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Neoproterozoic flood basalts of the upper beds of the Volhynian Series (East European Craton)

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The effusive rocks of the Ratno Beds of the Volhynian Series known from the western slope of the Ukrainian Shield are represented by lower Vendian flood basalts whose normative composition is that of quartz tholeiites. These are plagioclase-pyroxene basalts displaying intergranular, intersertal, doleritic, ophitic and amygdaloidal textures; they range from aphanitic to medium-grained and contain about 7 vol. % of palagonite — an altered glass with a high iron and considerable magnesium content. The range in composition of plagioclases (andesine-bytownite) and clinopyroxenes (augite-ferropigeonite) suggests that the Ratno Beds basalts formed by fractional crystallisation of a parent magma. Residual magma underwent liquation, producing a separate acid glass (69–73 wt. % of SiO_2) phase within a basic one considerably poorer in SiO_2 but rich in iron and magnesium. The Ratno Beds basalts are relatively rich in silica, iron, titanium and vanadium as well as in REE and LREE in particular but poor in Ni, Co and Cr. Normative composition, geochemical characteristics and tectonic position suggest classification as continental quartz tholeiites. Hydrothermal solutions are responsible for rich native copper mineralisation in basalts of certain parts of Volhynia (Ivance and Policy). The Vendian volcanism of the Volhynian Series lithologically correlated with the Sławatycze Series of eastern Poland, can be related to continental rifting accompanying the breakup of Rodinia, with crustal fractures mainly running concordantly with the suture zone between Fennoscandia and Sarmatia, thus almost perpendicular to the Tornquist rift; other fracture trends may also have controlled Vendian volcanism.

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Key words: Volhynian Series, Ratno Beds, flood basalts, fractional crystallisation, liquation, palagonite, copper mineralisation.

INTRODUCTION

In the early Vendian (Late Precambrian) widespread volcanism took place in eastern Poland, southwestern Belarus, western Ukraine and northern Moldavia, over an area of about 140 000 km^2 on the western margin of the East European Craton — EEC (Biryulev, 1969; *cf.* Fig.1). The resulting lavas and tuffs are only partly exposed at the surface (in the Ukraine and Belarus). The Late Precambrian volcanic activity on the western flank of the EEC was probably related to a fault system (Alenko *et al.*, 1990), perhaps active during the late stages of Rodinia rifting, and preceding the formation of the Tornquist Ocean (Poprawa *et al.*, 1999). In eastern Poland, Vendian volcanic activity manifested itself as four successive eruptive cycles of varying intensity (Juskowiakowa, 1971; Szczepanowski, 1977). The effusive-tuffogenic rocks, known exclusively from boreholes, have been named the Sławatycze Series (Areń and Lendzion, 1978; Compston *et al.*, 1995). The Volhynian basaltoids of the Goryn and Styr drainage basin we have studied have been lithologically correlated with the basalts of the IVth cycle of the Sławatycze Series (Szczepanowski, *op. cit.*).

Studies of the Volhynian basalts began in the 19th century and were continued by many Polish geologists (Małkowski, 1923, 1926, 1929, 1951; Kamieński, 1927, 1929; Bohdanowicz, 1932; Krajewski, 1935; Janczewski and Samsonowicz, 1936; Kowalski, 1936; Samsonowicz 1936*a*, *b*; Małkowski and Wojciechowski, 1937; Wojciechowski, 1939); a full list of publications, to 1960, is included in Lazarenko *et al.* (1960). Later studies include Volovnik (1971, 1975), Semenenko *et al.* (1976) and the papers edited by Semenenko (1972).

However, these have included no detailed modern account of mineralogy and petrology. The aim of our study was to give the petrographic and geochemical characteristics of the flood basalts belonging to the upper beds of the Volhynian Series in order to help understand their geotectonic setting and their rela-

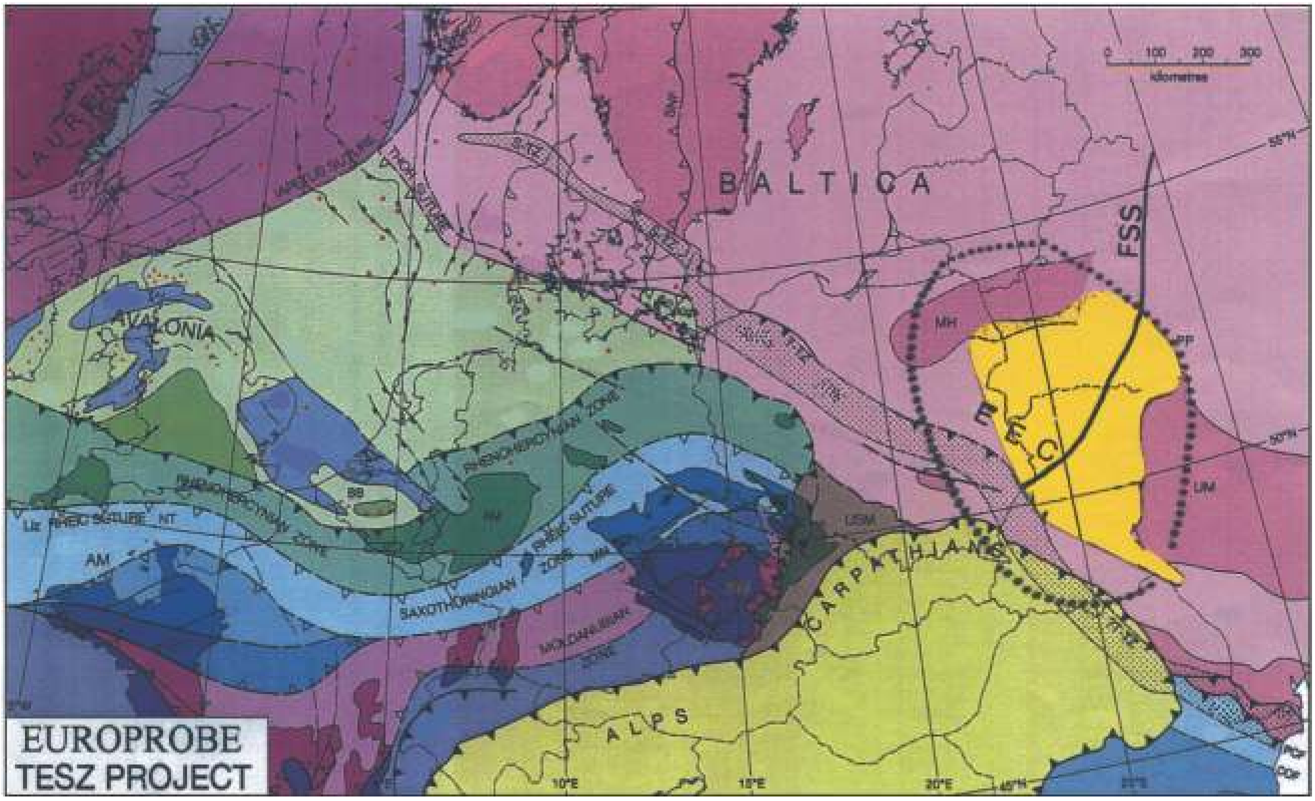

Fig. 1. Tectonic sketch map of the Trans-European Suture Zone and adjacent areas, according to Pharaoh (1999), modified

Open ticks — oceanic sutures, filled ticks — orogenic frontal zones; Proterozoic–Palaeozoic tectonic elements: AM — Armorican Massif, BB — Brabant Massif, BM — Bohemian Massif, FSS — Fennoscandia-Sarmatia Suture (Bogdanova, 1999), MH — Mazurska High, PP — Pripyat Trough, RM — Rhenish Massif, SNF — Sveconorwegian Front, S–TZ — Sorgenfrei-Tornquist Zone, T–TZ — Tornquist-Teisseyre Zone, UM — Ukrainian Massif, USM — Upper Silesian Massif; deep yellow color on the western margin of the EEC stands for the extension of flood basalts of the Volhynian Series according to Biryulev (1969); the dotted line delineates the maximum area of occurrence of pyroclastics connected with Vendian volcanic activity

tion to the protracted breakup of Rodinia, over the 1.0 to 0.5 Ga interval (Rogers, 1996).

Field work was carried out in June 1999 in the western Ukraine. Basaltoid and dolerite samples for mineralogical and geochemical analysis were collected from several quarries in the Rivne District, in the Goryn and Styr drainage basins near the villages of Policy, Ivance and Bazaltovoye (the last one known in geological literature as Janowa Dolina). Samples of effusive-tuffogenic rocks from borehole 5879 drilled by the Geological Exploration Company of Rivne on the left bank of the Styr river near Stary Chartoryjsk were also collected. All sample locations are shown in Figures 2–4.

GEOLOGICAL SETTING

The East European Craton (equivalent to Baltica) consists of three large terranes: Volgo-Uralia, Fennoscandia and Sarmatia (Bogdanova and Gorbatschev, 1997). The latter two abut upon the Trans-European Suture Zone, which originated from a continental rift within the craton (Żelaźniewicz, 1998). The suture zone between Fennoscandia and Sarmatia was formed during the Palaeoproterozoic between 2.0 and 1.7 Ga ago (Bogdanova, 1999, 2000). Along the suture, the Fennoscandian part consists of Palaeoproterozoic crustal domains, whereas the Sarmatian part is older, mainly Archean. Such an old crustal structure in the southwestern EEC controlled the localisation of faulting during Neoproterozoic rifting. In EEC, during the 1.3–1.0 Ga period, an aulacogen system developed, which including that of Orsha-Volhynia coinciding with the Fennoscandia-Sarmatia Suture zone (FSS). The NW trending Tornquist rift, however, was younger (*ca* 0.9 Ga; *cf.* Żelaźniewicz, *op. cit.*). On the Rodinia supercontinent, Baltica was juxtaposed with the Amazonian Craton until the latest stages of Rodinia breakup in the Neoproterozoic (Dalziel, 1997).

The study area lies within the Volhynian-Podolian Block constituting the northwestern part of the Ukrainian Shield, in the Sarmatian terrane of the East European Craton. Volcanic activity responsible for the formation of the lavas and tuffs in the area commenced at the turn of the Riphean (Volovnik, 1975; Alenko *et al*., 1990). Erosion of the volcanogenic formations during the Palaeozoic and Mesozoic resulted in the modern erosional boundary of the volcanic succession in the east running roughly northwards from Chmielnicki (Alenko *et al*., *op. cit*.). In the west the effusive-tuffogenic formations extend outside the Ukrainian

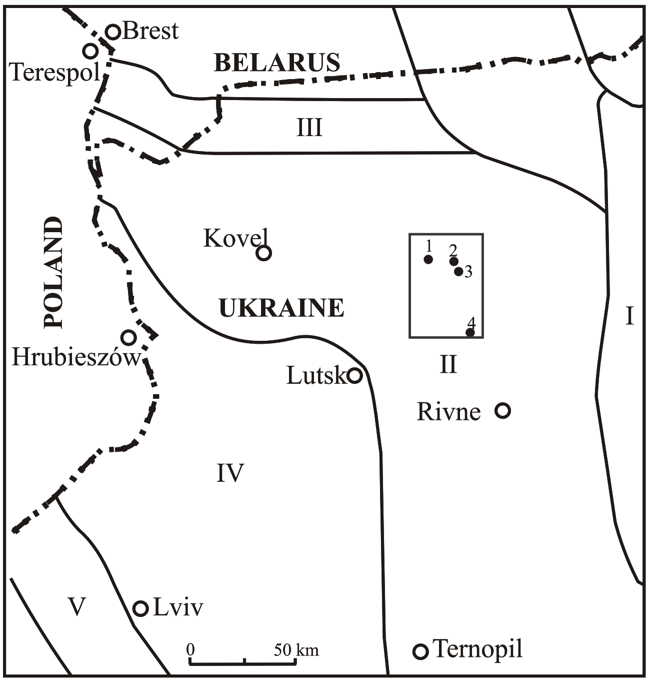

Fig. 2. Tectonic sketch map of the west Ukraine

I — Ukrainian Shield, II — Volhynian-Podolian Block (western slope of the Ukrainian Shield), III — Łuków-Ratno horst, IV — Palaeozoic Lviv Deep, V — Carpathian Foredeep; location of the samples collected: 1 — borehole 5879, 2 — Policy quarry, 3 —Ivance quarry, 4 — Bazaltovoye (Janowa Dolina) quarry; rectangle indicates Fig. 3

territory into Poland, in the north — into Belarus and in the south — into Moldavia (Biryulev, 1969). In the generalised sequence of the platform cover of the Volhynian-Podolian Block these rocks are termed the Volhynian Series (Fig. 5; Kosovski, pers. comm.). Below the Volhynian Series occur deposits of the Polesie Series (middle and upper Riphean, *cf.* Fig. 3). The Volhynian Series is overlain by upper Vendian volcanoclastic rocks forming the separate Mohylev-Podolia unit. Thus, the stratigraphic position of the Volhynian Series suggests an early Vendian age (Alenko *et al.*, *op. cit.*). The age of the Volhynian Series has been regarded as ranging between 590 and 625 Ma, whereas the overlying sedimentary rocks yield K-Ar ages ranging from 591 to 546 Ma (Sokolov and Fedonkin, 1990; fide: Compston *et al.*, 1995). However, Compston *et al.* (*op. cit.*) obtained U-Pb ages from zircons in the uppermost tuffs of the Sławatycze Series — lithologically correlated with the Volhynian Series of 551±4 Ma. Currently (Kosovski, pers. comm.; *cf.* Fig. 5) four units are separately distinguished in the composite succession of the Volhynian Series, three of them being volcanogenic whereas in the fourth, the lowermost, terrigenous material predominates. The lavas and tuffs are included within the volcanogenic Volhynian Series, while the hypabyssal rocks are regarded as late Riphean and placed in the Polesie Series (Volovnik, 1975).

