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Author(s): Daniel Demaiffe, Janina Wiszniewska, Ewa Krzemińska, Ian S. Williams, Holly Stein, Stéphane Brassinnes, Daniel Ohnenstetter, and Etienne Deloule

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GEOLOGICAL NOTE

A Hidden Alkaline and Carbonatite Province of Early Carboniferous Age in Northeast Poland: Zircon U-Pb and Pyrrhotite Re-Os Geochronology

Daniel Demaiffe,^{1,*} Janina Wiszniewska,² Ewa Krzemińska,² Ian S. Williams,³ Holly Stein,⁴ Stéphane Brassinnes,¹ Daniel Ohnenstetter,⁵ and Etienne Deloué⁵

1. *Laboratoire Géochimie Isotopique, Université Libre de Bruxelles (ULB), Département des Sciences de la Terre et de l'Environnement, CP 160/02, 50, avenue F. Roosevelt, 1050 Bruxelles, Belgium;*
2. *Państwowy Instytut Geologiczny, ul. Rakowiecka 4, 00-975 Warszawa, Poland;*
3. *Research School of Earth Sciences, Australian National University, Canberra, Australian Capital Territory 0200, Australia;*
4. *Applied Isotope Research for Industry and Environment Program, Department of Geosciences, Colorado State University, Fort Collins, Colorado 80512, U.S.A.;*
5. *Physics of Geological Processes, University of Oslo, 0316 Oslo, Norway;*
5. *Centre de Recherches Pétrographiques et Géochimiques—Centre National de la Recherche Scientifique, 54501 Vandoeuvre-les-Nancy, France*

ABSTRACT

Extensive geophysical investigations in NE Poland in the 1950s and 1960s led to the discovery of an alkaline and carbonatite magmatic province buried under thick (600–800 m) Meso-Cenozoic cover north of the Trans-European Suture Zone, or Tornquist Line. Drilling focused on geophysical anomalies identified three intrusions in the Paleoproterozoic metasedimentary and metavolcanic rocks of the Mazowsze Domain: the Pisz gabbro-syenite massif, the Ełk syenite massif, and the small, differentiated Tajno body consisting of clinopyroxenite cumulates and syenites crosscut by carbonatite veins. Emplacement ages for these intrusions have been obtained by (1) zircon U-Pb geochronology on a gabbro from Pisz, a syenite from Ełk, and an albitite from Tajno and (2) a Re-Os model age for pyrrhotite from a Tajno carbonatite. The ages measured by both methods fall in the narrow range 354–345 Ma (Early Carboniferous: Tournaisian). This is slightly younger than the Late Devonian (380–360 Ma) Kola Peninsula alkaline and carbonatite province (20 intrusions) of NW Russia and Karelia but is of comparable age to the first manifestations of the long-lasting (~100 m.yr.) Carboniferous to Permian magmatic event (360–250 Ma) manifest in northern Europe (from the British Isles to southern Scandinavia, the North Sea, and northern Germany) in the foreland of the Variscan orogeny (in the so-called West European Carboniferous Basin) and the East European Craton.

Introduction

Carbonatites are rare igneous rocks that contain more than 50% modal carbonate minerals (Le Maître 2002). They are commonly associated with either ultramafic rocks or a range of silica-undersaturated alkaline rocks. Alkaline-series rocks in general, and carbonatites in particular, are much less abundant than tholeiitic and/or calc-alkaline-series rocks. Nevertheless, they are important geologically because (1) they are windows into the geo-

chemical and isotopic composition of the subcontinental upper mantle (their very high Sr and rare earth element [REE] contents preclude crustal contamination) and (2) they can host important deposits of rare metals (Nb, Ta, REEs, etc.) and industrial materials (phosphates, vermiculites; see recent review by Petrov [2004]). Carbonatites occur mostly within stable continental (cratonic) areas; they are often located along lineaments (possibly rift zones) or within lithospheric domes (Woolley 1989). There are only two known oceanic occurrences, the Cape Verde and Canary Islands.

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* Author for correspondence; e-mail: ddemaif@ulb.ac.be.

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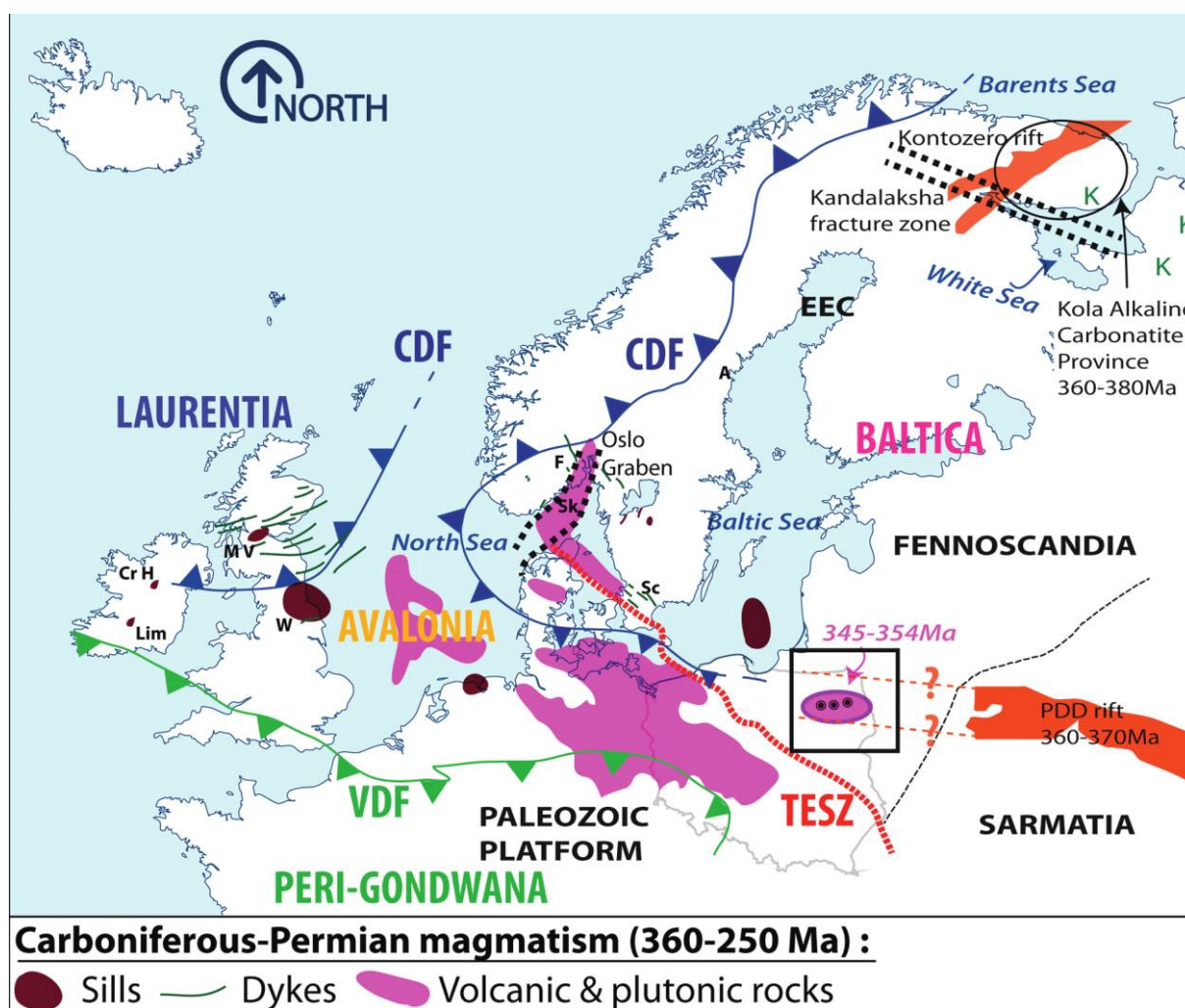


