THE MINDYAK PALAEOZOIC LHERZOLITE OPHIOLITE, SOUTHERN URALS: GEOCHEMISTRY AND GEOCHRONOLOGY

Jane H. Scarrow^{*1}, Galina N. Savelieva^{**}, Johannes Glodny^{***2}, Pilar Montero^{****}, Alexei N. Pertsev^{**}, Luciano Cortesogno***** and Laura Gaggero*****

* Dept GEOTER, University of Udine, Via Cotonificio 114, I-3100 Udine, Italy

** Geological Institute, Russian Academy of Sciences, Pyzhevski per. 7, 109017 Moscow, Russia

- *** Mineral-Geologisk Museum, Sars Gate 1, Toyen, 0562 Oslo, Norway
- **** Dept. of Mineralogy and and Petrology, Campus Fuentenueva, E-18002 Granada, Spain
- ***** Dept. of Earth Sciences, Corso Europa 26, I-16132 Genoa, Italy
- corresponding author: email jscarrow@ugr.es, present address: Department of Mineralogy and Petrology, Campus Fuente Nueva, 18002 Granada, Spain. 2
- present address: GeoForschungsZentrum, Potsdam, Telegrafenberg C2, D-14473 Germany.

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ABSTRACT

The Mindyak ophiolite, Southern Urals, preserves metamorphic garnet- and amphibole-bearing blocks, along with a diverse assemblage of ocean crust-derived clasts, in a serpentinite tectonic breccia in contact with its spinel-plagioclase/spinel lherzolite mantle and wehrlite/clinopyroxenite transition zone sequences. On the basis of petrological and geochemical data we suggest that the mantle section preserves variably depleted lherzolites generated by a two-stage process involving melting followed by magma-mantle interaction in a supra-subduction zone setting. The garnetiferous rocks are interpreted as high-temperature metamorphosed, rodingitized ocean crust gabbros that subsequently underwent later stage low-temperature retrogression. Previously determined radiometric U-Pb and Pb-Pb dates of 410-415 Ma, at the Silurian-Devonian boundary, for the peak metamorphic event affecting the metagabbros are confirmed with new Sm-Nd radiometric data. The complex, multistage evolution of the garnet metagabbros and their preservation in the Mindyak Iherzolitic ophiolite massif give insights into processes from plate divergence and ocean formation, to plate convergence and, ultimately, to preservation in the Uralian orogeny.

INTRODUCTION

Mindyak is a lherzolite ophiolite massif situated along the Main Uralian Fault (MUF), the main orogenic suture of the 2500 km-long, north to south-trending Urals chain (Fig. 1). The massif is one of a belt of ophiolites at the junction between the East European continental margin and the oceanic Magnitogorsk zone of the Southern Urals (Savelieva, 1987; Savelieva and Nesbitt, 1996). Here we report field, petrographic, and geochemical data for the main units of the massif and consider their petrogenesis. In addition, we present geochronological data for garnet metagabbros that crop out in a tectonic breccia between the mantle and transition zone sequences.

REGIONAL GEOLOGY

In the Late Cambrian to Early Ordovician the eastern edge of the East European Craton rifted and a passive margin developed (McKerrow, 1994; Puchkov, 1997; Dalziel, 1997; Smethurst et al., 1998). Then, through the Palaeozoic, an ocean formed as spreading followed after the rifting, subsequently arcs, part of one of which is preserved in the Mindyak ophiolite, and back-arc basins formed by intraoceanic convergence (Zonenshain et al., 1984; Savelieva and Nesbitt, 1996). Finally, a collision between the East European Craton, outboard terranes, and the Siberian Craton occurred in Late Carboniferous to Permian times (Matte, 1995; Otto and Bailey, 1995; Puchkov, 1997). Together with the Appalachian, Caledonian, and Variscan orogens, the Uralian orogeny contributed to the assembly of the late Palaeozoic supercontinent of Pangea (Wilson, 1966; Sengör et al., 1993).

