., SUWA K., 1985: Ammonium contents of biotites from Precambrian rocks in Finland: The significance of NH_4^+ as a possible chemical fossil. *Geoch. Cosm. Acta* 49, 1, 145–151.
- KOZŁOWSKI K., 1996: Al_2SiO_5 polymorphs in the Western Tatras — indicators of metamorphic conditions. *PTMin. Pr. Spec.* 7, 27–29.
- NEIVA A.M.R., HALL A., 1993: Ammonium in some Portuguese granitic rocks, and its petrogenetic implications. *Neues Jahrbuch für Miner., Monatshefte* 2, 49–62.
- URANO H., 1971: Geochemical and petrological study on the origin of metamorphic rocks and granitic rocks by determination of fixed ammoniacal nitrogen. *J. Earth Sci. Nagoya Univ.* 19, 1–24.
- VISSER D., 1992: On ammonium in upper-amphibolite facies cordierite-bearing rocks from Rød, Bamble Sector, south Norway. *Norsk Geol. Tidsskrift* 72, 385–388.
- WLOTZKA F., 1961: Untersuchungen zur Geochemie des Stickstoffs. *Geoch. Cosm. Acta* 24, 106–154.

POCHODZENIE WYBRANYCH SKAŁ KRYSTALICZNYCH TATR ZACHODNICH NA PODSTAWIE ZAWARTOŚCI JONU AMONOWEGO

Streszczenie

Jon amonowy w skałach metamorficznych uważany jest za „chemiczną ska-mieniałość”. Jego podwyższona zawartość, notowana zazwyczaj w skałach me-taosadowych, uważana jest za wynik „odziedziczenia” azotu związanego w po-łączeniach organicznych w pierwotnych osadach (Itihara i Suwa 1985). Podwyż-szone zawartości jonu amonowego odnotowano także w granitoidach pochodzenia anatektycznego (Hall et al. 1996).

Próbki skał metamorficznych, granitoidów, pegmatytów oraz wyseparowanych z nich minerałów z górnej części Doliny Kościeliskiej i zachodnich zboczy grani Ornak (Rys. 1) poddano badaniom na zawartość jonu amonowego. Stwierdzono, iż obserwowana duża zmienność zawartości tego składnika w badanych próbkach ma odniesienie w pochodzeniu rozpatrywanych skał.

Podwyższona zawartość NH_4^+ w niektórych pegmatytach oraz ich minerałach (Tab. 1) potwierdza wcześniejszą tezę o anatektycznym pochodzeniu pegmatytów z górnej części Doliny Kościeliskiej. Cechy geochemiczne tych skał są wynikiem „odziedziczenia” po metaosadowym protolicie.

Odnotowano obniżoną zawartość jonu amonowego w skałach o stwierdzonym parametamorficznym charakterze, zalegających w bliskości większych ciał gra-nitowych. Cecha ta może być tłumaczona oddziaływaniem agresywnych fluidów pochodzących z granitu i wymywaniem pierwotnych składników.

Zaobserwowano pozytywną korelację zawartości NH_4^+ oraz Th/Yb w amfiboli-tach. Istnieje prawdopodobieństwo, iż zawartość jonu amonowego w skałach ortometamorficznych, analizowana wspólnie z zawartością Th oraz pierwiastków ziem rzadkich, może być istotnym wskaźnikiem stopnia kontaminacji pierwotnej magmy materiałem krystalnym.