Phanerozoic tectonics led to erosion of the upper levels of the platform succession resting on the Ukrainian Shield including the volcanogenic rocks. As a result, the Cretaceous marine deposits covered rocks of various age exposed at the surface. The cross-section (Fig. 4) shows that the total thickness of the Volhynian Series increases gradually from the Ukrainian Shield to the west. Neotectonic processes led to exposure of the lavas and tuffs, which can be traced in many quarries and natural exposures in the Goryn riverbed — the southernmost investigation site.

As these volcanogenic rocks are poorly exposed, the role of fracture systems in the evolution of the Volhynian platform-type magmatism remains unclear. Such fractures, reaching deep into the upper mantle, constituted channels for the basaltic magma produced during partial melting of the mantle. Presumably, the Vendian volcanism involved rejuvenated fractures of the Fennoscandia and Sarmatia Suture zone (FSS, Fig.1) in the Orsha-Volhynia aulacogen and, to some extent, of the abortive triple junction of the FSS with the Tornquist rift. This fracture system was almost perpendicular to the Tornquist continental rift before the Tornquist Ocean opened (Poprawa *et al.*, 1999; Bakun-Czubarow *et al.*, 2000). However, other fracture systems of different trends may have played a role in the Vendian volcanism (Alenko *et al.*, 1990).

There are similarities between the rocks of the Volhynian Series and trap formations occurring elsewhere; Sobolev (1986) gives general characteristics of the latter. The main features of trap formations are: 1 — occurrence in platform areas, 2 — co-occurrence of lavas and tuffs with hypabyssal rocks and 3 — very small lateral variability of mineral composition.

An elevated copper content, in some places attaining economic concentrations, probably due to metasomatic-hydrothermal processes, characterises the Volhynian Series.

METHODS OF EXAMINATION

Effusive and hypabyssal rock samples of the Ratno Beds (Volhynian Series) were examined under the microscope both in transmitted and reflected light. In samples from borehole 5879 and the Policy, Bazaltovoye 4 and Bazaltovoye 5 quarries the contents of major and trace elements have been determined using ICP and INAA in Activation Laboratories Ltd. in Canada thanks to the Laboratory of Geological-Mineralogical Analyses in Cracow. Mineral chemistry was determined by electron microprobe in the Laboratory of Scanning Electron Microscopy and Microanalysis, Institute of Geological Sciences, Polish Academy of Sciences. A *JEOL* scanning electron microscope *JSM 840 A* equipped with an energy dispersive analytical system LINK AN 10000/85 S was used. Analytical results and values of atomic ratios of selected pairs of elements in rocks are given in Tables 1–3. Representative analytical results of minerals and glasses selected from about 500 analyses are given in Tables 4–7.

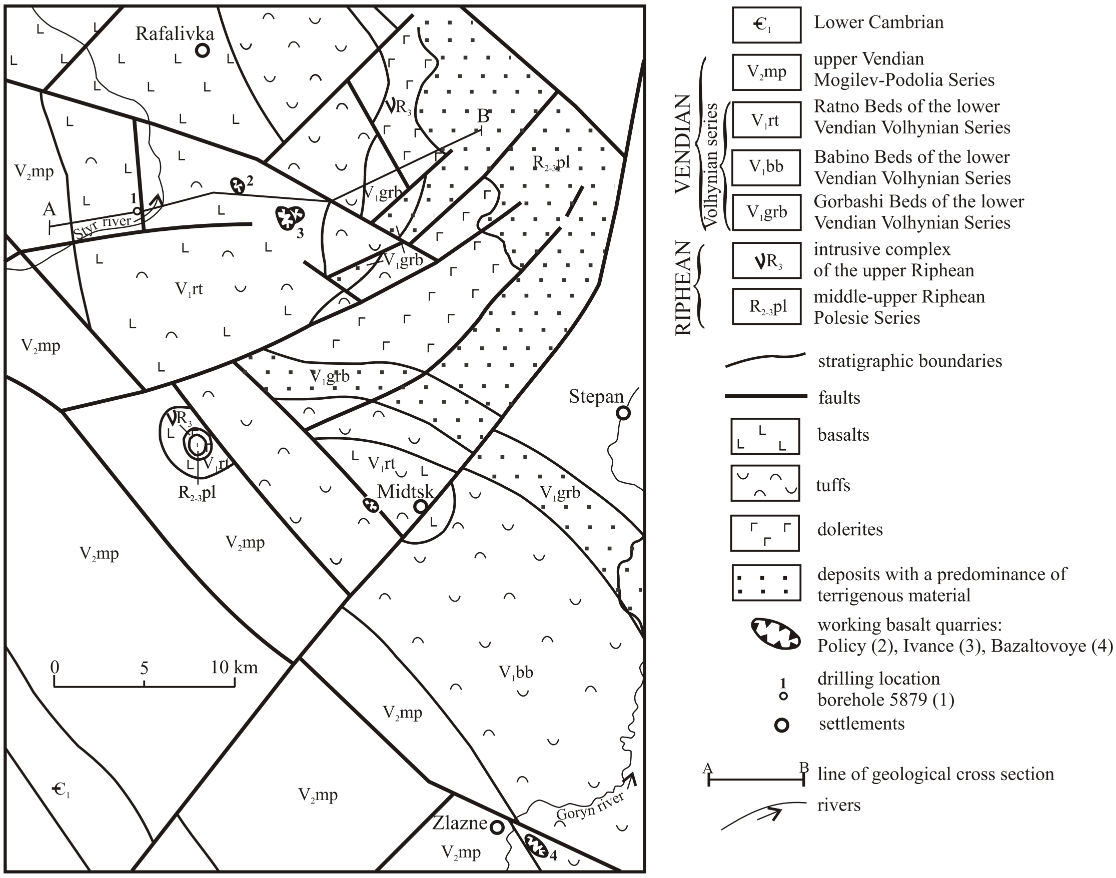

Fig. 3. Geological map of the area of investigations, according to Ya. Kosovski (unpublished)

PETROGRAPHY AND MINERAL CHEMISTRY

BOREHOLE 5879 NEAR STARY CHARTORYJSK

Basalts and dolerites in borehole 5879 at depths of 124 to 38 m (Fig. 5) have been examined microscopically.

Between 124.0 and 118.0 m there are dark grey massive palagonite-bearing basalts without any noticeable copper mineralisation. A doleritic texture is clearly visible. The main rock-forming minerals are plagioclases. Scarce plagioclase phenocrysts (earlier generation) differ from the remaining plagioclase crystals (later generation) in the matrix. Relatively large plagioclase phenocrysts (0.5 x 0.2 mm) have a distinctive tabular habit, with common twinning, indistinct zoning and poikilitic clinopyroxene inclusions. These crystals are of bytownite composition— An_{76-88}. The matrix is mainly built of plagioclase laths, clinopyroxene grains and subordinate ore minerals and palagonite. Matrix plagioclase laths, 0.05 x 0.5 mm in size, are randomly oriented. The composition of matrix plagioclase corresponds to andesine and labradorite (An_{38-56}). Locally, plagioclase laths are surrounded by palagonite. Clinopyroxene in the matrix forms minute aggregates but sometimes occurs as individual grains among plagioclase laths. Clinopyroxene grains are 0.01–0.02 mm across, less frequently 0.04 mm. Alteration in clinopyroxene grains has been locally accentuated by iron oxides. Some intergranular spaces are filled with green-brown or brown palagonite. Chalcedony and chlorite are among the products of palagonite alteration. The volume of palagonite in the rock does not exceed 5–7 vol. %. Ilmenite and titanomagnetite represent ore minerals. In the upper part of the borehole core more intense alteration is expressed by the presence of amygdales filled with a chlorite-goethite aggregate, the appearance of zeolite veinlets and secondary ore minerals.

Between 118.0 and 111.5 m depth there are greenish-grey, locally amygdaloidal, doleritic basalts. Amygdales range from 0.2 to 1 cm in diameter. A basalt sample from 116.9 m depth was chemically analysed (Table 1) and examined mineralogically. This basalt is composed mainly of lath-like, less frequently tabular, plagioclase and minute clinopyroxene grains occurring separately or in aggregates unevenly distributed throughout the rock. Two plagioclase generations have been recognised. Crystals of the early generation (phenocrysts) are chemically homogeneous and rich in anorthite (An_{75}). Fine plagioclase laths of the younger generation are significantly poorer in anorthite (An_{56}). Chemical compositions of the phenocrysts and the fine plagioclase laths are given in Table 4. Clinopyroxene grains within aggregates consistently show a composition of: $Wo_{41}En_{35}Fs_{24}$ (Table 5). The rock also contains rare silicates compositionally close to olivine (SiO_2: 33.5–34.5, MgO: 10.9–13.3, FeO: 47.9–49.1 wt. %). Accessory minerals include titanomagnetite (Table 6) and ilmenite containing about 4 wt. % of MnO. Chlorite is also present.

Within the 111.5–107.0 m depth interval occur green-grey amygdaloidal basalts of intersertal texture locally grading into intergranular (doleritic). The major minerals are plagioclase and clinopyroxene, with subordinate iron and titanium oxides. Clinopyroxene aggregates together with ore minerals and glass fill the space between plagioclase laths. The size of these grains is from 0.01 to 0.03 mm. Chloritisation of pyroxene and replacement of glass by green-brown aggregates of secondary minerals — palagonite — can be observed. The globular amygdales are 1.0–3.0 mm across and are filled with chlorite rosettes surrounded by chlorite and goethite rims.

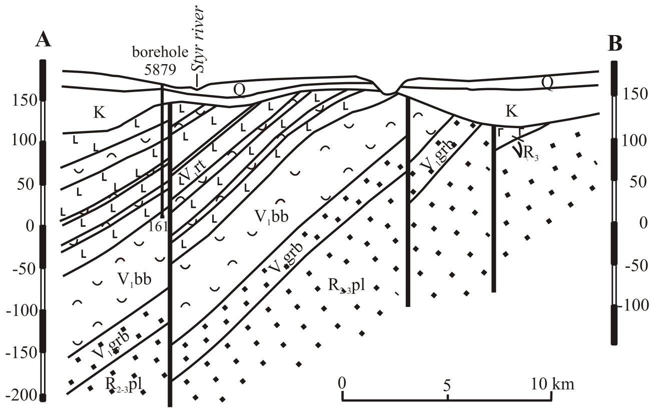

Fig. 4. Geological cross section along the line AB on the map (Fig. 3), according to Ya. Kosovski (unpublished)

K — Cretaceous, Q — Quartenary; vertical scale enlarged; other explanations see Fig. 3

Table 1

Chemical composition of the Ratno Beds basalts from the volcanogenic Volhynian Series (wt. %) together with their CIPW norms