The present-day Southern Urals comprise five main structural units, from west to east:

- 1. Pre-Uralian marginal depression: a foreland basin filled with Early Carboniferous-Early Permian molasse sediments (Kazansteva & Kamaletdinov, 1986; Brown et al., 1996).
- 2. West-Uralian folded zone: Ordovician-Carboniferous continental-margin sediments and mafic volcanic rocks.
- 3. Ural-Tau zone: Precambrian-early Palaeozoic schists and volcanic rocks of the East European Craton.
- 4. Tagil and Tagil-Magnitogorsk zone, including three sectors from north to south: i. Late Ordovician-Devonian oceanic and island arc volcanic rocks and capping sediments, ii. harzburgite-ophiolites and zoned ultramafic-mafic complexes, and iii. Ordovician oceanic crust, equivalent to i., and younger Devonian island arc volcanic rocks and mèlanges.
- 5. East-Uralian zone: Ordovician-Middle Palaeozoic volcanic and sedimentary rocks and Precambrian metamorphic rocks from the Siberian craton.

Units 1, 2, and 3 are part of the former passive margin of the East European Craton. Unit 3 is bounded to the east by the eastward-dipping MUF suture, which contains lherzolitic ophiolite massifs (Savelieva, 1987, Pertsev et al., 1997) and serpentinitic mèlanges (Gaggero et al., 1997). Unit 4 comprises allochthonous oceanic material and Unit 5 represents Siberian Craton continental crust.

GEOLOGIC SETTING: MINDYAK OPHIOLITE MASSIF

Like other southern Uralian ophiolite massifs, e.g., Nu-

rali and Kraka (Fig. 1), Mindyak has a predominantly spinel-lherzolite and plagioclase/spinel-lherzolite mantle section. The peridotite body is 20 km long by 8 km wide, internally thrust, east-dipping, and is overthrust onto Upper Riphean schists of the East European craton. The peridotite massif is bounded at its eastern and western margins by serpentinite tectonic mèlanges. In the lower, western, part of the massif, considered in this study, the lherzolite becomes more depleted upwards and grades into a wehrlite-pyroxenite-dunite transition zone. The serpentinite tectonic breccia in contact with the mantle and transition zone sequences at the lower western margin of the massif contains a diverse assemblage of ocean crust-derived clasts and the metamorphic garnet-bearing blocks considered in detail here.

PETROGRAPHY

Peridotites

The mantle rocks adjacent to the garnet metagabbrobearing tectonic breccia are medium- to coarse-grained, in places porphyroclastic, depleted spinel and plagioclase lherzolites. These lherzolites are banded and foliated and in some there is a lineation defined by preferred orientation of elongate blebs composed of turbid clay minerals and clinozoisite after plagioclase. The main minerals are diopside (>5%) and enstatite (Fig. 2a), predominantly serpentinized olivine (dominant) (Fig 2b), subordinate turbid clay minerals and clinozoisite after plagioclase and/or spinel (Fig. 2c). All the samples are extensively serpentinized, 45–90 modal % which negates the possibility of determining precisely the relative mineral proportions.

Banded, olivine-bearing wehrlites and clinopyroxenites have magmatic cumulus textures, and contain fresh, coarse, subhedral clinopyroxene, recrystallized diopside, and smaller anhedral olivine. These wehrlites and clinopyroxenites presumably represent a former mantle-crust transition zone. Serpentine partially replaces olivine, and intergranular, secondary magnetite is present along with rare, thin veins of chlorite and actinolite.

Garnet metagabbros

The metamorphic garnetiferous blocks are quite heterogeneous and medium- to coarse-grained (<0.2-9 mm, but generally 1–2 mm). They consist of varying proportions of garnet, diopside, amphibole, rutile, ilmenite, apatite, titanite, and zircon. The amount of accessory minerals and Fe/Mg of the garnet metagabbros allow us to distinguish two petrographic types, 1 and 2, which represent different protolith compositions. Both types show evidence of late-stage low-T rodingitization where they are in contact with their host serpentinite breccia.