Figure 1. Distribution of the two main Paleozoic magmatic provinces in northern Europe: the Late Devonian (380–360 Ma) province and the Carboniferous-Permian (360–250 Ma) province (based on the maps of Stephenson et al. 1996, Wilson and Lyashkevitch 1996, Heeremans et al. 2004, and Neumann et al. 2004). The main tectonic/structural features are also reported. CDF = Caledonian Deformation Front; EEC = East European Craton; PDD rift = Pripjat-Dniepr-Donets rift; TESZ = Trans-European Suture Zone; VDF = Variscan Deformation Front. Other abbreviations. A = Alnö carbonatite; CrH = Croghan Hill; F = Fen carbonatite; K = kimberlite occurrences; Lim = Limerick; MV = Midland Valley; Sc = Scania; Sk = Skagerrak; W = Whin Sill. The pink ellipse in the outlined box indicates the location of the three studied intrusions (black dots): from east to west, Tajno, Ełk, and Pisz.

Carbonatites are uncommon in the Fennoscandian Block of the East European Craton (EEC; Bogdanova et al. 2006) except in NW Russia, where more than 20 alkaline complexes, many of them with carbonatites, form the Late Devonian Kola-Karelia Province, which includes the well-known agpaitic nepheline syenite intrusions of Khibiny and Lovozero (Kukharenko et al. 1965; Kogarko et al. 1995). Few small Neoproterozoic alkaline complexes are known: Fen in southern Norway (Andersen 1988) and Alnö in Sweden (Meert et al. 2007) are examples.

This article presents new geochronological data on the buried alkaline and carbonatite province discovered in NE Poland in southern Fennoscandia. Three intrusions have been identified: the Tajno alkaline-carbonatite complex, the Ełk alkaline syenite massif, and the Pisz gabbro-syenite complex (figs. 1, 2). The province is located about 200 km NE of the Trans-European Suture Zone, which forms the southern boundary of the Baltica Block (Bogdanova et al. 2008). Zircon U-Pb ages for the three intrusions and a sulfide (pyrrhotite) Re-Os age for the Tajno carbonatite all indicate an Early Car-

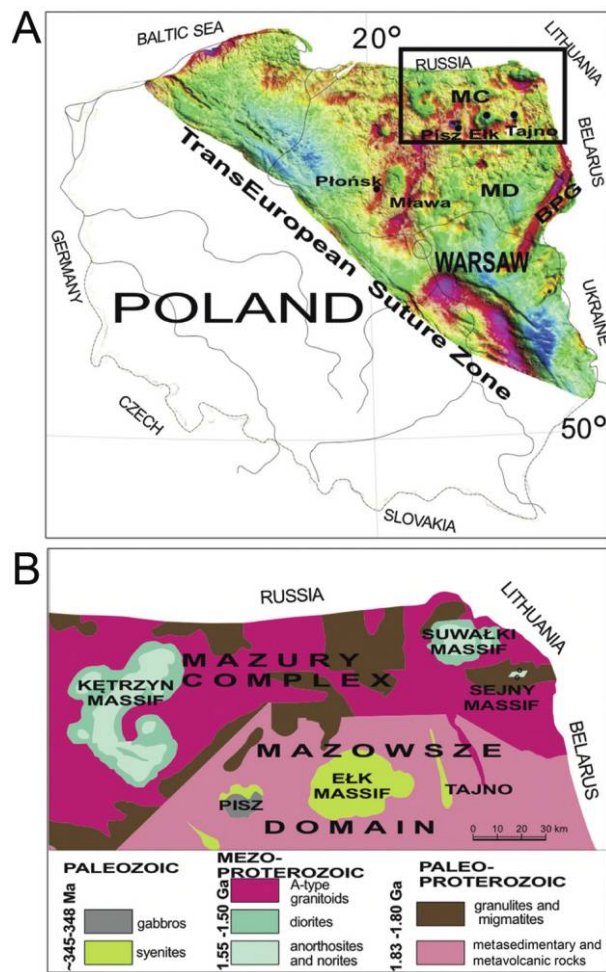


Figure 2. A, Transformed Bouguer anomaly for the basement of NE Poland (from S. Wybraniec, unpublished data 2007), showing major geologic structures and location of the studied boreholes. Main structural units: BPG = Belarus Podlasie granulite belt; MC = Mazury Complex; MD = Mazowsze Domain. B, Simplified geologic sketch map of northern Poland (from Kubicki and Ryka 1982, modified by Krzemińska and Wiszniewska [2007]).

boniferous (354–345 Ma) emplacement age. The Polish province is thus a new occurrence of the widespread Carboniferous to Permian rift-related magmatism that developed in NE Europe (fig. 1) between the Caledonian and Variscan deformation fronts (e.g., Neumann et al. 2004; Wilson et al. 2004).

Geological Setting

The crystalline basement of Fennoscandia in central NE Poland is covered by 600–800 m of Mesozoic to Cenozoic sedimentary rocks. Extensive geophysical investigations (regional magnetic and

gravity surveys) defined several pronounced anomalies in the basement (fig. 2) that have been explored through drilling. The regional basement consists of two main domains. The older domain, in the south (Mazowsze Domain), consists of Svecofennian metasedimentary rocks (Krzemińska et al. 2009; Williams et al. 2009) and Late Paleoproterozoic granitoids. Most of the granitoids have zircon U-Pb intrusion ages in the range 1.84–1.80 Ga (Krzemińska et al. 2007; Wiszniewska et al. 2007b). The younger domain, to the north (Mazury Complex), consists of several Mesoproterozoic A-type intrusions constituting an anorthosite-mangerite-charnockite-granite (AMCG) series: the Suwałki and Ketrzyn anorthosites, the Sejny norite, and a variety of outlying granitic bodies. Their zircon and titanite U-Pb ages are all in the range 1.52–1.50 Ga (Claesson 1996; Dörr et al. 2002; Wiszniewska et al. 2007a).

Three ultramafic and alkaline bodies were discovered by drilling (fig. 2): the Tajno pyroxenite-carbonatite complex, the Elk alkaline syenite massif, and the Pisz gabbro-syenite intrusion. The Pisz massif was discovered in the Johannesburg EG1 borehole (Fisher 1939), within the borders of the former East Prussia. The hole was located on a prominent magnetic and gravimetric high, now recognized as marking a large (~170 km²) body of augite-bearing gabbro (Görlich et al. 1960) locally interlayered with quartz syenite. The Elk nepheline syenite massif (~400 km²) and its metasomatized fenite aureole (Ryka 1994a) have been explored since 1954 by several boreholes (Elk IG 1–4, Klusy IG 1, Rydzewo IG 1, Drygaly IG 1–1a, Prostki IG 1–2, and Grajewo IG 1). The massif forms a ring structure, most probably of polyphase origin, dominated by silica-undersaturated rocks including foid-bearing syenites, foidites, and syenites. The Tajno massif is much smaller (~5 km²). It is penetrated by 12 drill holes (Tajno IG 1–12). The Tajno is a complex plutono-volcanic intrusion consisting of clinopyroxenites and syenites, various volcanic rocks, and a central diatreme breccia pipe (~800 m in diameter) cut by numerous carbonatite dykes.