Locality	Borehole 5879		Policy quarry	Bazaltovoye quarries		
Sample no.	SC 56	SC 116.9	P3	JD4b	JD5b	Janowa Dolina*
SiO_2	52.30	50.07	51.62	50.13	50.81	49.56
TiO_2	2.33	1.63	1.55	2.60	2.68	2.03
Al_2O_3	13.74	14.13	13.96	13.09	13.36	14.49
Fe_2O_3	13.41	14.14	12.81	14.57	14.43	11.75
MnO	0.23	0.18	0.21	0.21	0.21	0.17
MgO	4.84	5.34	6.08	5.35	5.09	5.10
CaO	8.74	9.66	10.06	9.13	9.06	8.50
Na_2O	2.84	2.45	2.27	2.55	2.49	2.10
K_2O	0.71	0.82	0.66	0.77	0.77	1.59
P_2O_5	0.23	0.29	0.21	0.31	0.29	0.20
LOI	0.75	1.76	0.54	0.77	1.02	
H_2O^+	nd	nd	nd	nd	nd	1.16
H_2O^-	nd	nd	nd	nd	nd	1.31
CO_2	nd	nd	nd	nd	nd	0.28
Sum	100.12	100.47	99.97	99.48	100.21	100.34
CIPW norms						
Qtz	8.68	5.10	6.88	6.62	7.99	4.50
Or	4.26	4.96	3.96	4.66	4.64	9.35
An	22.96	25.67	26.29	22.47	23.39	25.40
Ab	24.37	21.18	19.46	22.05	21.43	17.70
Di	16.03	17.68	18.76	17.92	16.83	12.70
Hy	11.91	14.71	15.03	13.39	12.87	17.00
Mt	6.79	6.90	6.18	7.14	7.03	6.25
Ilm	4.49	3.15	2.97	5.06	5.18	3.86
Ap	0.51	0.65	0.47	0.69	0.64	0.43
A/CNK	0.64	0.63	0.61	0.61	0.61	0.70
A/NK	2.53	2.87	3.14	2.60	2.71	2.80
mg	53.0	53.6	59.1	52.9	52.0	48.8

* Analysed by M. Kamieński (fide Małkowski, 1951); nd — not determined

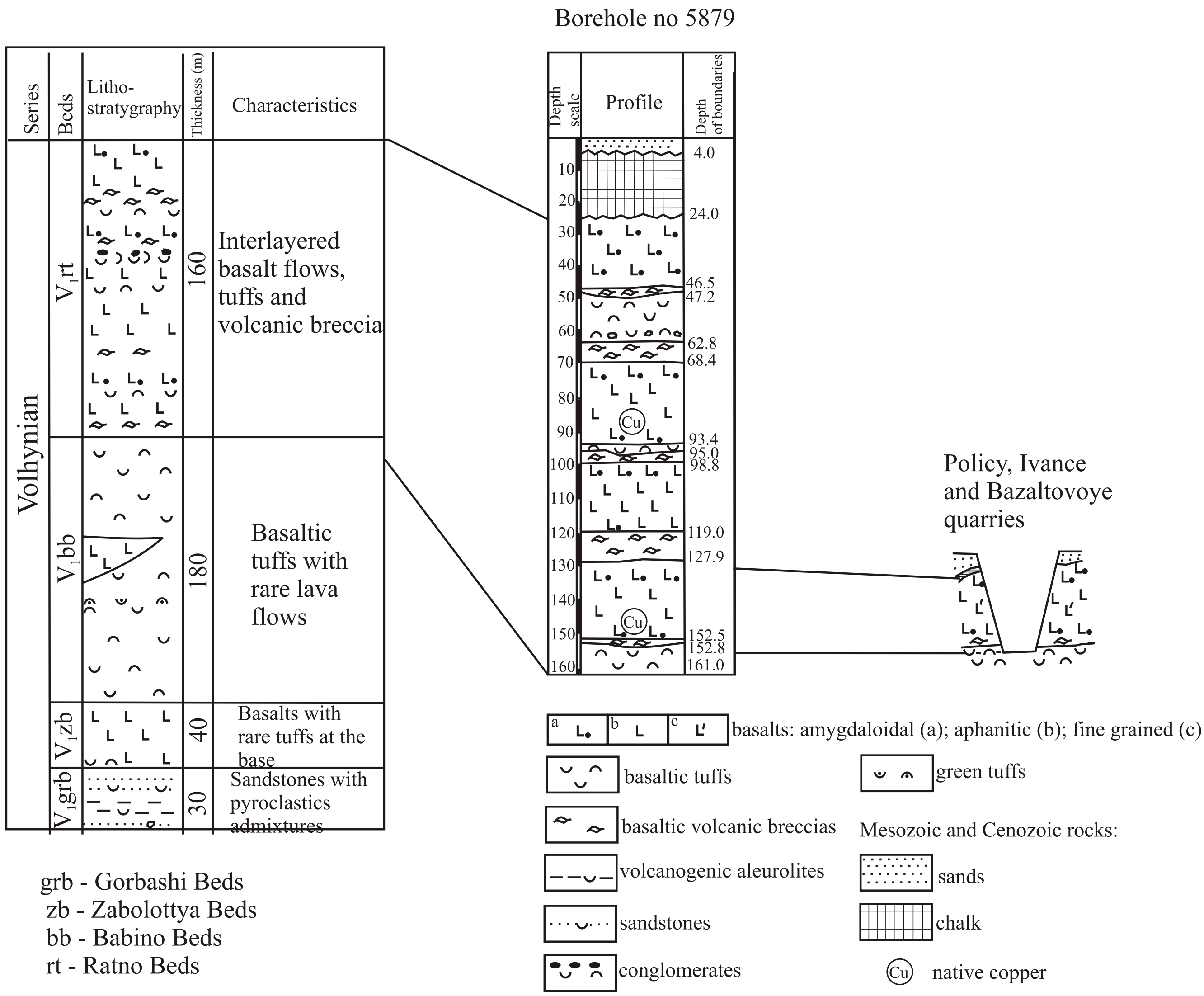

Fig. 5. Generalised stratigraphy of the lower Vendian Volhynian Series on the western slope of the Ukrainian Shield together with the geological section of borehole 5879 and lithostratigraphic position of the basalt quarries in Policy, Ivance and Bazaltovoye, according to Ya. Kosovski (unpublished)

At the depth of 107.0–100.0 m there occur agglomerates of grey-brown tuffs with fragments of altered palagonite-bearing basalts of doleritic and amygdaloidal texture.

The 100.0–82.0 m depth interval is represented by palagonite-bearing, doleritic, locally amygdaloidal basalts. Petrographically these rocks resemble basalts from the 124.0–118.0 m interval, the only difference being a more intensive alteration in the lower portion of the interval described. Secondary ore minerals and native copper occur throughout. The amygdales are filled with brown fibrous chlorite (Fig. 6a).

At the depth of 82.0–60.0 m there occur dark grey, green-tinged, porphyritic basalts (Fig. 6b). The lower basalts here are amygdaloidal and contain scoria fragments thus acquiring the appearance of volcanic breccia. The predominant texture is hyalopilitic and intersertal. Fragments of the oxidised black-brown scoria also have a hyalopilitic texture. Disseminated ore minerals include native copper. Amygdales less than 1 mm across are filled by chlorite-mica aggregate with a zeolitic rim.

Higher up in the succession (60.0–38.5 m) there are dark grey massive palagonite-bearing basalts of doleritic texture identical with those of the 124.0–118.0 m interval, with plagioclase and clinopyroxene phenocrysts. A basalt sample from 56.0 m depth was analysed (Table 1) as well as included plagioclases with the composition of labradorite and bytownite. Tabular, intensively corroded plagioclases of an earlier generation (Fig. 6b) have the composition of bytownite (An_{79}, *cf.* Table 4) while younger lath-like ones are of labradorite composition. The An content in the finest plagioclase laths is 53. Among the clinopyroxenes, augites relatively rich in Ca occur as strongly corroded phenocrysts, their composition being $Wo_{45}En_{37}Fs_{18}$, and as inclusions in tabular plagioclase phenocrysts of bytownite composition. The matrix also includes pigeonite the Ca content of which drops to $Wo_{09}En_{57}Fs_{34}$. The

Table 2

Minor and trace element contents in the Ratno Beds basalts from the Volhynian Series (ppm; Au — in ppb)

Locality	Borehole 5879		Policy quarry	Bazaltovoye quarries	
Sample no.	SC 56	SC 116.9	P3	JD4b	JD5b
Ni	45	44	42	54	56
Co	44	51	50	50	51
Cr	38	55	28	50	49
V	344	372	313	368	368
Mn	1780	1394	1626	1626	1626
Ti	13968	9772	9292	15587	16066
Zr	144	145	121	184	174
Hf	5	4	4	6	6
Zn	125	111	112	129	132
Cu	65	167	246	94	97
Au	X	X	6	X	X
Ba	372	631	299	305	327
Sr	335	309	282	346	352
Rb	X	24	X	12	X
Sc	33	41	40	33	34
Y	32	33	28	34	34
La	21.8	22.70	15.90	22.3	22.4
Ce	49	44	33	51	52
Nd	27	25	18	28	28
Sm	6.85	5.78	4.80	7.28	7.42
Eu	2.28	1.92	1.52	2.54	2.56
Tb	1	1	0.80	1	1
Yb	2.78	3.16	2.50	2.71	2.72
Lu	0.42	0.48	0.39	0.41	0.41
Th	2.70	1.60	1.80	2.10	2.00
U	0.4	X	0.3	0.4	0.5

X — below the detection limit

chemical composition of selected clinopyroxene grains is listed in Table 5. Ilmenite and titanomagnetite (Table 6) represent ore minerals. In addition, this basalt sample also contains about 5 vol. % of palagonite and acid glass containing about 73 wt. % of SiO_2 (Table 7).

QUARRIES AROUND BAZALTOVOYE

In the Bazaltovoye 4 quarry fresh basalts occur with distinct columnar jointing, the diameter of columns being 0.7–0.8 m. The basalts have a doleritic, locally porphyritic texture. Among the basalts appear dark grey to black palagonite-bearing dolerites. Two samples (basalt and dolerite) were analysed (Table 1). The basalt examined comprised plagioclases and clinopyroxenes, with subordinate ore minerals (titanomagnetite and ilmenite). Plagioclase phenocrysts are developed as thin laths 0.2–0.3 x 0.8 in size, less frequently as plates. These plagioclases have the composition of labradorite and bytownite An_{68-73} and in zoned crystals the Ca content clearly drops towards the rim (core — An_{72}, rim — An_{52}; *cf.* Table 4). Fine plagioclase laths of the matrix have a labradorite composition (An_{55}). Clinopyroxenes are also represented by various crystal generations (Fig. 6c and d). The largest individuals (about 0.2 x 0.8 mm) of $Wo_{40}En_{39}Fs_{21}$ composition contain about 2 wt. % of Al_2O_3 and are thus low-alumina augites frequently with a zoned structure. Compared with the rims, the cores of the zoned grains are richer in magnesium and calcium and poorer in iron. Among the smallest clinopyroxene grains (0.02–0.04 mm) occur pigeonites — $Wo_{11}En_{43}Fs_{46}$ (Table 5, *cf.* Fig. 7a). In addition, basalts of the Bazaltovoye 4 quarry con-

Table 3

Atomic ratios of the selected elements in the Ratno Beds basalts of the volcanogenic Volhynian Series

Locality	Borehole 5879		Policy quarry	Bazaltovoye quarries	
Sample no.	SC 56	SC 116.9	P3	JD4b	JD5b
Fe/Mg	1.40	1.34	1.06	1.38	1.43
(Ni/Mg) x 10^4	6.38	5.65	4.74	6.93	7.55
Ni/Cr	1.05	7.07	1.31	0.97	1.01
(Cr/V) x 10^2	10.77	14.52	8.86	13.18	13.10
(V/Fe) x 10^4	40.20	41.24	38.28	39.56	39.96
(V/Ti) x 10^2	2.31	3.58	3.16	2.22	2.15
(Ti/Fe) x 10^2	17.39	11.52	12.09	17.80	18.54
(Cr/Ti) x 10^4	24.90	51.96	28.04	29.29	28.24
(Co/Fe) x 10^4	4.48	4.91	5.28	4.63	4.79
(Co/Ni) x 10^2	98.33	116.00	118.62	91.83	90.74
(Ni/Fe) x 10^4	4.56	4.23	4.46	5.04	5.28
(Mn/Fe) x 10^2	1.90	1.43	1.84	1.62	1.64
(Sc/Fe) x 10^4	4.40	5.33	5.56	4.04	4.19
(Sr/Ca) x 10^4	24.50	20.49	17.95	24.26	24.88
Sr/Ba	1.41	0.77	1.48	1.78	1.69