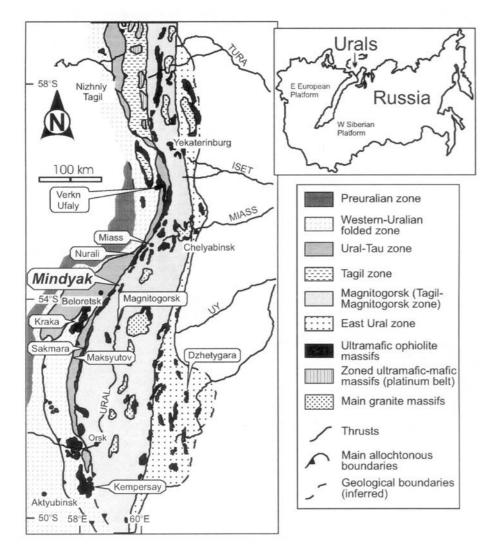


Fig. 1 - Geological map of the Urals showing the location of the Mindyak ophiolite massif.

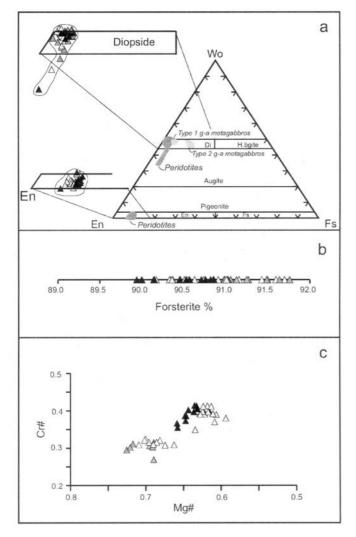


Fig. 2 - Representative mineral analyses from Mindyak Iherzolites. **a**. pyroxenes: *dark grey triangles* SU505, *black triangles* SU505-1, *white triangles* SU505-2, *light grey triangles* SU505-3, *g-a metagabbros* garnet amphibole metagabbros, *Di* diopside, *Hbgite* hedenbergite, *En* enstatite, *Fs* ferrosilite, *Wo* wollastonite. **b**. olivines, symbols as in a. **c**. spinels, symbols as in a.

Type 1 has a massive texture and comprises predominantly grossular-rich garnet (Py₃₈₋₄₀Alm₂₅₋₂₆Grs₂₉₋₃₄), tschermakite-pargasite, diopside (Fig. 2a), zoisite-clinozoisite, and scarce accessory minerals such as apatite. The peak equilibrium metamorphic assemblage is represented by the garnet and its inclusions (diopside, tschermakite-pargasite, and zoisite). At a later time the peak assemblage retrogressed to an assemblage of clinozoisite and hornblende. Following retrogression, the rocks were affected by late-stage alteration with chlorite replacing hornblende and clinozoisite replacing garnet. Clinozoisite/chlorite/prehnite-infilled cracks cutting across all other minerals give evidence for late-stage brittle deformation.

Type 2 is weakly foliated and contains more Fe-rich garnet (Py43-53Alm₁₅₋₂₁Grs26-33) and diopside (Fig. 2a) than Type 1 as well as pargasite, zoisite-clinozoisite, and up to 6 modal % accessory minerals including rutile, titanite, apatite, and zircon. The peak metamorphic assemblage is represented by garnet, diopside, tschermakitic amphibole, zoisite, titanite, rutile, ilmenite, apatite, zircon, and phlogopite. Diopside and tschermakite subsequently retrogressed to green, zoned hornblende, and chlorite, respectively. After retrogression, the rocks were partially altered to epidote- and secondary chlorite-bearing assemblages. Finally, actinolite- and chlorite-filled microfractures record late stage brittle deformation.

GEOCHEMISTRY

Selected, representative major and trace element variations of the peridotites, garnet metagabbros, and an olivine clinopyroxenite are presented in Figs. 3 and 4.