More recent drilling shows that there are other intrusions in the same province, southwest of the three massifs described (fig. 1). Drilling at Plonsk IG 2, Ciechanow 1, Konopki Wielkie, and Gradzanowo has intersected a sequence—consisting of quartz syenite, microsyenite, and microsyenite veins—that crosscuts Silurian to Permian sedimentary rocks. The petrogenetic relationships between these alkaline bodies have yet to be established, but many are thought to be of Carboniferous age. Collectively, this region of geophysical anom-

alies has been termed the Mława (or Olsztynek) anomaly (Wybraniec and Cordell 1994).

Petrography of the Alkaline Complexes

Preliminary geological, geophysical, and geochemical investigations of the Tajno and Ełk intrusions have been published as monographs of the Polish Geological Institute edited by Ryka (1992*b*, 1994*b*). The Tajno alkaline massif was also briefly reviewed and compared to the intrusions of the Kola Province by Demaiffe et al. (2005).

The Tajno Massif. The plutonic component of the Tajno massif consists mostly of clinopyroxenites and syenites. The clinopyroxenites are medium-grained cumulates of diopside + magnetite + titanite ± apatite, with interstitial phlogopite, amphibole, and alkali feldspar. The clinopyroxene has two distinct habits: (1) large (>3 mm), zoned, inclusion-rich crystals (Mg# of the cores: 0.86–0.75) that occur locally as broken clasts embedded in a fine-grained matrix and (2) elongate, prismatic, unzoned, and inclusion-free crystals (Mg#: 0.78–0.61). Grain size and deformation texture (cataclasis) differ from sample to sample. The syenites are also varied. Two end members have been recognized: (1) syenites (with minor melanosyenites) containing early-formed tabular and weakly zoned clinopyroxene (Mg# in the core: 0.76–0.63; low Na₂O content: 0.75–1.22 wt%), titanite, and apatite embedded in large poikilitic, perthitic alkali feldspar; and (2) nepheline syenites with large twinned microperthitic alkali feldspar laths and late-stage, strongly zoned clinopyroxene with colorless augite cores (Mg#: 0.76) and dark green aegirine-augite to augite rims (Mg# as low as 0.23; Na₂O up to 4.35 wt%). The nepheline syenites are not agpaitic in the restricted sense of Sørensen (1997; see also Le Maitre 2002), as they do not contain complex Zr-Ti silicates such as eudialyte and rinkite, although some samples contain lamprophyllite.

Ryka (1992*a*) recognized three stages of carbonatite emplacement: (1) early carbonatites found as fragments in the central breccia, (2) main-stage carbonatites occurring as veins (a few centimeters to 1 m thick) crosscutting the clinopyroxenites and syenites and as cement within the central breccia, and (3) thin, late-stage, Fe-rich carbonatites composed mainly of ferroan dolomite and ankerite (Brassinnes et al. 2005). Grain size differs from one borehole to another. Most carbonatites are fine grained (~1 mm), but locally the calcite grains can be larger than 10 mm. Textures are mainly granular, sometimes porphyroclastic. Comb texture with elongate calcite grains (similar to those observed in

the Kaiserthul carbonatite veins; Katz and Keller 1981) has been described by Ryka (1992*a*). Sr-rich calcite is the main carbonate; it locally contains numerous strontianite inclusions (exsolutions?). Other carbonates (dolomite, ankerite, burbankite, and REE-bearing fluorocarbonates) have been identified but are of minor importance. Fluorite occurs as cement in the central breccia. Sulfides (mainly pyrite and pyrrhotite) are quite abundant; they sometimes occur as large (>5 mm) grains. Coarse (up to 10 mm), euhedral, twinned alkali feldspar is the main silicate phase; phlogopite and aegirine are subordinate. Perovskite and pyrochlore are generally absent but do occur locally.

The albitites are mainly composed of anhedral albite grains. Most grains are small (<1 mm), but locally larger (up to 5 mm) zoned and corroded crystals (former alkali feldspars?) have been observed. Accessory magnetite and apatite have been found, but Fe-Mg silicates are absent. Carbonates occur as small interstitial grains, sometimes aggregated, sometimes as diffuse veinlets. Zircon grains (50–200 μm) are closely associated with the carbonate seams. These albitites could result from the thorough metasomatic transformation (albitization) of former syenites or former country rocks induced by the infiltration of carbonatitic melts.

The Ełk Complex. The Ełk complex consists mainly of various types of foid-bearing syenites. Quartz syenites occur near the margins of the intrusion. The rocks have been described petrographically by Krystkiewicz and Ryka (1994) and Ryka (1994*a*) and geochemically by Armbrustmacher and Modreski (1994). Most nepheline syenites have been variously affected by late-stage hydrothermal alteration. Rocks of intermediate composition (syenogabbro to monzonite) were intersected in the Grajewo drillhole. Mafic rocks and carbonatites are absent.

The sample for zircon U-Pb geochronology was collected from fresh syenite in the upper part of the Ełk IG 1 drill hole (~816 m depth), the same interval previously sampled for K-Ar dating (Depciuch et al. 1975). This interval consists of about 100 m of massive gray sodalite-bearing syenite, the principal components of which are alkali feldspar (microperthite), aegirine-augite, sodalite, biotite, and thorium-rich titanite.

The Pisz Complex. The Pisz mafic complex was intersected near the bottom of only one drill hole (Johannisburg EG 1 1206, at 1359.5 m). The core sampled olivine-free gabbro and two syenite veins (6–10 m thick), as well as a few meters of gabbro permeated by quartz syenite microveins. The coarse-grained main gabbro body consists of cli-

nopyroxene, plagioclase of mostly labradorite composition (An_{60-65}), Ca-amphibole, and biotite. Accessory minerals include abundant Fe-Ti oxides and apatite. Rare zircon grains were recovered from the massive gabbro, but none were observed in the several thin sections studied. The clinopyroxene is a diopside with oriented, rod-like to tabular inclusions of biotite and ilmenite "dust" distributed along two intersecting planes. Such "Schiller structures" are common in all the unaltered gabbro samples. The plagioclase grains are regularly zoned from $\sim An_{60}$ cores to $\sim An_{40}$ rims. Clinopyroxene is commonly altered to amphibole along its margins and along fractures. Some new-grown amphibole is postmagmatic, probably formed during cooling and/or emplacement of the quartz syenite veins.

Backscattered electron (BSE) images of the veins reveal the presence of very fine (2–5 μm) zircon grains within amphibole coronas around altered pyroxene crystals. The upper part of the Pisz complex (1200–1262 m) consists of syenite-permeated gabbro and quartz syenite. The fine-grained syenite is composed chiefly of K-feldspar, quartz (up to 5 vol%), and Na-rich plagioclase. Locally, hornblende, biotite, and titanite are common. The sample selected for geochronology was from massive gabbro near the bottom of the drill hole (depth ~ 1330 m).