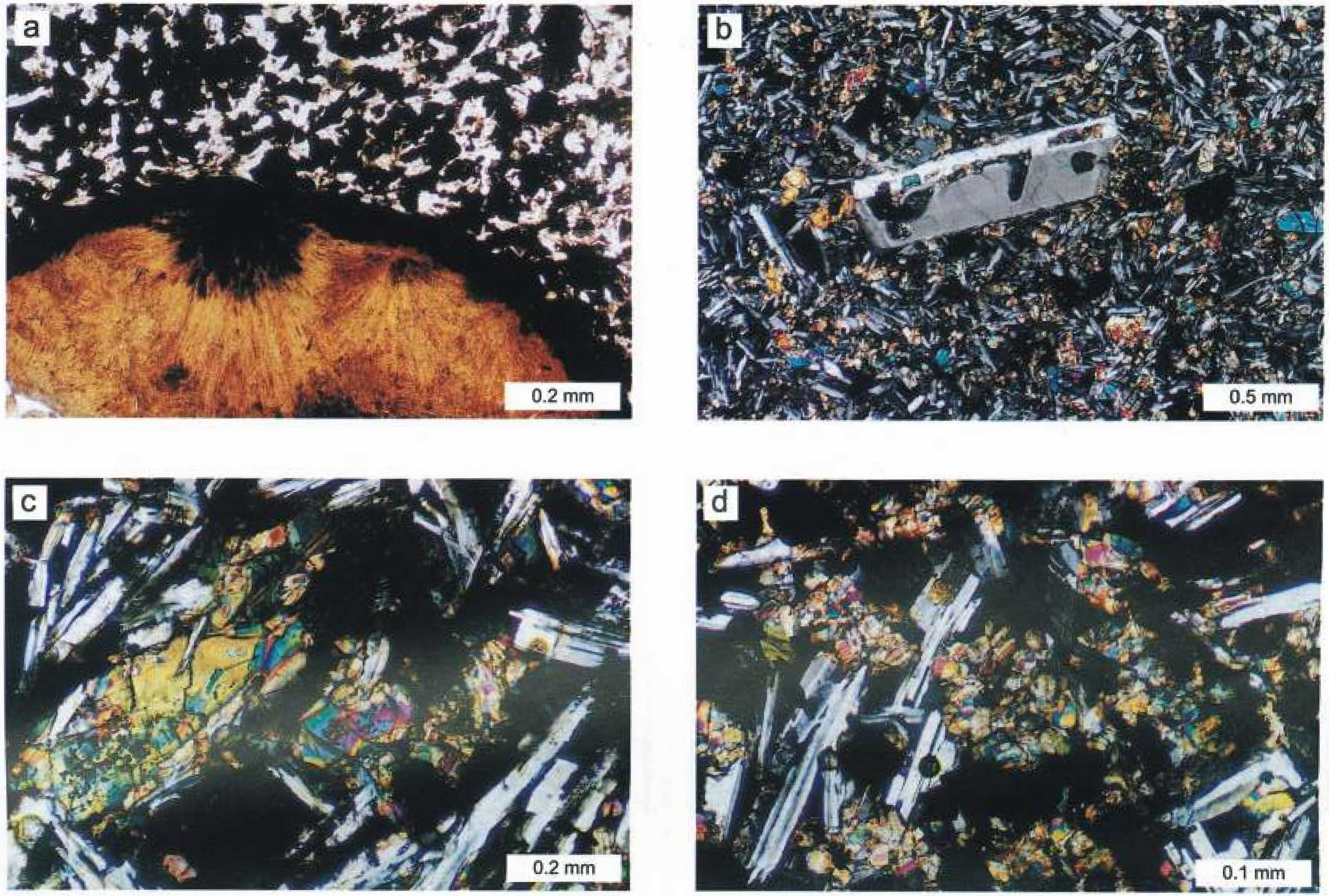

Fig. 6. **A** — brownish, fibrous chlorite filling up an amygdale in amygdaloidal basalt, sample SC 97 from borehole 5879, one polar; **B** — strongly corroded and deformed plate of bytownite forming the phenocryst, which belongs to the early generation of plagioclases, the phenocryst is set in the basalt matrix, sample SC 95 from borehole 5879, crossed polars; **C** — augite phenocryst of the early generation of pyroxenes, the phenocryst contains small iron oxide grains and is surrounded by fine clinopyroxene crystals, fine plagioclase laths and palagonite (black), basalt sample JD4b from the Bazaltovoye quarry, crossed polars; **D** — numerous aggregates of fine clinopyroxene grains with plagioclase laths, black spots are palagonite and titanomagnetite, basalt sample JD4b, crossed polars

Table 4

Microprobe analyses of plagioclases from the Ratno Beds basalts of the Volhynian Series (wt. %)

Analysis no.	1	2	3	4	5	6	7	8
SiO_2	53.38	52.50	56.46	52.47	51.26	57.32	56.45	54.71
TiO_2	0.26	0.08	0.17	0.12	0.11	0.18	0.19	0.23
Al_2O_3	27.46	27.91	25.82	27.74	28.17	25.78	25.31	26.78
FeO	1.31	1.35	1.17	1.15	0.94	0.98	1.06	1.22
CaO	13.21	14.15	11.51	14.20	14.73	10.15	10.72	11.96
Na_2O	3.89	3.20	4.45	3.53	3.14	4.78	5.03	4.46
K_2O	0.31	0.64	0.60	0.33	0.12	0.55	0.47	0.36
Sum	99.82	99.83	100.18	99.54	98.47	99.74	99.23	99.72
cations per 8 oxygens								
Si	2.438	2.409	2.552	2.413	2.376	2.588	2.570	2.489
Al	1.478	1.510	1.375	1.503	1.539	1.372	1.358	1.436
Fe	0.050	0.052	0.044	0.044	0.036	0.037	0.040	0.046
Ti	0.009	0.003	0.006	0.004	0.004	0.006	0.006	0.008
Ca	0.647	0.696	0.557	0.700	0.731	0.491	0.523	0.583
Na	0.345	0.285	0.390	0.315	0.282	0.419	0.444	0.394
K	0.018	0.037	0.032	0.020	0.007	0.032	0.027	0.021
Sum	4.985	4.992	4.956	4.999	4.975	4.945	4.968	4.977
An	64.0	68.3	56.8	67.7	71.6	52.2	52.6	58.4
Ab	34.1	28.0	39.7	30.4	27.7	44.5	44.6	39.4
Or	1.9	3.7	3.5	1.9	0.7	3.3	2.8	2.2

1 — relatively big homogenous plagioclase lath in basalt SC 56 from borehole 5879; 2 — the core of the big plagioclase plate in basalt SC 116.9 from borehole 5879; 3 — fine homogenous plagioclase lath in basalt SC 116.9 from borehole 5879; 4 — big deformed plagioclase lath in basalt P3 from the Policy quarry; 5 — the core of the big plagioclase plate in basalt JD4b from the Bazaltovoye quarry 4; 6 — the rim of the plate of plagioclase 5; 7 — plagioclase lath in dolerite JD4d from the Bazaltovoye quarry 4; 8 — the core of the plagioclase relict in basalt from the Ivance quarry

Table 5

Microprobe analyses of clinopyroxenes in the Ratno Beds basalts of the Volhynian Series (wt. %)

Analysis no.	1	2	3	4	5	6	7	8	9	10	11
SiO_2	48.36	52.62	49.34	50.27	50.73	49.58	48.27	47.45	52.61	49.95	50.65
TiO_2	1.14	0.30	0.88	0.31	0.56	0.45	1.36	0.79	0.58	1.32	0.70
Al_2O_3	3.80	0.64	1.62	1.26	0.57	0.62	1.85	1.15	0.72	1.77	1.98
Cr_2O_3	0.22	0.11	0.00	0.04	0.00	0.08	0.04	0.00	0.00	0.00	0.08
MgO	12.60	20.32	12.00	16.44	15.18	14.43	10.64	8.14	16.77	13.71	13.85
NiO	0.00	0.03	0.05	0.09	0.00	0.02	0.14	0.03	0.07	0.00	0.00
MnO	0.18	0.66	0.53	0.50	0.66	0.62	0.42	0.55	0.41	0.47	0.36
FeO	10.84	21.44	15.12	25.83	28.58	28.15	18.51	28.07	25.69	17.11	12.01
CaO	21.18	4.23	19.61	4.06	4.64	5.65	18.09	14.32	4.39	14.21	20.20
Na_2O	0.22	0.06	0.17	0.10	0.00	0.00	0.42	0.20	0.02	0.20	0.02
K_2O	0.00	0.00	0.03	0.00	0.04	0.00	0.00	0.00	0.01	0.03	0.04
Sum	98.54	100.41	99.35	98.90	100.96	99.60	99.74	100.70	101.27	98.77	99.89
cations per 6 oxygens											
Si	1.856	1.969	1.909	1.954	1.959	1.948	1.886	1.901	1.985	1.926	1.916
Al^{IV}	0.144	0.028	0.074	0.046	0.026	0.029	0.014	0.054	0.015	0.074	0.084
Al^{VI}	0.028			0.012			0.071		0.017	0.006	0.004
Ti^{IV}		0.003	0.017		0.015	0.013					
Ti^{VI}		0.005	0.006				0.040	0.024	0.017	0.038	0.020
Cr	0.007	0.003	0.000	0.001	0.000	0.002	0.001	0.000	0.000	0.000	0.002
Mg	0.721	1.133	0.692	0.953	0.874	0.845	0.620	0.486	0.943	0.788	0.781
Ni	0.000	0.001	0.001	0.003	0.000	0.001	0.005	0.001	0.002	0.000	0.000
Mn	0.006	0.021	0.017	0.017	0.022	0.021	0.014	0.019	0.013	0.015	0.011
Fe	0.348	0.671	0.489	0.840	0.923	0.925	0.605	0.941	0.811	0.552	0.380
Ca	0.871	0.170	0.813	0.169	0.192	0.238	0.758	0.615	0.178	0.587	0.819
Na	0.017	0.004	0.013	0.008	0.000	0.000	0.032	0.016	0.001	0.015	0.002
K	0.000	0.000	0.001	0.000	0.002	0.000	0.000	0.000	0.000	0.002	0.002
Sum	4.031	4.008	4.034	4.012	4.014	4.022	4.046	4.057	3.982	4.003	4.021

1 — the core of the relatively big, strongly corroded clinopyroxene grain in basalt SC 56 from borehole 5879; 2 — the fine clinopyroxene grain in basalt SC 56; 3 — clinopyroxene from the aggregate of the grains in basalt SC 116.9 from borehole 5879; 4 — the core of the fine clinopyroxene grain in basalt P3 from the Policy quarry; 5 — the rim of the grain of clinopyroxene 4; 6 — small clinopyroxene grain in basalt JD4b from the Bazaltovoye quarry 4; 7 — the core of the big clinopyroxene grain in dolerite JD4d from the Bazaltovoye quarry 4; 8 — the rim of the grain of clinopyroxene 7; 9 — the core of the clinopyroxene grain in basalt JD5b; 10 — the rim of the grain of clinopyroxene 9; 11 — the clinopyroxene grain included in magnetite of basalt from the Ivance quarry

Table 6

Electron microprobe analyses of Fe-Ti oxides from basalts of the Ratno Beds of the Volhynian Series

Mineral	Titanomagnetites								Ilmenites	
Analysis no.	1	2	3	4	5	6	7	8	9	10
SiO_2	0.49	0.38	0.24	0.12	0.27	0.42	0.22	1.09	0.20	0.43
TiO_2	24.26	7.46	8.70	24.18	19.29	25.51	27.29	6.56	50.40	53.13
Al_2O_3	1.30	4.15	3.73	1.25	1.82	1.22	1.85	1.00	0.04	0.36
Cr_2O_3	0.09	0.00	0.30	0.26	0.11	0.14	0.16	0.04	0.00	0.09
MgO	0.03	0.07	0.10	0.80	0.78	0.02	0.60	0.25	0.27	1.33
NiO	0.12	0.20	0.00	0.08	0.12	0.00	0.00	0.15	0.14	0.09
MnO	1.26	0.13	0.09	0.96	0.63	0.76	0.96	0.00	0.66	1.14
FeO	70.81	82.72	81.76	68.61	73.33	68.70	69.43	86.31	49.00	43.40
CaO	0.08	0.23	0.18	0.05	0.03	0.03	0.00	0.25	0.12	0.10
Na_2O	0.14	0.21	0.20	0.25	0.30	0.17	0.00	0.08	0.17	0.19
K_2O	0.03	0.03	0.00	0.00	0.02	0.01	0.02	0.01	0.05	0.00
Sum	98.61	95.58	95.30	96.56	96.70	96.98	100.53	95.74	101.05	100.26
	cations per 4 oxygens								per 3 oxygens	
Si	0.019	0.017	0.011	0.005	0.011	0.017	0.008	0.055	0.005	0.011
Ti	0.726	0.250	0.292	0.736	0.602	0.769	0.784	0.227	0.958	0.990
Al	0.061	0.218	0.196	0.060	0.089	0.058	0.083	0.055	0.001	0.011
Cr	0.003	0.000	0.011	0.008	0.004	0.004	0.005	0.002	0.000	0.002
Mg	0.002	0.004	0.007	0.048	0.048	0.001	0.034	0.017	0.010	0.049
Ni	0.004	0.007	0.000	0.003	0.004	0.000	0.000	0.006	0.003	0.002
Mn	0.042	0.005	0.004	0.033	0.022	0.026	0.031	0.000	0.014	0.024
Fe	2.356	3.097	3.056	2.321	2.546	2.302	2.217	3.322	1.036	0.899
Ca	0.004	0.010	0.008	0.002	0.001	0.001	0.000	0.012	0.003	0.003
Na	0.011	0.019	0.017	0.019	0.024	0.013	0.000	0.008	0.008	0.009
K	0.001	0.018	0.000	0.000	0.001	0.000	0.001	0.001	0.002	0.000