Peridotites

The Mindyak peridotites have some major and trace element compositional similarities to lherzolites from other Uralian ophiolites, e.g., Kraka and Nurali (Savelieva, 1987; Savelieva et al. 1997) and typical lherzolite of Maaløe and Aoki (1977). In detail, however, some of the Mindyak lherzolites have higher SiO₂, MgO, Al₂O₃, and CaO, and lower Na₂O than the Uralian and typical lherzolites (Fig. 3a). The peridotites show clear negative correlations between MgO and all the incompatible trace elements, whereas Ni correlates positively. These features and the absence of trends in the major and trace element plots versus Mg# is attributed to variable olivine/pyroxene proportions.

In the most depleted Mindyak peridotites analysed for REE, the REE concentrations are lower than in chondrites, LREE 0.09-0.3 times chondritic and HREE 0.2-0.4 times chondritic, as is typical of alpine-type peridotites (Loubet and Allègre, 1982). The LREE/HREE ratios of ~ 1 are not typical, however, of alpine-type peridotites. This is discussed in more detail below.

Garnet metagabbros

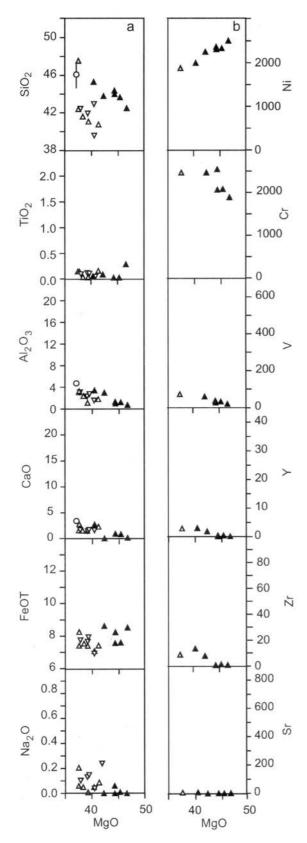
The garnetiferous rocks have lower SiO₂, alkalis and Al₂O₃ and higher CaO and Fe₂O₃ than typical mafic melt compositions (Fig. 4a), which is reflected in the high modal abundance of Ca-rich garnet. Furthermore, when dry magmatic norms are calculated, extra, non-magmatic components (hematite, wollastonite, monticellite) are present.

Type 1 garnet metagabbros have high MgO, slightly LREE-depleted to flat chondrite-normalised REE patterns (Lan/YbN of 0.3-1.3), positive Eu anomalies (Eu/Eu* = 1.33-1.51) (Fig. 5a), and LILE enrichments. In contrast, Type 2 garnet metagabbros have lower MgO, higher LREE/HREE (Lan/YbN of 2-5.5) (Fig. 5a), and LILE depletions. Both types have low 87 Sr/ 86 Srⁱ of 0.7040–0.7044 and high eNdⁱ 5.0–7.5 (authors' unpublished data) indicating derivation from a depleted source.

The analysed transition-zone olivine pyroxenite has some major (CaO, TiO₂, P₂O₅, and K₂O) and trace (Ni, Y, and Zr) element contents similar to the Type 1 garnet metagabbros (Fig. 4), but there are significant compositional differences at comparable MgO, i.e., the former has higher SiO₂ and lower Al₂O₃ and Sr.

GEOCHRONOLOGY

Sm-Nd data from the Type 2 garnet metagabbros (samples SU339 and SU424) measured on garnet at Mineral-Geologisk Museum Oslo, Norway are presented in Table 1. Details of analytical techniques are given in the Appendix.