Previous Age Determinations

Previously, the emplacement ages of the three massifs studied (Tajno, Ełk, and Pisz) were not precisely determined. A biotite Rb-Sr age of 329 ± 13 Ma (recalculated for $\lambda^{87}Rb = 1.42 \times 10^{-11} \text{ yr}^{-1}$) was measured by Przewłocki et al. (1962) on the Ełk syenite. Depciuch et al. (1975) measured a K-Ar age of ~ 318 Ma on biotite, and K-feldspars from several drill holes in the Ełk massif yielded a range of ages between 323 and 264 Ma. Titanite and apatite (29 samples) have yielded a very large range of fission-track ages (331–206 Ma) that has been divided into four stages (Blusztajn 1994) inferred to relate to uplift and cooling of the massif. A Rb-Sr whole-rock age indication of 355 ± 4 Ma was measured by Blusztajn (1994) on nine syenites (both foid-bearing and quartz-bearing varieties). There is a small amount of scatter about the regression line (MSWD = 5.8), so the Rb-Sr isotopic system might have been disturbed by hydrothermal alteration, which is commonly observed in alkaline-peralkaline rocks. Fewer age measurements are available for the Pisz massif. Depciuch et al. (1975) obtained K-Ar ages of ~ 349 Ma on biotite from a gabbro and ~ 291 Ma on K-feldspar from a syenite. Feldspars

from a coarse-grained syenite and a microsyenite from the Tajno massif yielded similar K-Ar ages: ~ 327 and ~ 289 Ma, respectively. Mineral K-Ar and Rb-Sr ages (as well as fission-track ages) must be interpreted as minimum ages that record the cooling and postcrystallization history of the intrusions.

Samples for U-Pb and Re-Os Geochronology

Zircon was separated from a Pisz gabbro, an Ełk syenite, and a Tajno albitite. The zircon from the massive Pisz gabbro sample 1330 occurred as medium-grained (100–200 μm), clear, weakly colored, stubby subhedral crystals with few well-developed crystal faces. Cathodoluminescence (CL) images (fig. 3A) showed mostly banded or weak concentric growth zoning that is almost certainly of igneous origin (see Corfu et al. 2003). There were no metamorphic overgrowths. Truncated zoning on many grains indicated that they were fragments of larger crystals.

The two Pisz gabbro samples analyzed for major and trace elements by x-ray fluorescence spectrometry and inductively coupled plasma-mass spectrometry had Zr contents in the range 74–82 ppm. Zircon crystallizing from a mafic magma with such a low Zr content is likely to be late-stage, because the magma initially would have been zircon undersaturated. Despite very careful microscopic investigations, zircon was not observed in thin section. Interstitial crystallization from fractionated liquid might explain the incomplete development of the zircon crystal faces (Corfu et al. 2003). The zircon grains also appear to be devoid of older cores (fig. 3A), which suggests that they accurately record the emplacement age, free from the effects of inheritance. The zircon grains from the gabbro are distinctive and much larger than the tiny (2–5 μm) interstitial zircon grains from the late quartz syenite veins. From these features, we conclude that the gabbro zircon crystallized as the gabbro magma crystallized, not as a result of a later hydrothermal event.

Very little zircon was extracted from the Ełk alkaline syenite (sample 816), despite the relatively high Zr content of the rock (360 ppm). Zircon was difficult to identify in thin section because of its "poor quality." It was not observed within biotite or within the other ferromagnesian minerals but instead occurred mainly within the large alkali feldspar crystals (not at their rims) in association with fine-grained titanite, consistent with the zircon being a relatively early crystallizing phase. The zircon grains, although coarse ($\sim 250 \mu m$), were in

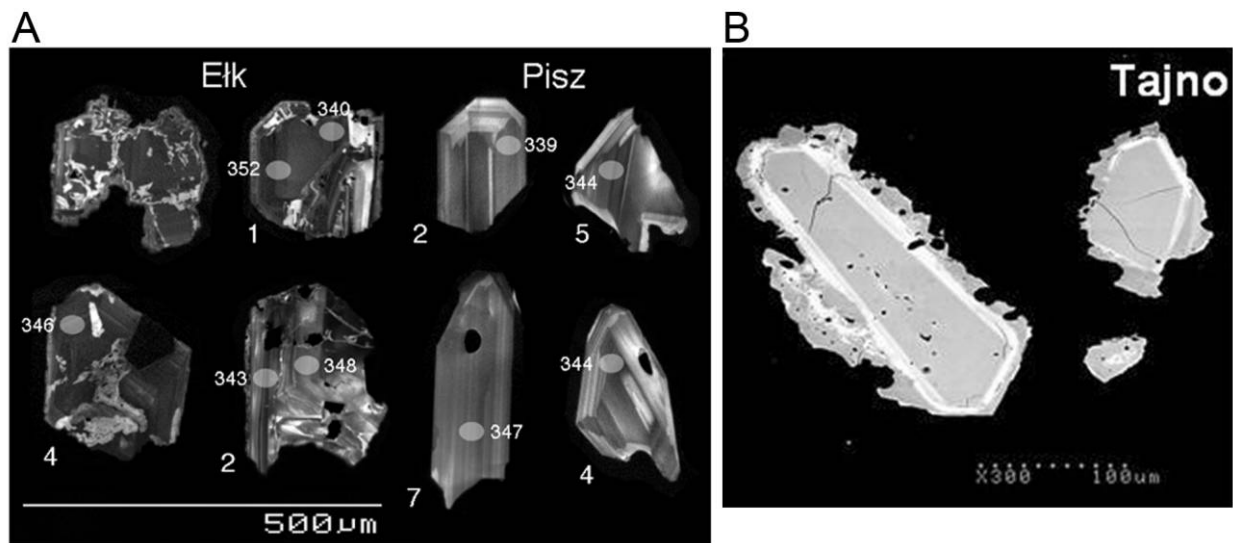


Figure 3. *A*, Cathodoluminescence images of analyzed zircon grains from the Elk and Pisz intrusions. Ellipses show the location and approximate size of the dated areas. Ages in Ma. *B*, Backscattered electron image of selected zircons from the Tajno albitite.

very poor condition (fig. 3A); they were turbid, dark in color, and anhedral. CL imaging nevertheless showed a few areas with preserved remnants of oscillatory igneous zoning, and those were targeted for U-Pb dating. All grains had large areas of alteration in which primary zoning was completely replaced by secondary “cauliflowers” of CL-bright zircon at grain margins and penetrating into the crystals along healed fractures. This recrystallized zircon had a very high Th content (1328–3554 ppm in five of seven analyzed grains), which is not unusual for syenite zircons (Belousova et al. 2002).

The zircon from Tajno was separated from an albitite (sample 10–1091) in which it occurred closely associated with carbonate-rich pockets and/or diffuse veinlets. The Tajno albitites have intermediate SiO₂ contents (61.0–63.5 wt%), very high Na₂O (9.0–11.5 wt%), and low K₂O (0.5–1.5 wt%). Zr contents are high: 845–1150 ppm. The zircon grains were large (commonly >200 μm) and generally euhedral to subhedral, with oscillatory zoning, and had thick, porous, deeply corroded overgrowths (fig. 3B).