1 — titanomagnetite in basalt SC 56 from borehole 5879; 2 — titanomagnetite in basalt SC 116.9 from borehole 5879; 3 — another grain of titanomagnetite from basalt SC 116.9; 4 — relatively big grain of titanomagnetite from basalt P3 from the Policy quarry; 5 — small grain of titanomagnetite from the basalt P3; 6 — titanomagnetite from dolerite JD4d from the Bazaltovoye quarry 4; 7 — titanomagnetite from the basalt JD5b from the Bazaltovoye quarry 5; 8 — magnetite forming rim on the ilmenite grain from basalt from the Ivance quarry; 9 — ilmenite from dolerite JD4d from the Bazaltovoye quarry 4; 10 — ilmenite rimmed by the magnetite 8 in basalt from the Ivance quarry

tain considerable amounts (about 5 vol. %) of brown palagonite and brown basic glass (Table 7). Local acid glass exsolutions (Table 7) frequently in globular form are visible in basic glass and palagonite. Sometimes the acid glass forms rims on palagonite aggregates. A dolerite sample (Fig. 8a) from a small body of undefined shape occurring among the basalts (probably within a lava cover) contains large plagioclase laths (up to 2.0 mm) frequently with a zoned structure where the Ca content drops towards the rim (from An_{52} to An_{47}). The composition of a homogeneous plagioclase lath is given in Table 4. The clinopyroxenes, similar to those derived from basalts of the same quarry, have a very differentiated composition. Besides low-alumina augites the rock contains ferroaugites, sub-calcic ferroaugites and ferropigeonites (Fig. 7b). Large clinopyroxene individuals of augite composition are frequently characterised by a zoned structure. Their cores contain $Wo_{38}En_{32}Fs_{30}$ and their rims $Wo_{30}En_{24}Fs_{46}$. Thus, the Ca and Mg content in these augites decreases towards the rims while the iron content increases (Table 5). Augite grains included in palagonite were also noted. Titanomagmetite and ilmenite (Table 6) represent ore minerals. Brown and green interstitial palagonite in the dolerite examined amounts to about 7 vol. %. As doleritic dykes were not observed within the Ratno Beds, the dolerites most likely crystallised in the centres of thick basaltic lava flows. One basalt sample from Bazaltovoye 5 quarry was analysed (Table 1) The predominant mineral is lath-shaped plagioclase while clinopyroxene is less abundant, as well as ilmenite and titanomagnetite are only accessories. Frequently plagioclases have a zoned structure. Their cores contain $An_{70–74}$ and their rims $An_{40–58}$. Most often, clinopyroxenes have the composition of low-alumina augite. They too often exhibit zoned structures. Their cores have a composition of $Wo_{27}En_{48}Fs_{25}$ and their rims of $Wo_{27}En_{40}Fs_{33}$. Pigeonite individuals ($Wo_{09}En_{49}Fs_{42}$), locally rimmed by clinopyroxene richer in Ca and impoverished in iron, are found among clinopyroxenes. Oxides are represented by titanomagnetite. The basalt described contains about 7 vol. % of interstitial chlorophaeite and palagonite (Table 6). Palagonite is brown in colour (Fig. 8b) or green grading into brown in the marginal zones (Fig. 8c). In the rock acid glass is also present (73 wt. % of SiO_2, *cf*. Table 6).

Table 7

Microprobe analyses of glass and products of its alteration from basalts of the Ratno Beds of the volcanogenic Volhynian Series (wt. %)

Phase	Chlorophaeite			Palagonite			Acid glass			
Analysis no.	1	2	3	4	5	6	7	8	9	10
SiO_2	43.18	44.02	42.73	47.36	40.28	46.67	72.96	68.56	72.44	73.32
TiO_2	0.29	0.47	0.13	0.22	0.15	0.24	0.69	0.00	0.08	0.82
Al_2O_3	6.14	6.16	7.01	6.76	5.85	6.85	13.97	5.16	5.68	11.58
Cr_2O_3	0.00	0.004	0.04	0.00	0.00	0.10	0.00	0.06	0.04	0.04
MgO	9.44	10.15	11.92	2.17	2.13	2.85	0.08	0.00	0.02	0.00
NiO	0.12	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.18	0.00
MnO	0.14	0.00	0.22	0.08	0.08	0.13	0.18	0.00	0.00	0.06
FeO_{tot}	28.16	28.87	23.01	24.96	22.45	26.25	0.79	0.49	0.48	1.37
CaO	2.84	2.69	2.90	1.92	1.97	2.02	0.29	1.87	1.95	0.34
Na_2O	0.11	0.43	0.00	0.28	0.37	0.12	1.12	0.30	0.41	0.18
K_2O	0.19	0.24	0.10	0.40	0.42	0.50	2.35	0.56	0.66	0.30
Sum	90.61	93.07	88.06	84.15	73.70	85.73	92.46	77.00	81.94	88.01
cations per 10 oxygens										
Si	3.112	3.091	3.086	3.541	3.475	3.460	4.157	4.583	4.568	4.212
Ti	0.016	0.025	0.007	0.012	0.009	0.014	0.030	0.000	0.004	0.035
Al	0.522	0.510	0.596	0.596	0.596	0.599	0.938	0.407	0.422	0.784
Cr	0.000	0.002	0.002	0.000	0.000	0.006	0.000	0.000	0.002	0.002
Mg	1.014	1.063	1.283	0.241	0.274	0.315	0.007	0.000	0.002	0.000
Ni	0.007	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.009	0.000
Mn	0.009	0.000	0.014	0.005	0.006	0.008	0.009	0.000	0.000	0.003
Fe	1.697	1.696	1.390	1.561	1.620	1.628	0.038	0.028	0.025	0.066
Ca	0.220	0.203	0.224	0.153	0.182	0.161	0.017	0.048	0.132	0.021
Na	0.016	0.058	0.000	0.041	0.062	0.018	0.124	0.040	0.051	0.178
K	0.010	0.021	0.010	0.038	0.047	0.047	0.171	0.048	0.053	0.297
Sum	6.629	6.668	6.612	6.188	6.271	6.256	5.492	5.160	5.268	5.598

1 — chlorophaeite from JD5b basalt of the Bazaltovoye quarry; 2 — another grain of chlorophaeite from JD5b sample; 3 — chlorophaeite from basalt SC 116.9 from borehole 5879 near Stary Chartoryjsk; 4 — the centre of the brown palagonite in basalt JD4b from the Bazaltovoye quarry 4; 5 — the rim of the concentration of palagonite 4; 6 — the centre of another concentration of the brown palagonite in basalt JD4b; 7 — acid glass in basalt SC 56 from borehole 5879; 8 — acid glass forming small sphere in palagonite 4; 9 — another spherical acid glass found in palagonite from basalt JD4b; 10 — acid glass occurring in interstices between silicate minerals of basalt JD5b from the Bazaltovoye quarry 5

QUARRY NEAR POLICY

The Policy quarry has several exploitation levels and its bottom is flooded. In its upper part the volcanogenic rocks are covered by Cretaceous deposits represented by a basal breccia (up to 0.5 m thick) grading upwards into chalk. A series of samples was taken from the northern face of the quarry. The following rocks can be identified in the sequence from the water table upwards: 1 — volcanic basalt breccia of porphyritic and locally amygdaloidal texture; 2 — amygdaloidal basalts of intersertal texture locally grading into dolerite with noticeable local porphyritic texture; 3 — doleritic palagonite-bearing basalts analogous to those described from the 124.0–118.0 m depth interval in borehole 5879.

In the volcanic breccia from the lower level (1) lava fragments and matrix show an intersertal texture. The matrix is made up of fine plagioclase laths, glass and its alteration products and of ore minerals. The amygdales are filled with chlorite-chalcedony aggregate with an oxide admixture.

The major minerals of basalts of the middle level (2) are plagioclases (mostly lath-shaped) and fine-grained clinopyroxenes occurring in aggregates. Dark brown glass and

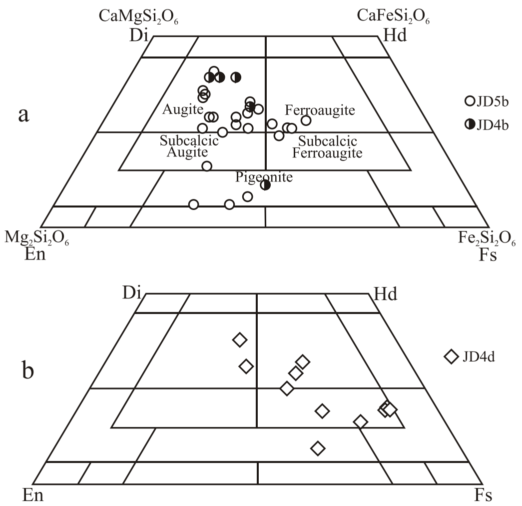

Fig. 7. Composition of clinopyroxenes in basalts and dolerite from the Bazaltovoye quarries

a — basaltic clinopyroxenes from sample JD5b and sample JD4b; b — doleritic clinopyroxenes from sample JD4d

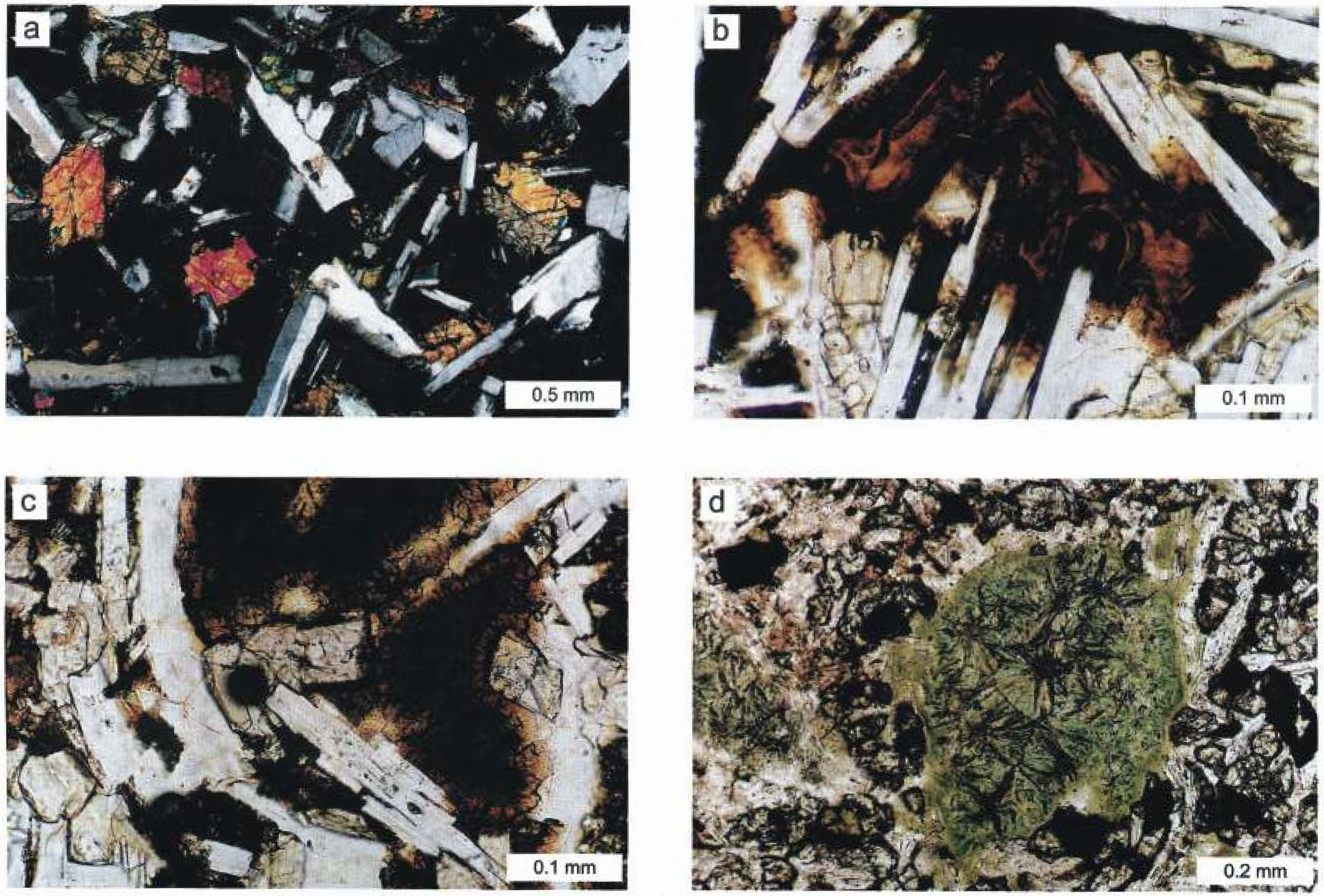

Fig. 8. **A** — laths of twinned plagioclases with single crystals of clinopyroxene between them in dolerite from Bazaltovoye quarry 4, sample JD4d, crossed polars; **B** — basalt from the Bazaltovoye quarry 5 with a concentration of brown palagonite, sample JD5b, one polar; **C** — basalt sample JD5b with concentrations of dark green palagonite rimmed by brown palagonite, one polar; **D** — green chlorite filling amygdales in basalt from the Ivance quarry, one polar

ore minerals are also present. Amygdales 1.0–3.0 mm in size are filled with green and brown chlorite aggregate rimmed with goethite. A basalt sample from this level has been analysed (Table 1). The predominant plagioclase grains differ between each other in habit, size and composition and probably belong to different generations. The tabular plagioclases (phenocrysts) bearing evidence of protoclastic deformation are the largest and have a labradorite composition An_{68} (Table 4). The lath-like plagioclases vary in size. The largest laths have a zoned structure, the An content in cores reaching 74, in marginal zones dropping to 48–60. Clinopyroxenes also show a variable chemical composition. The larger grains are augites containing $Wo_{39}En_{35}Fs_{26}$ while the smaller grains have the composition of pigeonites (Table 5) ranging as follows: $Wo_{09}En_{43–49}Fs_{48–42}$. Present in the rock is titanomagnetite (Table 6) and palagonite (Table 7) together making up to about 5 vol. %.