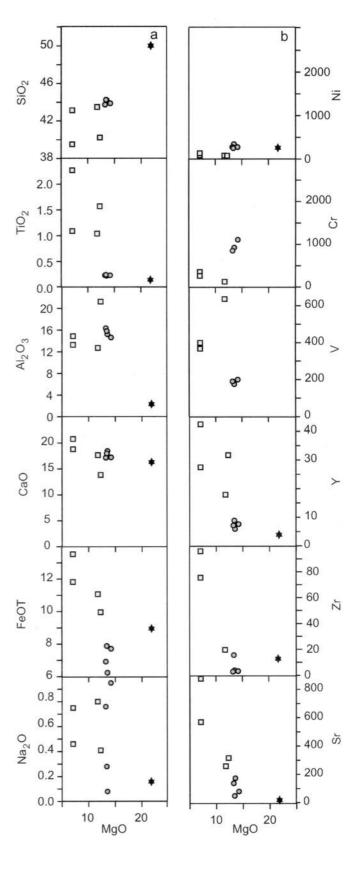


Fig. 3 - MgO versus selected major and trace elements of the Mindyak lherzolites. Symbols:

filled triangle peridotites, *grey triangle* most fertile Mindyak lherzolite SU335, *hollow triangles* Kraka Massif spinel and plagioclase mantle lherzolites, *hollow inverted triangles* Nurali Massif spinel and plagioclase mantle lherzolites, *crosses* Primitive mantle of Hart and Zindler (1986).

Fig. 4 - MgO versus selected major and trace elements of the Mindyak garnet metagabbros and a transition zone olivine pyroxenite. *circles* Type 1 garnet metagabbros, *squares* Type 2 garnet metagabbros, *star* transition zone olivine pyroxenite.

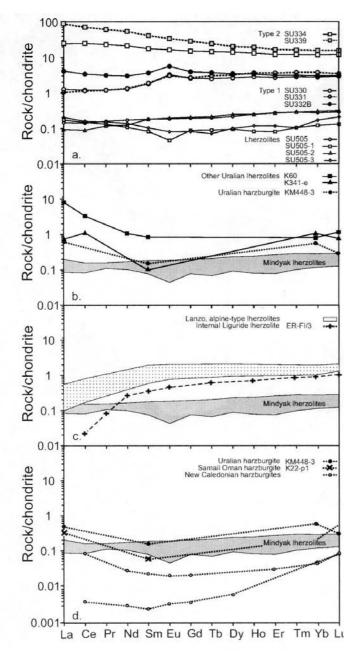


Fig. 5 - Chondrite normalised rare earth element diagram. **a**. Mindyak garnet metagabbros and peridotites. **b**. Uralian peridotites (data from Savelieva et al., 1997). **c**. Typical alpine-type lherzolites (data from McDonough and Frey, 1989 and references therein; Rampone et al., 1996). **d**. Uralian and ophiolitic harzburgites (data from Pallister and Knight 1981; Prinzhofer and Allègre, 1985; Savelieva et al., 1997). Normalization factors are those of Nakamura (1974).

A whole rock analysis for SU339, performed at Granada (see Appendix), and two garnet analyses, one from SU339 and the other from SU424, form a common isochron, with an age of 414 ± 4 Ma (Fig. 6).

Previous U-Pb dating of zircon populations carried out on a Type 2 garnet metagabbro at the Vernadsky Institute of Geochemistry in Moscow gave nearly concordant U-Pb ages of 410 ± 5 which is interpreted as the age of zircon growth (Saveliev et al., in press). Furthermore, radiometric Pb-Pb single zircon dating using the Kober method (Kober, 1986) was undertaken at the University of Granada, Spain. Zoned and unzoned zircons separated from two Type 2 samples were analysed. The preliminary data allowed calculation of a mean rim age of 411 ± 4 Ma and an older Pb com-

Table 1 - Sm-Nd analytical data.

Sample			Sm (ppm)	Nd (ppm)	$^{147}\mathrm{Sm}/^{144}\mathrm{Nd}$	143 _{Nd} /144 _{Nd}
SU339, whole rock			9.40	37.96	0.1497	0.51277
SU339, garnet			2.1442	0.8419	1.5527	0.516578
SU424, garnet			2.0676	1.1883	1.0603	0.515245
¹⁴³ Nd/ ¹⁴⁴ Nd	0.518- 0.517- 0.516- 0.515- 0.514- 0.513- 0.512-	Mindya garnet :	es SU339, SL k massif, So amphibole py 1339 WR	414 A14 A14	SU424 garn 4 +/- 4 Ma (MSWD 0.51236 +/- 0.000 silon Nd(414)+5.1	<1) 001
	(0.2	2 0.4 (0.6 0.8 ¹⁴⁷ Sm/		.4 1.6 1.8

Fig. 6 - Sm/Nd whole rock-garnet isochron from Type 2 samples SU339 and SU424. See text for details.

ponent, from inherited cores, provided a minimum age of 467 Ma (P. Montero, pers. comm. 1999).