Sulfides were relatively rare in the Tajno carbonatites. Pyrite is the most common; it occurs as euhedral (up to 10 mm) crystals, and it may contain intergrowths and/or rims of pyrrhotite. Dzierżyc and Ryka (1983) observed small (<0.05 mm) euhedral crystals of pyrrhotite associated with pyrite. For this study, a single occurrence of pyrrhotite from drill core T10 at a depth of 1047.0 m was analyzed (fig. 4). Two small, fine-grained pyrrhotite masses,

identified as having similar occurrence and separated by a few centimeters, were extracted with a small diamond-tipped drill rotated at slow speed. Visually and magnetically, the two masses consisted of fine-grained pyrrhotite disseminations, whereas another nearby sulfide patch consisted of a pyrrhotite rim on a pyrrhotite core.

Analytical Methods

The zircon U-Pb analyses were performed by secondary ion mass spectrometry (SIMS) in two laboratories: the Pisz and Elk samples were analyzed at the Research School of Earth Sciences (RSES) of the Australian National University (ANU; Canberra) and the Tajno sample at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Centre National de la Recherche Scientifique (Nancy, France).

The reference materials used at RSES were zircons from Sri Lanka (SL13, 238 ppm U) and Temora 2 (²⁰⁶Pb/²³⁸U = 0.06683). Before analysis, the internal zoning of the sectioned zircon grains was imaged by CL with a Hitachi S-2250N scanning electron microscope (SEM). The U-Th-Pb isotopic analyses were carried out with the ANU SHRIMP II ion microprobe, following the procedures described by Williams and Claesson (1987) and Williams (1998).

The reference material used at CRPG was zircon 91500, dated at 1062.4 ± 0.4 Ma (Wiedenbeck et al. 1995). BSE and CL images of the sectioned zircon



Figure 4. Drill core sample T-10, at 1047 m, shows carbonatite vein material with pyrrhotite. Fine-grained pyrrhotite masses selected for Re-Os dating are shown within black circles. A pyrrhotite patch with a thin pyrrhotite rim around a pyrrhotite core is circled in gray. Length of core is 10 cm. A color version of this figure is available in the online edition or from the *Journal of Geology* office.

crystals were taken with a Philips XL30 SEM (Service Commun de Microanalyse, Université Henri Poincaré Nancy 1) in order to select locations for analyses with respect to zircon zoning. U-Pb isotopic compositions were determined with the CRPG-CNRS Cameca IMS-1270 ion microprobe (Nancy, France) and instrumental conditions and data reduction procedures as described by Delouie et al. (2002).

The Re-Os sulfide analyses were performed by isotope dilution–negative thermal ion mass spectrometry (ID-NTIMS) at the Applied Isotope Research for Industry and Environment (AIRIE) Program, Colorado State University (Fort Collins). The Re-Os isotopic composition of the Tajno pyrrhotite sample was determined via Carius tube dissolution and single ^{185}Re and ^{190}Os spikes (AIRIE run LL-291). Inverse aqua regia (3 mL 6N HCl + 8 ml H_2O_2 -treated concentrated HNO_3), accurately weighted spike solutions, and accurately weighted sample powder were sealed in a Carius tube and heated at 250°C for 12 h. Os and Re were separated from the aqua regia via CHCl_3 -HBr solvent extraction and anion-exchange chromatography, respectively. Further purification and extraction of Os and Re utilized microdistillation and single-bead chromatography, respectively. Sample-spike mixtures were measured on a Thermo-Finnigan Triton NTIMS using outgassed Pt filaments. Re ratios were determined using the total evaporation method, whereas Os ratios were determined by time-corrected, peak-hopping SEM detection. All ratios were measured as negative oxides and corrected for oxygen isotope

composition; Os ratios were corrected for mass fractionation. Final Re and Os concentrations were corrected for blank contributions. At the time of analysis, the Re blank was 2.89 ± 0.01 pg and the Os blank was 0.252 ± 0.003 pg, with a $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition of 0.160 ± 0.006 .

Geochronological Data

The U-Th-Pb isotopic analyses of the selected zircon grains from the three samples are listed in table 1 and plotted on Tera-Wasserburg concordia diagrams in figure 5. The Re-Os results are discussed in the text.

Pisz Gabbro. Nine zircon grains were analyzed, four with oscillatory zoning and five with banded growth zoning. All had moderate to low U concentrations (<230 ppm), but the grains with banded zoning were the lowest on average (<125 ppm), consistent with their earlier crystallization. Th/U was consistently high (1.22–1.76), a common feature in gabbro zircon. Common-Pb contents were all low. All the analyses were concordant within analytical uncertainty, and all gave the same radiogenic $^{206}\text{Pb}/^{238}\text{U}$ within error (0.05506 ± 0.00029 , MSWD = 0.5), equivalent to a weighted mean age of 345.5 ± 5.1 Ma (95% confidence level), the uncertainty including 0.4% uncertainty in the Pb/U calibration.

Ełk Syenite. It was difficult to locate Ełk zircon of sufficiently high quality to date, even with a spatial resolution of $25 \mu\text{m}$. Seven measurements were attempted on five grains in areas where the

Table 1. U-Th-Pb Isotopic Data for Zircons from the Pisz Gabbro, Elk Syenite, and Tajno Albitite