In basalts of the top part of the upper level (3) fine-lenticular aggregates of ore minerals appear imparting a layered structure to the rock. The thickness of the layers is 1.5–2.0 cm.

QUARRY NEAR IVANCE

The Ivance quarry exposes doleritic, locally porphyritic and amygdaloidal basalts showing a varying degree of alteration and mineralisation, mainly by native copper. Basalt samples both with and without copper mineralisation have been analysed as regards mineral chemistry. The principal basalt minerals are plagioclases in the form of fine laths and minute clinopyroxene grains often surrounding amygdales filled with chlorite aggregate (Fig. 8d). Iron and titanium oxides represent magmatic accessory minerals. Plagioclases have been affected by strong alteration and most often are oligoclase. However, relics indicate that the original composition of plagioclase was that of labradorite An_{60} (Table 4). In the altered basalt pure albite and potassium feldspar are common. Clinopyroxenes have a varied composition — besides augites ($Wo_{41}En_{39}Fs_{20}$) containing about 2 wt. % of Al_2O_3 (Table 5) pigeonites are also present. Augites occasionally form inclusions in ore minerals. Titanomagnetite, ilmenite and magnetite (Table 6) represent iron and titanium oxides. Magnetite usually forms small grains, and locally rims around ilmenite.

ORE MINERALISATION

In the basalts and dolerite examined, ore minerals are represented chiefly by iron and titanium oxides and native copper. Among iron and titanium oxides, titanomagnetite and ilmenite crystallising from basaltic magma can be distinguished. With the drop of temperature in the course of exsolution magnetite and ilmenite appeared at the cost of titanomagnetite. Native copper, on the other hand occurs in typical hydrothermal paragenetic associations.

In the Volhynian basalts from the Bazaltovoye 4 and 5, Policy and Ivance quarries, as well as from depths of 56 and 116.9 m from borehole 5879, titanomagnetite and ilmenite occur in varying amounts and proportions, the total content of these two minerals not exceeding 3 vol. %. In all the basalts examined and in the dolerite titanomagnetite prevails over ilmenite. The highest ilmenite content has been found in basalt samples from Bazaltovoye 4 and 5 quarries and in the dolerite from the Bazaltovoye 4 quarry. The chemical composition of these titanomagnetites is close to that of titanomagnetites from basalts from the depth of 56 m from borehole 5879 and from the Policy quarry. They contain more than 20 wt. % of TiO_2 (Table 6), which indicates of a high ulvospinel molecular content (up to 74 mol. %). In some titanomagnetite grains ilmenite lamellae or irregular inclusions have been noted. Besides ilmenite forming intergrowths with titanomagnetite, individual elongated acicular ilmenite crystals are also present. Titanomagnetites with elevated titanium contents and ilmenites are usually richer in Mn (Table 6). As a rule the marginal zone of ilmenite individuals is made up of magnetite containing about 6 wt. % of TiO_2 (Table 6). Minute magnetite grains of similar composition occur in the basalt matrix. Thus magnetite rims around ilmenite grains could have formed simultaneously with the crystallisation of small magnetite crystals. Hematite and goethite has been found in altered basalt zones.

In some Volhynian basalts (Policy, Ivance, Stary Chartoryjsk — borehole 5879, depth 117 m) copper mineralisation has been found; reflected light microscopy showes this to have a relatively simple mineral composition. The prevailing mineral is native copper with addition of chalcopyrite, chalcosine, covellite and bornite. Cuprite, probable tenorite and occasional malachite represent oxides and oxy-acid salts. According to Y. Kosovski (pers. comm.) basalts of the Ivance area contain trace amounts of native gold, silver and electrum. We have confirmed the presence of native gold and silver in basalts of Janowa Dolina (quarry 4) by electron microprobe analysis.

The biggest massive copper aggregates are found in quartz-chlorite veins in the Ivance basalt quarry where native copper forms plates in the central parts of the veins and is accompanied by chlorite and goethite or fills fissures in quartz (Fig. 9). This implies that fissures constituted pathways for the migrating copper-bearing fluids. Usually native copper precipitated near chlorite and goethite. The size of the largest copper concentrations reach up to several tens of cm in length and about 1.5 cm in thickness. The margins of native copper plates have the form of dendrites where copper is partly replaced by cuprite and malachite.

Abundant native copper concentrations in the Policy quarry occur as veinlets and inclusions in volcanic breccias containing fragments of porphyritic basalt (Fig. 10a). Dispersed native copper mineralisation occurs in borehole core (borehole 5879). In this case two copper generations are probable: the earlier one represented by equant, frequently cuprite-rimmed, inclusions in pyroxene (Fig. 11a) and the later ones related to goethite or quartz-goethite mineralisation (Figs. 10b and 11b). Usually the copper content does not exceed 1% of the rock volume but locally (in the doleritic basalt sample from the depth of 89.8 m in borehole 5879) a 1–2 cm thick mineralisation zone built of goethite, quartz, chalcedony and chlorite contains up to 10 vol. % of native copper. Here copper grows over hematite pseudomorphs after magnetite (Fig. 11c), forms fine aggregates with goethite (Fig. 11d) and narrow rims around quartz

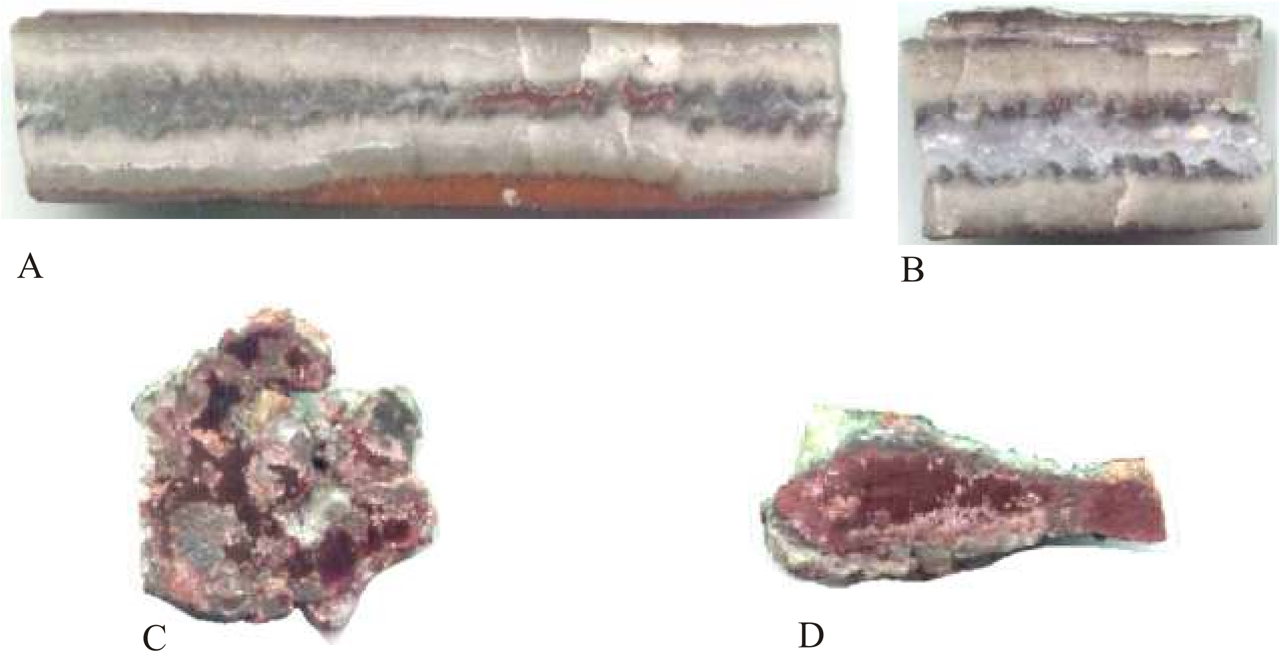

Fig. 9. Native copper in quartz-chlorite veinlets: **A** — platy copper concentrations in central parts of the veinlets, in the rims of the veinlets goethite is present; **B** — fissures in quartz are filled with copper and fine inclusions of copper are visible in chlorite; **C** and **D** — platy and compact copper concentrations, respectively, are visible in the basalt from the Ivance quarry, natural size

crystals (Fig. 12a). Native copper also forms dendrites in quartz (Fig. 12b). In amygdaloidal basalts copper forms rims around amygdales filled with quartz, chalcedony, chlorite, calcite, zeolites and goethite (Fig. 12c) as well as veinlets leading to the quartz concentrations.

In the volcanic breccias of the Ivance quarry chalcopyrite and covellite represent the copper sulphides. In some parts of the quarry only native copper is present. Elevated chalcopyrite contents (1–2 vol. %) occur in contact zones between volcanic breccias and dolerites. Occasionally, covellite pseudomorphs after native copper are noted (Fig. 12d).

The copper mineralisation of the Volhynian volcanic breccias and altered basalts is of economic value and so further examinations are advisable.

GEOCHEMICAL CHARACTERISTICS

Geochemical analysis included basalts from Bazaltovoye 4 and 5 and Policy quarries as well as from borehole 5879 (depth 56 and 116.9 m) drilled near Stary Chartoryjsk in Volhynia. According to the TAS (total alkali-silica) classification (Le Bas *et al*., 1986) the chemical composition of the rocks examined is equivalent to that of basalts and some of the projection points fall close to the basaltic andesite field. The rocks are saturated with silica and their normative CIPW composition corresponds to metaluminous quartz tholeiites (Table 1). The basalts are moderately differentiated in their major, subordinate and trace element contents (Tables 1 and 2).

Fig. 10. **A** — knotty and veinlet-like concentrations of native copper in the basaltic volcanic breccia from the Policy quarry, natural size; **B** — fine grains of the native copper in goethite, sample SC 89.8 from borehole 5879, natural size

The quartz tholeiites examined are relatively poor in Ni (42–56 ppm) and Cr (28–50 ppm) which elements concentrate in early basaltic magma differentiates. Also the cobalt content is low (44–51 ppm). Szczepanowski (1977) notes a strong Cr content decrease with fractional crystallisation of the basaltic magma — the source of the Sławatycze Series rocks found in boreholes in the eastern parts of Poland.

Basalts of the Ratno Beds, have high and strongly differentiated contents of titanium (9770–16 070 ppm) and manganese (1390–1780 ppm) bound chiefly in iron and titanium oxides (Table 5). The strontium content is relatively high and little differentiated (282–352 ppm). The carrier of this element is the main rock-forming mineral — plagioclase of labradorite and bytownite composition. Barium content ranges from 299 to 631 ppm. The highest barium content has been recognised in basalt from a depth of 116.9 m in borehole 5879 and, together with the highest rubidium content found in the basalts (Table 2) may be due to the effect of hydrothermal solutions. This basalt, similar to that of the Policy quarry, shows an elevated copper content (Table 2). Some basalts from borehole 5879 and from the Policy and Ivance quarries have native copper mineralisation in the form of veinlets and irregular concentrations (Figs. 9 and 10a).