DISCUSSION

Petrogenesis of the peridotites

The peridotites form the major part of the ophiolite body in which the garnet metagabbro-bearing tectonic breccia crops out. For this reason, their petrogenesis, geodynamic significance, and possible primary relations with the protoliths of the garnet metagabbros are considered.

The linear trends defined in the major and trace element plots (Fig. 3) of the peridotites are indicative of an extraction line resulting from increasing degree of partial melting of a homogeneous source. A suitable source is perhaps represented by the most fertile peridotite SU335 which has a composition similar to the primitive upper mantle of Hart and Zindler (1986) (Fig 3a). In contrast, the mineral chemistry data (Fig. 2) for the more depleted lherzolites do not corroborate this simple interpretation. For example, the Fo content of the olivines, 90-91.5%, are rather high, and Al²O³ of orthopyroxene, <3%, rather low for lherzolites associated with a mid-ocean-ridge environment for all but the most mature North Atlantic-type ocean basins (Bonatti and Michael, 1989). In contrast, such values are typical for supra-subduction zone peridotites (Bonatti and Michael, 1989), but these are more typically harzburgites or dunites (Parkinson and Pearce, 1998 and references therein). In fact, high olivine Fo in pyroxene-rich peridotites has been interpreted as evidence of a two-stage genetic model (Kelemen et al., 1992; Kelemen et al., 1998) for cratonic peridotite xenoliths and lherzolitic ophiolite massifs in which harzburgitic compositions may be produced by clinopyroxene dissolution and consequent orthopyroxene and olivine precipitation when basaltic melts interact with lherzolitic material. Kelemen et al. (1992) did not, however, consider this model to be generally applicable for abyssal peridotites which they considered to be, most commonly, partial melt residues.

The suggestion, from the mineral chemistry, that the Mindyak peridotites are not simply lherzolitic residues of a low degree partial melting event is also supported by some trace element features, e.g., low levels of REE without LREE-depletion (Fig. 5a), and the lack of correlation between Al₂O₃ and Yb (not shown). In contrast, other Uralian lherzolites are less depleted particularly in LREE (Fig. 5b). Furthermore, typical abyssal and ophiolitic lherzolites, interpreted to be partial melt residues (e.g., McDonough and Frey, 1989; Rampone et al., 1996) show characteristic, marked LREE-depletion (Fig 5c). So, assuming that REE have not been significantly modified by serpentinization, the compositional features of the Mindyak lherzolites (Figs 2, 3, and 5) are not consistent with them being simply residues of variable degrees of partial melting. In detail, their mildly Ushaped patterns (Fig. 5) are characteristic of peridotites, typically harzburgites, that have had a two-stage history involving post-melt-extraction melt/fluid-rock reaction (Menzies et al., 1987; Navon and Stolper, 1987; Vasseur et al., 1991; Kelemen et al., 1992; Kelemen et al., 1998; Gruau et al., 1998).