Grain spot	Zoning ^a	Pb* (ppm)	U (ppm)	Th (ppm)	²⁰⁴ Pb/ ²⁰⁶ Pb	% ²⁰⁶ Pb comm. ^b	²⁰⁸ Pb/ ²³² Th	²⁰⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²³⁵ U	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²³² Th	²⁰⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²³⁵ U	Apparent ages (Ma)			
														²⁰⁸ Pb/ ²³² Th	²⁰⁷ Pb/ ²³⁵ U		
Pisz gabbro, zircon:																	
4.1	CZ	17	228	401	1.76	9.33E-05	± 5.05E-05	.002	.5416 ± .0062	.0169 ± .0003	.0548 ± .0007	.399 ± .012	.0528 ± .0013	338 ± 6	344 ± 4	341 ± 8	319 ± 57
5.1	CZ	16	217	375	1.73	4.43E-05	± 3.10E-05	.001	.5349 ± .0072	.0170 ± .0003	.0548 ± .0007	.432 ± .010	.0572 ± .0011	341 ± 6	344 ± 4	365 ± 7	498 ± 44
1.1	CZ	11	153	244	1.60	1.56E-04	± 2.00E-04	.003	.487 ± .011	.0170 ± .0006	.0557 ± .0012	.416 ± .030	.0542 ± .0036	340 ± 11	349 ± 7	353 ± 22	379 ± 159
6.1	CZ	9	126	184	1.46	5.73E-04	± 1.97E-04	.010	.430 ± .017	.0161 ± .0008	.0545 ± .0019	.358 ± .032	.0476 ± .0037	322 ± 17	342 ± 11	311 ± 24	80 ± 175
2.1	BZ	8	121	158	1.30	4.84E-04	± 2.12E-04	.009	.391 ± .017	.0162 ± .0008	.0541 ± .0011	.375 ± .029	.0503 ± .0036	325 ± 16	339 ± 7	323 ± 21	209 ± 175
9.1	BZ	8	113	153	1.36	5.85E-04	± 1.78E-04	.011	.407 ± .018	.0164 ± .0008	.0546 ± .0007	.368 ± .024	.0489 ± .0031	328 ± 15	343 ± 4	318 ± 18	145 ± 143
3.1	BZ	7	95	136	1.43	1.71E-04	± 1.27E-04	.003	.441 ± .013	.0171 ± .0006	.0553 ± .0008	.415 ± .025	.0544 ± .0032	343 ± 11	347 ± 5	352 ± 18	388 ± 135
7.1	BZ	6	87	112	1.28	6.39E-04	± 2.03E-04	.012	.364 ± .016	.0158 ± .0008	.0556 ± .0010	.374 ± .034	.0489 ± .0043	317 ± 15	348 ± 6	323 ± 25	141 ± 192
8.1	BZ	5	67	82	1.22	3.65E-04	± 1.69E-04	.007	.380 ± .012	.0177 ± .0007	.0566 ± .0012	.420 ± .027	.0537 ± .0032	354 ± 14	355 ± 7	356 ± 20	360 ± 139
Elk syenite, zircon:																	
4.1	CZ	45	179	2472	13.8	4.97E-05	± 5.83E-05	.001	4.180 ± .032	.0167 ± .0003	.0551 ± .0009	.409 ± .016	.0539 ± .0018	334 ± 6	346 ± 5	348 ± 11	366 ± 76
3.1	CZ	50	126	2945	23.3	1.21E-03	± 2.63E-04	.022	7.10 ± .10	.0169 ± .0005	.0557 ± .0012	.410 ± .041	.0534 ± .0050	339 ± 10	349 ± 8	349 ± 30	346 ± 228
1.2	CZ	58	122	3554	29.1	1.12E-03	± 2.26E-04	.020	8.74 ± .15	.0169 ± .0005	.0562 ± .0011	.323 ± .032	.0417 ± .0040	339 ± 9	352 ± 7	284 ± 25	...
1.1	CZ	28	106	1647	15.5	2.45E-03	± 7.55E-04	.045	4.62 ± .12	.0161 ± .0006	.0541 ± .0015	.343 ± .095	.046 ± .013	323 ± 12	340 ± 9	300 ± 75	6 ± 835
2.2	CZ	8	46	424	9.28	6.75E-04	± 4.15E-04	.012	2.779 ± .17	.0166 ± .0008	.0554 ± .0019	.420 ± .059	.0550 ± .0072	333 ± 15	348 ± 11	356 ± 43	412 ± 323
5.1	CZ	21	44	1328	29.8	7.30E-04	± 7.06E-04	.013	8.87 ± .17	.0164 ± .0006	.0551 ± .0017	.437 ± .089	.058 ± .011	328 ± 13	345 ± 10	368 ± 65	514 ± 503
2.1	CZ	4	20	175	8.99	2.99E-03	± 9.96E-04	.055	2.784 ± .088	.0169 ± .0010	.0546 ± .0024	.311 ± .133	.041 ± .017	339 ± 20	343 ± 15	275 ± 109	...
Tajno albitite, zircon:																	
5.1	CZ	33.4	715	720	1.01				.651 ± .06	.016 ± .071	.0543 ± .002	1.376 ± .12	.184 ± .013	713 ± 50	341 ± 15	879 ± 49	2686 ± 115
6.1	CZ	18.0	358	191	.54	2.43E-04	± 3.82E-05	.004	.174 ± .009	.0120 ± .0100	.0587 ± .001	.443 ± .01	.058 ± .004E-04	358 ± 5	368 ± 9	373 ± 9	404 ± 32
6.2	OR	16.0	345	301	.87	3.07E-04	± 3.47E-05	.005	.272 ± .01	.013 ± .011	.0541 ± .001	.484 ± .02	.069 ± .001	307 ± 5	340 ± 8	401 ± 11	770 ± 45
7.1	CZ	24.3	476	420	.88	1.21E-02	± 8.11E-04	.156	.318 ± .168	.011 ± .173	.0589 ± .003	.415 ± .19	.229 ± .012	312 ± 53	369 ± 17	352 ± 129	245 ± 812
7.3	OR	4.0	81	78	97	3.34E-04	± 9.22E-05	.006	.303 ± .013	.0120 ± .015	.0569 ± .001	.381 ± .02	.053 ± .004E-04	331 ± 6	357 ± 9	327 ± 12	125 ± 78
8.1	CZ	21.4	449	595	1.32	7.35E-03	± 2.37E-04	.099	.564 ± .036	.013 ± .045	.0551 ± .0020	.694 ± .07	.194 ± .005	387 ± 18	346 ± 12	535 ± 39	1453 ± 158
8.2	OR	4.9	101	84	.84	3.54E-03	± 2.65E-04	.057	.256 ± .031	.01 ± .037	.0562 ± .002	.318 ± .04	.094 ± .002	307 ± 12	353 ± 11	281 ± 31	0 ± 11
9.1	CZ	15.8	316	125	.40	2.15E-03	± 2.09E-04	.085	.124 ± .084	.012 ± .085	.0583 ± .002	.434 ± .04	.085 ± .003	328 ± 28	365 ± 10	366 ± 29	373 ± 193
10.1	CZ	31.6	693	718	1.04	4.27E-04	± 7.64E-05	.007	.343 ± .01	.009 ± .016	.053 ± .001	.433 ± .02	.065 ± .002	340 ± 7	333 ± 9	366 ± 14	578 ± 78
10.2	CZ	5.1	99	92	.93	2.95E-04	± 1.32E-04	.005	.3080 ± .049	.0140 ± .049	.0598 ± .002	.537 ± .03	.069 ± .002	364 ± 18	375 ± 9	437 ± 20	779 ± 106
10.4	OR	10.0	200	107	.54	2.01E-03	± 2.71E-04	.033	.213 ± .089	.013 ± .092	.0583 ± .0020	.505 ± .05	.092 ± .004	430 ± 39	365 ± 12	415 ± 35	705 ± 195
10.5	OR	0.9	19	5	.28	1.06E-02	± 6.36E-04	.133	.213 ± .126	.025 ± .132	.0549 ± .002	.751 ± .12	.245 ± .006	623 ± 81	344 ± 15	569 ± 69	1611 ± 266

Note. Pb* = radiogenic Pb, corrected for laboratory-derived surface common Pb using ²⁰⁷Pb. Ratios and ages are reported ± 2σ.

^a BZ = banded zoning, CZ = concentric zoning, OR = overgrowth rim, SZ = sector zoning.

^b Percentage of common ²⁰⁶Pb.