The REE — La, Ce, Nd, Sm, Eu, Tb, Yb and Lu — concentrations in the Volhynian Series basalts correspond to those in continental tholeiites listed by Werner (1984). Distribution patterns of REE normalised to C1 chondrite (data by Evensen *et al*., 1978) for the Volhynian basalts investigated are given in Figure 13. The observed REE differentiation is small as the basalts examined represent a small portion of fractional crystallisation of magma. However, enrichment in LREE is clearly visible. The LREE/HREE ratio expressed as La_N/Yb_N lies within the 4.3–5.6 range and the extreme values correspond to the basalts of borehole 5879 (depth 56 m) and to those of the Bazaltovoye 5 quarry (Fig. 13). The discussed REE distribution patterns of the studied basalts resemble those of the tholeiitic flood basalts recognised in trap rocks worldwide (Campbell, 1998).

The measure of the degree of fractional crystallisation is the petrochemical ferruginity coefficient expressed by the $Fe_{tot.}/Mg$ atomic ratio. This coefficient ranges for the tholeiites examined from 1.06 to 1.43. The lowest coefficient value is related to the basalts of Policy also characterised by the lowest Ni/Mg, V/Fe, Cr/V, Cr/Ti and Sr/Ca atomic ratios (Table 3). Among the basalts examined they are distinctive also by the highest Co/Ni, Co/Fe and Sc/Fe atomic ratios. High Co/Ni, Co/Fe and Sc/Fe atomic ratios and, unlike the Policy basalts, also the highest V/Fe, V/Cr and Cr/Ti as well as V/Ti and Ni/Cr (Table 3) have been found in basalts at the depth of 116.9 m in borehole 5879. Basalts from the Bazaltovoye 4 and 5 quarries show similar atomic ratio values for the respective element pairs whereas in samples from different depths (56 and 116.9 m) from borehole 5879 the atomic ratio values for the respective element pairs vary.

The geochemical data, particularly the contents of trace elements in the Ratno Beds basalts were also applied for recognition of their geotectonic setting. Three types of discrimination diagrams were used for this purpose (Fig. 14): 1 — the Ti-Zr-Y diagram (Pearce and Cann, 1973), where the studied basalts plot in the field of within-plate basalts and partly in the field of MORB and other basalts; 2 — the Zr/Y versus Zr graph (Pearce and Norry, 1979), where all the samples investigated lie in the field of within-plate basalts; 3 — the V versus Ti discrimination diagram (Shervais, 1982), where the rocks studied plot mainly in the field of continental flood basalts.

DISCUSSION OF THE RESULTS

Vendian volcanic activity in the western part of EEC was probably caused by the rise of a mantle plume and the appearance of continental rifts during the late stages of breakup of the Rodinia supercontinent.

The lower Vendian effusive-tuffogenic rocks of the Volhynian Series occurs on the western slope of the Ukrainian Shield. Within this series the following beds are distinguished: Gorbashi, Zabolottya, Babino and Ratno Beds (Figs. 3–5). The age of the Volhynian Series is probably between 590 and 625 Ma (Sokolov and Fedonkin, 1990). According to the new chronostratigraphic table recommended by the International Commission on Stratigraphy (Remane *et al*., 2000) and taking into account the Phanerozoic time scale of Gradstein and Ogg (1996) the Volhynian Series should be classified as Neoproterozoic III (NP_3).

Flood basalts described in this paper are classified into the Ratno Beds occurring in the top portion of the Volhynian Series. The normative composition of the basalts examined (Table 1) is equivalent to that of metaluminous quartz tholeiites. The composition of the major minerals, plagioclases and pyroxenes, suggests that the parent magma of the Volhynian basalts underwent fractional crystallisation. The composition of plagioclase, the major mineral of both basalts and dolerite (50–70 vol. %), varies from bytownite ($An_{70–74}$) forming tabular phenocrysts of earlier generations to andesine ($An_{49–50}$) typical of late generations and developed as minute laths. The variation in clinopyroxene composition is shown in Table 5 and illustrated in Figure 7. In the Ca-Mg-Fe diagrams the projection points for clinopyroxenes of the basalts from Bazaltovoye 4 and 5 quarries (Fig. 7a) and of the dolerite from Bazaltovoye 4 quarry (Fig. 7b) show even in individual samples a considerable scatter from augite and ferroaugite through augite and subcalcic ferroaugite to pigeonites and ferropigeonites. The composition of clinopyroxenes from dolerite (Fig. 7b) indicates that these pyroxenes crystallised from the most differentiated magma i.e. that richest in iron. The differentiation of pyroxene composition in the course of fractional crystallisation of tholeiitic magmas is thoroughly discussed by Deer *et al.* (1978). Following their standpoint it can be assumed that in the earlier differentiation stages of the parental magma of the Volhynian basalts, augites crystallised simultaneously with pigeonites while further differentiation and enrichment in iron produced exclusively ferroaugites. The decline of pigeonite crystallisation could have been accompanied by the appearance of ephemeral olivine rich in iron, a product of reaction between clinopyroxene poor in calcium and magma rich in iron, and showing a decrease in silica activity. Basalts described in this paper do not contain olivine. Only in one basalt sample SC 116.9, borehole 5879, aggregates, showing a composition close

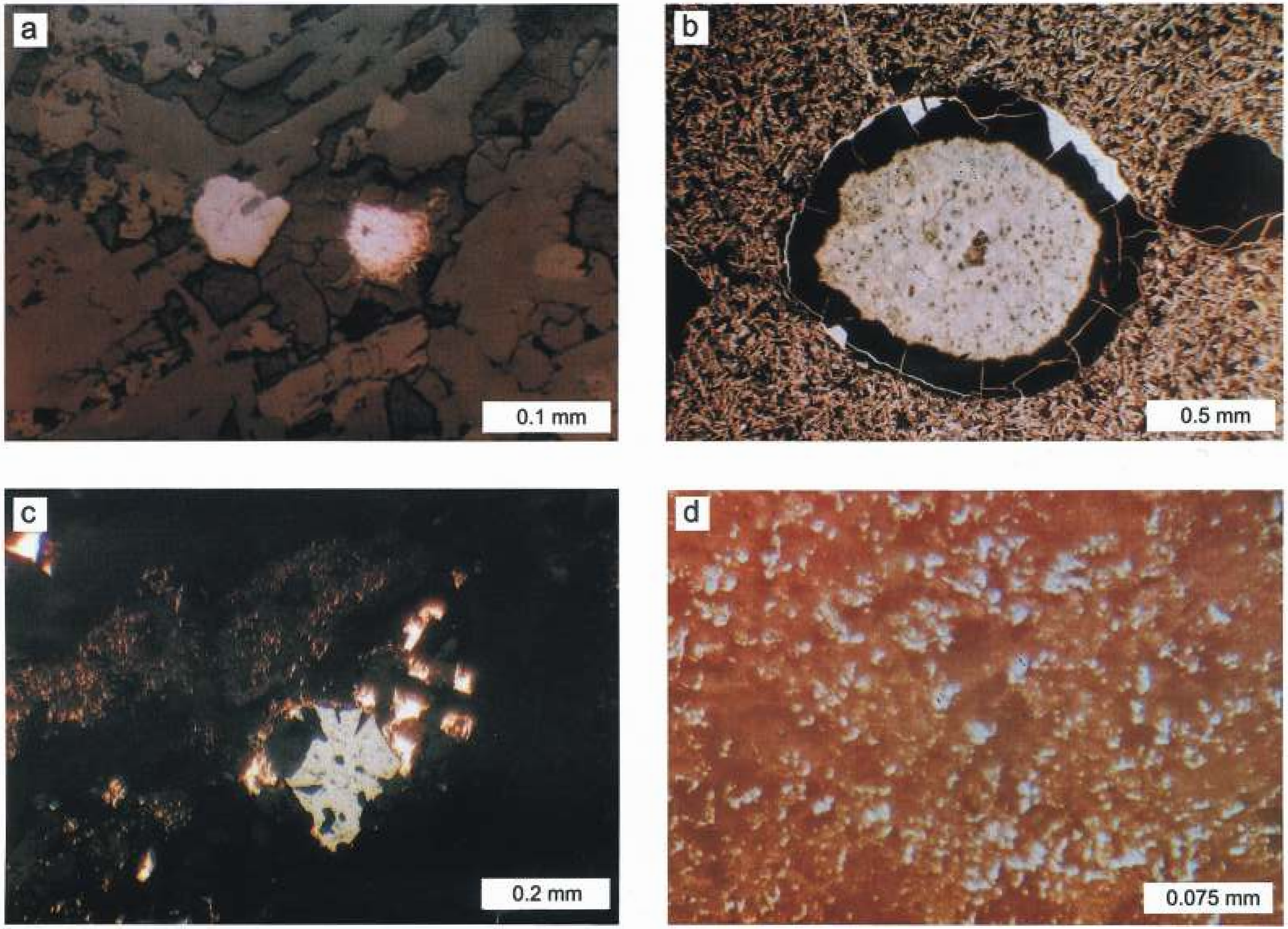

Fig. 11. **A** — a native copper grain rimmed by cuprite, forming an inclusion in the clinopyroxene crystal, on the pyroxene-plagioclase boundary magnetite is present, sample SC 89.8 from borehole 5879, reflected light; **B** — concentric amygdale with chlorite in the centre and goethite in the rim, one polar; **C** — native copper growing on hematite concentration, sample SC 89.8 from borehole 5879, reflected light, immersion; **D** — fine grained aggregate of goethite and native copper in sample SC 89.8 from borehole 5879, reflected light, crossed polars, immersion

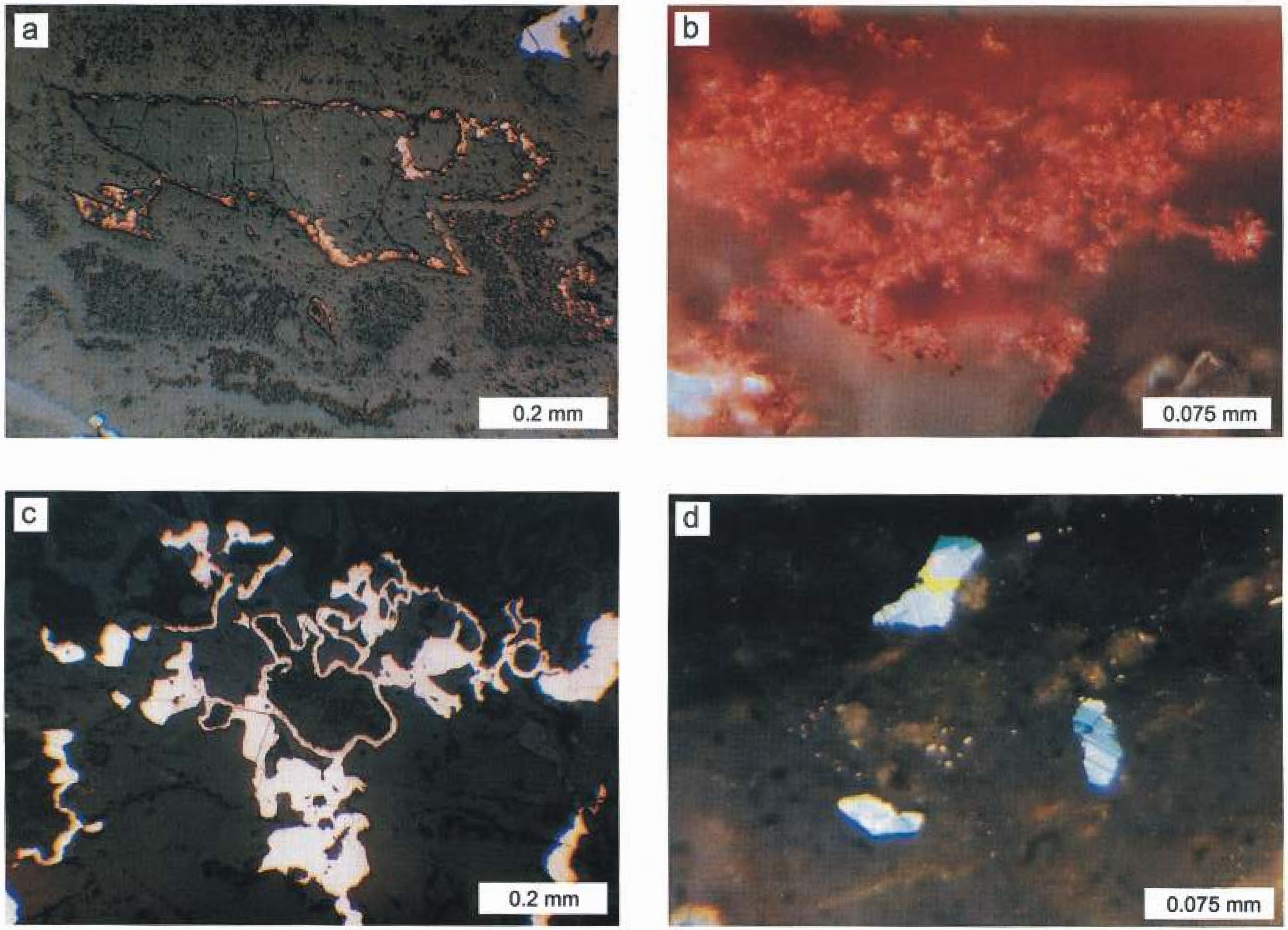

Fig. 12. **A** — native copper bordering the quartz crystal in goethite, sample SC 89.8 from borehole 5879, reflected light; **B** — dendrites of native copper in quartz, sample SC 89.8 from borehole 5879, reflected light, crossed polars, immersion; **C** — lacelike concentration of native copper in the basaltic volcanic breccia from the Policy quarry, the form of concentration is connected with amygdaloidal texture, reflected light; **D** — covellite pseudomorphs after native copper, a sample from the Ivance quarry, reflected light, crossed polars, immersion