Kelemen et al., (1992) concluded that the magma-mantle interactions they invoked to produce pyroxene-rich peridotites without LREE-depletions, may occur beneath oceanic spreading centres, but that in such a setting the geochemical effects of the process would be masked by the increasing magma mass resulting from rapid decompression of the entire system. In contrast, they noted that the compositional effects of magma-mantle interaction would be enhanced in the cold lithosphere beneath cratons. Subduction-related magmatic arcs were suggested as a scenario intermediate between the two above extremes. Compared with the subcratonic environment this setting has a lower average pressure of interaction, a smaller solid/liquid ratio, less modified mantle compositions, and more liquid products. The preponderance of evidence for magma-mantle interaction in ophiolitic lherzolites as opposed to abyssal lherzolites (Kelemen et al., 1992) probably reflects the observation that ophiolites usually preserve arc-related rather than mid-ocean ridge lithosphere. In agreement with this, we suggest that the harzburgitic mineral chemistry and trace element affinities of the Mindyak peridotites, coupled with their lherzolitic mineralogy, likely result from a two-stage process involving an initial melting phase, possibly in an ocean ridge environment, and a subsequent melt-peridotite interaction indicative of a supra-subduction setting. This is consistent with the environment of preservation of the ophiolite at the western margin of the Magnitogorsk arc adjacent to the East European Craton (Fig. 1).

Petrogenesis of the garnet metagabbros

From the field and compositional data presented above we suggest that the garnet metagabbros, now cropping out in the tectonic breccia in the Mindyak ophiolite massif, are metamorphosed, metasomatised ocean crust gabbros that, based on their geochemistry, are not cogenetic with the cumulate rocks in the transition zone of the Mindyak ophiolite. We attribute the major and LIL element compositional differences between the metagabbros and common mafic melts to rodingitization, i.e., low-T metasomatism related to serpentinization of the host peridotite in an oceanic environment that resulted in addition of Ca and removal of Si, Na, and K (c.f. Coleman, 1977). In contrast, in agreement with the findings of previous workers (e.g., Sun and Nesbitt, 1978; Dubinska, 1997), the immobile trace element abundances and ratios in the garnet metagabbros are apparently unaffected by the rodingitization and are typical of depleted and enriched mafic igneous rocks (Fig. 5a).

LREE-depleted to flat REE patterns, with positive Eu anomalies (Eu/Eu* = 1.33-1.51) in Type 1 are consistent with a plagioclase cumulate protolith that crystallised from a mantle-derived melt. Moreover, the LREE-enriched patterns of Type 2 may reflect protoliths that were melts derived from a similar source and crystallised from residual liquids after cumulate formation (c.f., Kelemen et al., 1997). The protoliths were rodingitized (reducing SiO₂ and alkalis and increasing CaO and FeO) and then metamorphosed, possibly during subduction of ocean lithosphere in the Devonian Magnitogorsk arc, thus giving the observed Ca-rich metamorphic mineral assemblage. No exact metamorphic pressure and temperature conditions are available because the mineral assemblages present do not exactly match any published geothermometer or geobarometer. Nevertheless, Cortesogno et al. (1998) estimated conditions of 800°C to 900°C and pressures in excess of 1 GPa from some of the mineral phases present.

The ages obtained for the metagabbros record tectonic processes prior to the main Uralian Carboniferous-Permian orogenic event (c.f. Puchkov, 1997). We tentatively suggest that the older core age of 467 Ma might be a zircon crystallisation age of the oceanic gabbro protolith. The 410-415 Ma age at the Silurian-Devonian boundary, determined by the U-Pb population zircon, Pb-Pb single zircon rim, and Sm-Nd garnet-whole rock methods, gives an age for the subduction related metamorphic event affecting the gabbros. The whole-rock and mineral Sm-Nd analyses for Type 2 samples SU339 and SU424 all fall on a common isochron (Fig. 6), which means that they probably have a common origin. In any case, it seems that their Nd isotopic characteristics were derived from the same source at the same time; they could, perhaps, be lithological variations of the same block. It is noteworthy that the whole rock Sm/Nd data on other Type 2 and Type 1 garnetiferous blocks do not fall on this same isochron suggesting more than one or a heterogeneous source.