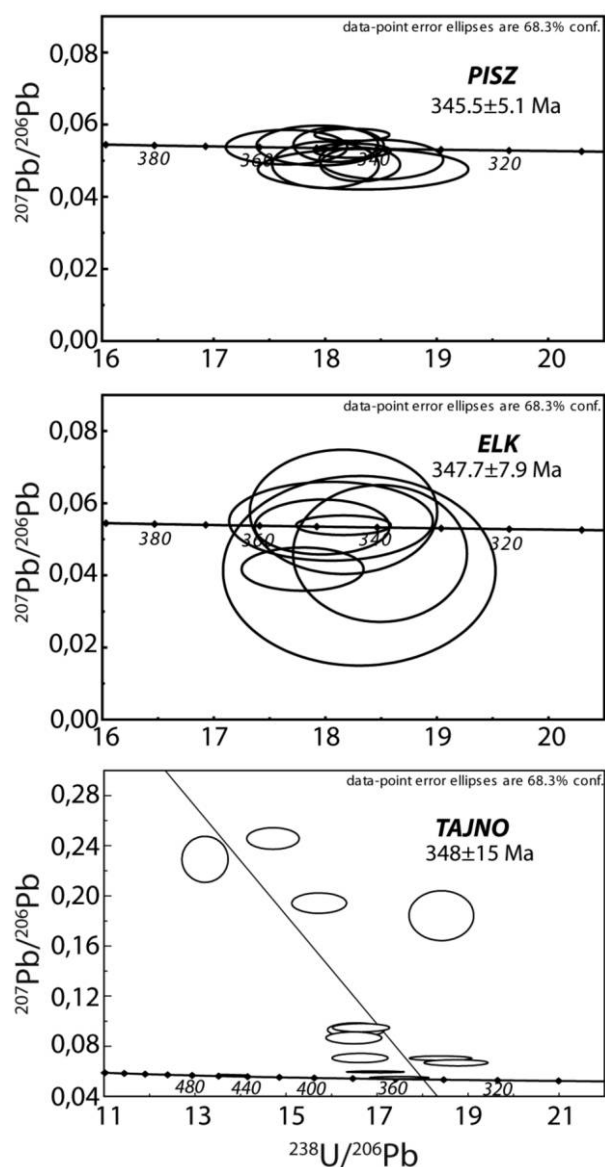


Figure 5. Tera-Wasserburg concordia diagrams showing all U-Pb geochronological data obtained for zircons: *top*, Pisz, sample 1330; *middle*, Elk, sample 816; *bottom*, Tajno, sample 10–1091.

zircon preserved igneous zoning, was transparent, and appeared to be unaltered. U contents were low to very low (179–20 ppm), but Th contents were mostly very high (1300–3550 ppm), resulting in extreme Th/U ratios (9–30), typical for zircons from syenites (Belousova et al. 2002). Common-Pb contents were also moderately high. Zircon with such high Th/U is normally not particularly suitable for precise or accurate geochronology. Nevertheless, all U-Pb analyses were concordant or nearly so within error, and all gave the same radiogenic $^{206}\text{Pb}/$

^{238}U within analytical uncertainty (0.05543 ± 0.00048), equivalent to a weighted mean age of 347.7 ± 7.9 Ma (95% confidence level). The large uncertainty reflects the low uraniumogenic Pb contents of most analyzed areas.

Tajno Massif. Six zircon grains from an albitite crosscut by thin carbonatite veins were investigated. In four of them, both the core zone with concentric zoning and the surrounding overgrowth were analyzed. The Th and U contents were quite varied: 81–715 ppm U and 78–720 ppm Th (one overgrowth zone had 19 ppm U and 5 ppm Th). All the grains had rather low Th/U ratios (from 1.04 down to 0.28). The overgrowths mostly had lower U and Th contents than the core zones (three of four grains). There was no detectable difference in age between the cores and the overgrowths. The measured $^{204}\text{Pb}/^{206}\text{Pb}$ ratios were not as low as those in the Pisz and Elk zircons, and the data points were slightly more scattered than those from Pisz and Elk. A line drawn through the 12 points (eight close to concordia and four more discordant) yielded an intercept age of 348 ± 15 Ma. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age was 354 ± 9 Ma. This age is interpreted as recording the crystallization of the carbonate melts that infiltrated the albitite or possibly its protolith.

Some zircon grains from Tajno had high measured $^{207}\text{Pb}/^{206}\text{Pb}$ dates (zircon 5.1 at 2686 Ma, zircon 8.1 at 1453 Ma, and zircon 10.5 at 1611 Ma) that are related to the presence of an old crustal component. Some albitites are indeed considered to be strongly modified (metasomatized = fenitized) country rocks that have interacted with carbonatitic melts and/or fluids (Le Bas 1987). At Tajno, the country rocks are Paleoproterozoic (1.8 Ga) metasedimentary and metaigneous rocks.

The Re-Os analyses (2σ uncertainties) were made on fine-grained pyrrhotite from a carbonatite. The Re concentration in the pyrrhotite was 17.06 ± 0.03 ppb, and total Os was 0.096 ± 0.007 ppb. Common Os was very low ($^{192}\text{Os} = 0.0056$ ppb); the $^{187}\text{Os}/^{188}\text{Os}$ ratio was 14.52 ± 0.002 . A $^{187}\text{Re}/^{188}\text{Os}$ ratio of 2466 ± 5 indicated an LLHR (low level, highly radiogenic) sample (Stein et al. 2000), and thus a direct age determination for this single occurrence of pyrrhotite was possible. Assuming an initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.2, the Re-Os age was 348 Ma. Although our analytical error, combined with the ^{187}Re decay constant, would put the uncertainty in the Re-Os age at under 0.5% (less than about 1.7 Ma), selection of the initial Os ratio for the age calculation limits the accuracy of age. We cannot know the initial Os ratio with certainty. If the initial $^{187}\text{Os}/^{188}\text{Os}$ is increased to 0.3, the age becomes

346 Ma; for a ratio of 0.5, it is 341 Ma. An initial Os ratio of 0.2 is a reasonable value for the carbonatite setting at Tajno. For highly radiogenic samples, such as this Tajno pyrrhotite, the calculated age is moderately insensitive to selection of the Os initial ratio (348–341 Ma, noted above); the extreme case for which selection of the initial Os ratio has no effect on the age is presented in the mineral molybdenite (Stein et al. 2001).

Discussion

The emplacement age of the hidden alkaline and carbonatite province in NE Poland is well constrained by new zircon U-Th-Pb ages (354–345 Ma) for three sampled intrusions (Pisz gabbro, Elk syenite, and Tajno carbonatite complex). A Re-Os model age of 348 Ma, obtained from fine-grained masses of pyrrhotite hosted in the Tajno carbonatite, is in excellent agreement with the U-Pb ages, demonstrating that pyrrhotite is capable of preserving its Re-Os age in this high-temperature carbonatite setting. These results contrast with the disturbed Re-Os data from pyrrhotite of the Homestake gold mine, hosted in mixed metavolcanic and metasedimentary rocks of the Black Hills, South Dakota (Morelli et al. 2010).

With these new geochronologic data, we document an Early Carboniferous (Tournaisian) alkaline and carbonatite province in NE Poland. The tectonic setting of this province cannot be established from fieldwork because the intrusions are known only from drilling through the thick (600–800 m) Mesozoic-Cenozoic cover of the East European Platform (EEP). On the interpretive sketch geological map drawn from geophysical data (gravity and magnetic measurements), it nevertheless appears that the three intrusions are roughly aligned along a preexisting east-west structural trend that is parallel to the east-west-trending faults and possibly to a tectonic contact between two Proterozoic basement units (fig. 2*b*).

Two large, rift-related, Mid- to Late Paleozoic magmatic provinces have been recognized in northern Europe: a Late Devonian (Frasnian-Famennian) province and a Carboniferous-Permian province. The Late Devonian province, largely developed on the EEC and the EEP (e.g., Ziegler 1988), has been related to a period of intense rifting and might be associated in part with basement uplift. Alkaline-ultramafic magmatism, locally with kimberlitic affinities, is widespread in the Barents Sea area (Ziegler 1988), the Pripyat-Dniepr-Donets (PDD) rift, and especially the Kola alkaline and carbonatite province. The PDD rift, which extends more than 2000 km from

Belarus to Ukraine (Stephenson et al. 1996; Wilson and Lyashkevitch 1996) and where rifting was accompanied by uplift of the neighboring Ukrainian shield and Voronezh massif (fig. 1) is “the largest and best documented Late Paleozoic rifted basin” (Stephenson et al. 1996, p. 71).