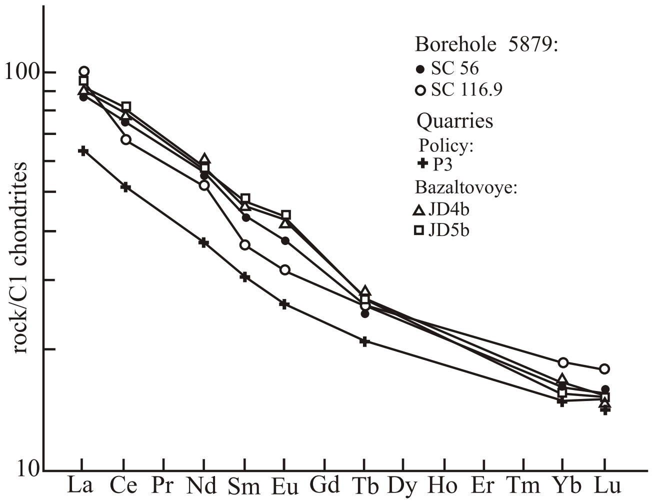

Fig. 13. Chondrite-normalised REE distribution patterns for basalt samples of the Ratno Beds of the Volhynian Series

to olivine ($Fo_{32}Fa_{68}$) were found. These aggregates could form in the way described above.

The residual magma underwent liquation and solidified as a basic glass rich in iron, magnesium and calcium and an acid glass poor in these elements. In the basic glass chlorophaeite has been identified — a mineraloid whose composition is close to that of chlorite. Usually basic glass was transformed into palagonite while the subordinate acid glass forms rims around palagonite aggregates and basic glass or distinct globular and oval inclusions armoured by palagonite and basic glass. The chemical composition of acid and basic glasses including chlorophaeite and palagonite is given in Table 7. Palagonite has been described in detail by Lazarenko *et al*. (1960). They have found palagonite to be common in the Volhynian basalts reaching usually up to 10 and less frequently 12–13 vol. %. Palagonite fills interstices among the rock-forming individuals or forms separate rounded concentrations from < 1 mm to several cm in diameter. Lazarenko *et al*. (1960) envisage yet another possible genesis of palagonite — direct separation of gel from residual magma rich in water during the final stage of solidification. The palagonites are distinctive by their variable chemical composition and varying degree of hydration resulting in different colouring — from green-brown to the less common rusty red. Literature devoted to liquation in residual tholeiitic magmas commonly describe basic glass inclusions in a prevailing acid glass (Meyer and Sigurdsson, 1978; Philpotts, 1979, 1982; Rabov, 1989). Concentrations of acid glass in a prevailing basic glass or its alteration products are — with the exception of the Volhynian basalts — considerably less frequently described (Gelinas *et al*., 1976).

Of particular importance, as regards alteration processes in the basalts, is the origin of native copper present in basalts in some parts of Volhynia (Midtsk Velki, Dovgoye Pole as well as Policy and Ivance — our study area). Copper mineralisation in the Midtsk Velki basalts has been described by Małkowski (1929), and in the Janowa Dolina (Bazaltovoye) by Krajewski (1935). According to Kowalski (1936), Wojciechowski (1939) and Małkowski (1951) the source for native copper was the basaltic volcanic glass from which it was released by hydrothermal solutions and precipitated locally. But we believe that copper mineralising the effusive-tuffogenic formations might have been brought by hydrothermal solutions from outside the Ratno Beds, as the basalts investigated are relatively poor in copper (Table 2) and weakly altered as a whole. Most likely copper migrated in the form of chloride complexes. In the varying pH and Eh environments the complex compounds decayed and copper was reduced to Cu^0. Moreover, all simple salts of univalent copper can in aqueous environment be subjected to disproportionation following the reaction $2Cu^+ \rightarrow Cu^0 + Cu^{2+}$ (Frost and Ebsworth diagram; fide: Bielański, 1994). According to Małkowski (1951) the nature and mode of occurrence of native copper in Midtsk Velki and Janowa Dolina (Bazaltovoye) show many features in common. On both sites copper crystallised in the basal, fractured part of the basalt flow which, according to Małkowski (*op. cit.*) "most probably formed a strong cover of a seemingly huge autoclave" preventing the hot solutions, steam and gases from escaping to the surface. The latter certainly contained hydrogen, a common component of mantle fluids. At high temperatures hydrogen has strong reducing properties, enabling reduction of metals to lower oxidation states or to native metal. The reaction $CuO + H_2 \rightarrow Cu^0 + H_2O$ proceeds at a relatively low temperature (420 K). But trivalent iron can be reduced by hydrogen to metallic iron at higher temperatures — about 900 K (Bielański, 1994). Elemental carbon can also act as a reducing agent for iron. Pedersen (1979) has described such an example in a Tertiary basalt dyke from the Disko Island (West Greenland). Native iron in the Berestovec basalt (Volhynia) has been first described by Karpinskij (1873) and its content has been estimated by Pfaffius (1886) at 0.04 wt. %. Native iron is a strong reducing agent for copper, as it reduces Cu^{2+} to metal at room temperature, which could account for the occurrence of copper in a dispersed form in the Volhynian basalts.

To explain the origin of copper-bearing fluids and the further modification of their composition more detailed examination is needed, both of basalts and of ore mineralisation of beds older than the Ratno Beds (Babino, Zabolottya and Gorbashi). Such examination is in progress.

CONCLUDING REMARKS

1. The basalts of the Ratno Beds are poorly differentiated and have the composition of metaluminous quartz tholeiites. On discrimination diagrams, which may be used to determine the tectonic setting of basalts, these tholeiites plot mainly in the fields of within-plate basalts (Fig. 14). As far as REE distribution patterns are concerned (Fig. 13) these rocks show similarities to continental tholeiitic basalts of the Deccan, Siberia and Karoo trap formations (Campbell, 1998).

2. We believe that the magmas for the Ratno Beds flood basalts were predominantly derived from the underlying subcontinental lithospheric mantle melted to a relatively high degree during its interaction with the hot convecting, plume-forming mantle.

3. The mineral chemistry of clinopyroxenes, particularly their great variability in individual samples (from augites to ferropigeonites; *cf*. Fig. 7) as well as an ephemeral appearance of fayalite-rich olivine, point to the solidification and crystallisation of the rocks studied under conditions of disequilibrium.

4. Two kinds of glass — basic and acid — occur in the tholeiitic basalts of the Ratno Beds probably due to liquation, which took place in relatively small volumes of residual magma, on a microscopic scale.

5. Some of the Ratno Beds contain native copper. Copper mineralisation is of hydrothermal origin and — most likely — copper was supplied from outside the Ratno Beds, probably in the form of chloride complexes. This hypothesis can be supported by the following observations: 1 — unaltered, fresh basalts and their glass are relatively poor in copper; 2 — the degree of alteration of the Ratno Beds basalts, as a whole, is relatively low; 3 — the native copper mineralisation in the Ratno Beds has been found, exclusively, in strongly hydrothermally altered rocks, in parageneses with quartz, chlorite, calcite and K-feldspar.

6. The effusions of basaltic magma of the Volhynian Series were, most likely, mainly fissure-fed. The origin of faults and deep fractures constituting pathways for the magma can be related to continental rifts appearing during the breakup of the Rodinia supercontinent, that may have started with continental rifting in South China about 820 Ma ago (Li *et al*., 1999) and then continued during mid-Neoproterozoic times (Powell *et al*., 1993) when the Pacific Ocean was formed. Most likely, the main fracture trend responsible in the EEC for the Volhynian flood volcanism relates to the suture between Fennoscandia and Sarmatia (Fig. 1) i.e. the trend of the Orsha-Volhynia aulacogen. Although the Fennoscandia-Sarmatia Suture was formed in Palaeoproterozoic, and, later on, at the turn of Mesoproterozoic times, the abortive rift (Orsha-Volhynia aulacogen) formed there, fissures in this area might have been rejuvenated in Neoproterozoic III times. This direction is almost perpendicular to the Trans-European Suture Zone (TESZ), where the continental Tornquist rift was active preceding the formation of the Tornquist Ocean.

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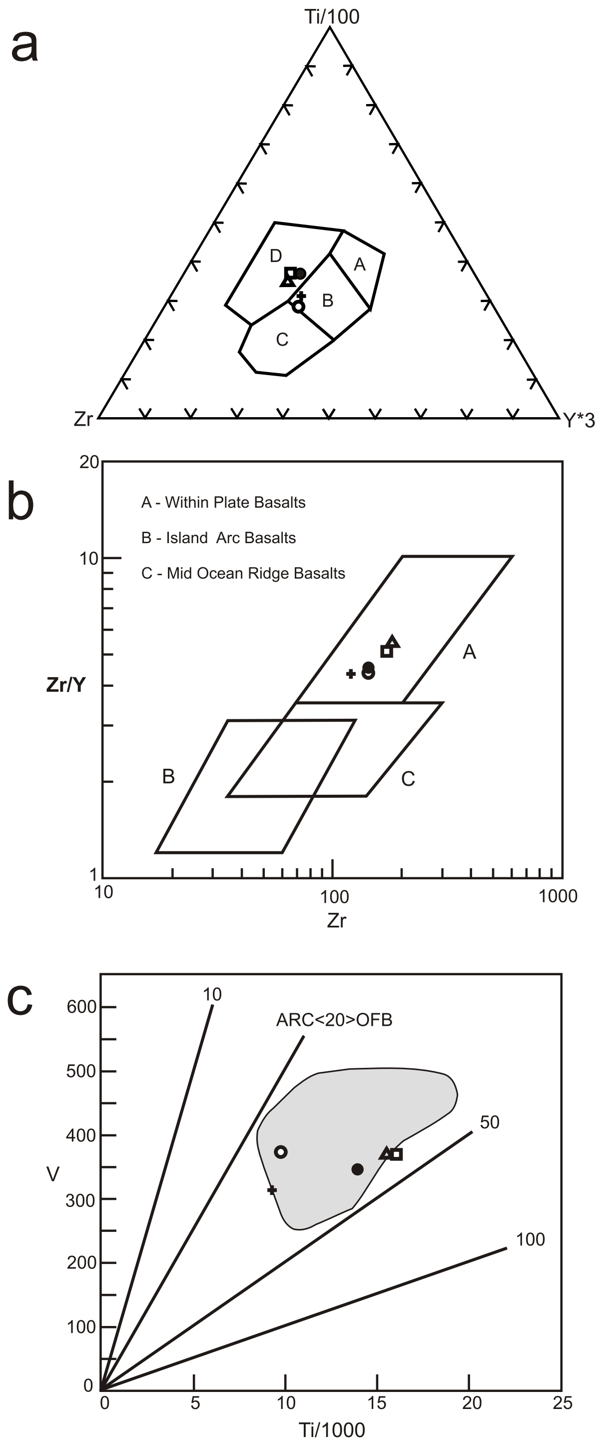

Fig. 14. Discrimination diagrams for the Ratno Beds basalts of the Volhynian Series

a — the Ti-Zr-Y diagram for basalts according to Pearce and Cann (1973): A — the field of island-arc tholeiites, B — the field of MORB, island-arc tholeiites and calc-alkaline basalts, C — the field of calc-alkaline basalts and D — the field of within-plate basalts; **b** — diagram based upon Zr/Y–Zr variations in basalts according to Pearce and Norry (1979); **c** — the Ti–V discrimination diagram for basalts after Shervais (1982), shaded area is the field of continental flood basalts; filled circle — sample SC 56, open circle — sample SC 116.9 — both from borehole 5879; cross — sample P3 from the Policy quarry; triangle — basalt JD4b, square — sample JD5b — both from the Bazaltovoye quarries

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