Other Uralian events were happening, to the south of Mindyak, at the same time as dates obtained for the metagabbros. Considering the older, 467 Ma, zircon core event, oceanic magmatism, some of which has been interpreted as being associated with ocean opening, was occurring at this time in Kraka, Kempersay, and Sakmara (Fig 1) (Savelieva and Nesbitt, 1996; Knipper and Perfiliev, 1979; Saveliev and Savelieva, 1991; Puchkov, 1993; Savelieva et al., 1997). Compared with the ~410 Ma metamorphic event that affected the metagabbros, similar, but somewhat younger ages were obtained for Emsian age boninites (~390 Ma) from the Western Magnitogorsk Zone associated with initiation of subduction (Spadea et al., 1998). It is possible that subduction was diachronous in the Southern Urals. Alternatively, the ~410 Ma age for Mindyak garnet metagabbros could record a different, previous, aborted subduction event. Finally, the 375 Ma to 390 Ma high-P/low-T metamorphism which is recorded by the Maksyutov complex (Fig. 1) associated with the thinned leading edge of the East European Craton entering the Magnitogorsk subduction zone (Shatsky et al., 1997; Matte et al., 1993; Hetzel, 1999) post-dates the metamorphism of the Mindyak garnet metagabbros. Post-metamorphic exhumation of the metagabbros during the Uralian orogeny is evidenced by reequilibration to amphibolite and greenschist facies. So, in summary, the garnet amphibole metagabbros record a change from Middle Ordovician plate divergence and ocean formation to Early Devonian plate convergence and, ultimately, to the Carboniferous-Permian Uralian orogeny.

SUMMARY

- 1. Metamorphic garnet and amphibole bearing blocks are preserved in a serpentinite tectonic breccia at the contact between the lherzolite mantle and transition zone sequences of Mindyak ophiolite, Southern Urals.
- The Mindyak ophiolite preserves supra-subduction lherzolitic mantle generated by partial melting followed by magma-mantle interaction.
- 3. Type 1 and 2 garnet metagabbros represent metasomatised and rodingitized oceanic crust subsequently metamorphosed in an early stage of subduction.
- 4. A variously determined (U-Pb, Pb-Pb, Sm-Nd) age of 410-415 Ma, at the Silurian-Devonian boundary, gives an age for the peak metamorphic event affecting the ocean crust protoliths of the metagabbros and records pre-collisional tectonic processes, associated with oceanic subduction, that are older than the main Uralian Carboniferous-Permian orogenic event.

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APPENDIX ANALYTICAL TECHNIQUES

Quantitative electron microprobe analyses of mineral phases were made on a WDS Camebax SX50 Cameca equipment (at Padua University) and on a SE-EDS microprobe equipped with an X-ray dispersive analyser, EDAX PV 9100, (at Genoa University). Operating conditions for both machines were 15 kV accelerating voltage, 2.2 nA beam currents. Synthetic and natural standards were used.

Sm-Nd dating of the garnet metagabbros was undertaken at Mineral-Geologisk Museum, Oslo, Norway. Minerals were obtained from fist-size samples using standard mineral separation techniques (magnetic separation, heavy liquids) and purified carefully by hand-picking prior to analysis. The mineral samples (approx. 150 mg for garnet) were spiked with a mixed ¹⁴⁹Sm-¹⁵⁰Nd spike before being digested in a mixture of HF and HNO₃ using screw-top Savillex Teflon

beakers. After evaporation, the samples were dissolved in 6N HCl, evaporated to dryness and redissolved in 2.5N HCl for cation exchange chromatography. The REE were separated as a group using a 5 ml BioRad AG50W-X8 exchange resin bed. Sm and Nd were separated on 5 ml HDEHP-PTFE columns. For analysis, Sm and Nd were loaded separately on Re double filaments and run as metals on a Finnigan MAT 262 TIMS instrument (University of Oslo). Sm was analysed in static multicollector, and Nd in dynamic multicollector mode. All Nd isotope ratios were normalised to ${}^{146}Nd/{}^{144}Nd = 0.7219$. The total procedural blanks for Nd and Sm were in the range of 100 pg, a negligible amount compared to the amount of Nd obtained from the mineral separates. For isochron calculation, the uncertainty for the Sm/Nd ratio was taken to be \pm 1%. For Nd isotopic composition, the internal precision of the individual analyses was used. The error on the age is reported as 2s.