Recent age compilations and discussions (Kramm and Sindern 2004; Downes et al. 2005) confirm the earlier assertion of Kramm et al. (1993) that the magmatic event at Kola was of relatively short duration and that most of the intrusions there (more than 20) were emplaced between 380 and 360 Ma. The Polish alkaline province is slightly but significantly younger (by 5–20 m.yr.) than the Kola Province. Although rifting activity on the EEC-EEP appears to have decreased during the Famennian, it nevertheless continued into the Early Carboniferous, perhaps until the Late Viséan (Stephenson et al. 1993). Field evidence being impossible to obtain, we tentatively suggest that the Polish alkaline and carbonatite province was emplaced during the northwestward propagation of the PPD rift after its main Late Devonian activity (Wilson and Lyashkevitch 1996).

The Carboniferous-Permian magmatic event developed mainly within the northern foreland of the Variscan orogeny, more particularly in the region between the Caledonian and Variscan fronts (Heermans et al. 2004; Neumann et al. 2004; Timmerman 2004; Upton et al. 2004; Wilson et al. 2004). The area is related to the development of the West European Carboniferous Basin (Maynard et al. 1997), which narrows from west (>500 km in the British Isles) to east (<100 km in North Germany and Poland). Magmatic activity extended over a vast area, including SW Ireland, the British Isles, Scandinavia, the North Sea, the Baltic Sea, and North Germany. The NE Polish province is located just to the east of this magmatic trend. The activity is not uniformly distributed within this long (~100-m.yr.) time interval (Timmerman et al. 2009); several pulses have been recognized, in the British Isles and in the Oslo graben, for example. The main activity peaked during two distinct time periods, the Viséan and the Permian, when large volumes of magmas intruded the Oslo graben (~48,000 km³; Neumann et al. 2004) and the NE German basin. Although less important in volume, Tournaisian magmatism, as recorded in the studied Polish province, has been identified (see compilations in Timmerman 2004 and Wilson et al. 2004) in Ireland (e.g., Limerick volcanics: 345 Ma), in the Midland Valley of Scotland (352–342 Ma), and in a large sill sampled by drilling in the Baltic Sea (355 Ma; Monaghan and Pringle 2004).

That last occurrence is located north of the Tornquist Line, just west-northwest of the Polish province. The magmatic activity appears to be fault controlled (Upton et al. 2004; Kirstein et al. 2006). It has been related to extensional tectonics (lithospheric stretching), which induced reactivation of old lineaments in the Variscan foreland and subsequent decompression melting of the mantle. Magmatism is dominantly (but not exclusively) represented by alkaline to mildly alkaline rocks, as observed in Scotland, southern Scandinavia, the North Sea, and northern Germany (Neumann et al. 2004; Upton et al. 2004; Kirstein et al. 2006). Large composite nepheline syenite intrusions, locally associated with small gabbro intrusions, are abundant in the Oslo-Skagerrak graben (they represent rift stages 2 and 4; Neumann et al. 2004; Andersen et al. 2010). In contrast, carbonatites have not been reported yet (they are common in the Late Devonian Kola Province), but silica-undersaturated alkaline mafic magmas are known in the Carboniferous-Permian province. Basanites, foidites, and camptonites have been found in Scania dikes (South Sweden; Neumann et al. 2004; Timmerman et al. 2009), trachybasalts and tephrites have been intersected by drilling in the Lublin Trough of SE Poland (Timmerman 2004), and alkaline lamprophyres and olivine nephelinites have been reported in dikes in Scotland (Kirstein et al. 2006). Most of these alkaline magmatic rocks are characterized by the presence of halogen-rich (mainly F) volatiles; some are carbonated and less-commonly S-rich. Enrichment in F is a particular feature of most Tajno carbonatites, in which fluorite occurs as an interstitial phase and as cement in the central diatreme breccia (Ryka 1992a; Kozłowski and Wiszniewska 2006) as well as in Oslo graben nepheline syenite pegmatites, in which F enrichment is interpreted as a liquidus phase (Andersen et al. 2010).

As discussed by Neumann et al. (2004) and Kirstein et al. (2006), the primary alkaline mafic magmas from which the various Carboniferous-Permian magmatic rocks were formed were probably derived from different variable, small-degree partial melts of a mantle source that had previously been enriched either by ancient (Caledonian or Variscan) subduction or by metasomatism related to carbonatitic fluids (possibly derived from the Late Proterozoic Fen and Alnö carbonatites). In that respect, it is interesting to note that the most volatile- and F-rich intrusions (in NE Poland [Tajno] and in the Oslo graben) are located in Baltica (EEC) to the north of the Caledonian orogenic front, where the lithosphere is significantly thicker (>100 km) than that in Laurentia (<80 km in Scotland; Pascal et al.

2004). The range of radiogenic Sr and Nd isotopic compositions (see compilations and discussion in Neumann et al. 2004) indicate the involvement of both asthenospheric and lithospheric mantle-derived melts as well as crustal contamination.

Conclusions

A newly recognized alkaline and carbonatite province in NE Poland consists of several massifs that have been sampled and dated. The province, located north of the Trans-European Suture Zone, lies beneath 600–800 m of Mesozoic-Cenozoic meta-sedimentary and metavolcanic cover of the Paleoproterozoic Mazowsze Domain.

Zircons have been separated from a gabbro of the Pisz gabbro-syenite complex, from a syenite of the Ełk intrusion, and from an albitite invaded by carbonatite veins in the Tajno massif. U-Pb geochronological data on these zircons were obtained by SIMS and SHRIMP methods. Zircons from Pisz (nine grains) and from Ełk (seven grains) yielded concordant (or nearly so within errors) ages: weighted mean emplacement ages are 345.5 ± 5.1 and 347.7 ± 7.9 Ma, respectively. For Tajno, eight data points plot close to concordia and four are slightly discordant: a 12-point line provides an intercept age of 348 ± 15 Ma. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is 354 ± 9 Ma.

A pyrrhotite from a Tajno carbonatite vein was dated by the Re-Os method. Assuming an initial $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratio of 0.2, the pyrrhotite yields a Re-Os age of 348 Ma. Given the rather high analytical uncertainty for the U-Pb age for Tajno, the Re-Os result is in good agreement, even if the assumption of the Os initial ratio is somewhat higher.

These new age data document an Early Carboniferous (Tournaisian) emplacement age for the NE Poland alkaline province. This province constitutes a new occurrence, farther east, of a vast domain in which magmatic activity developed during a long-lasting period—from Early Carboniferous to Late Permian—in northern Europe, in the foreland of the Variscan orogeny, from west (Ireland and the British Isles) to east (northern Germany) through the North Sea and southern Scandinavia (Oslo and Skagerrak grabens, the Baltic Sea).

The dominantly alkaline primary magmas of the various suites are strongly enriched in volatiles (water, CO_2 , SO_3) and especially in F (e.g., in the Tajno carbonatite and the Oslo graben nepheline syenites). They were probably formed by small-degree melt of an enriched mantle source in response of a period of extension (lithosphere stretching).

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