

Protolith Signatures and Element Mobility of the Maksyutov Complex Subducted Slab, Southern Ural Mountains, Russia

RACHEL J. BEANE¹

Department of Geology, Bowdoin College, Brunswick, Maine 04011

AND SORENA S. SORESENSEN

Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, P.O. Box 37012, Washington, District of Columbia 20013-7012

Abstract

Geochemical data from the Maksyutov Complex in the southern Ural Mountains provide evidence for the nature of the protoliths of eclogite boudins and sedimentary gneiss from the ultra-high-pressure metamorphosed (UHPM) subducted slab, and for an evaluation of fluid-mediated mass transfer in the Devonian to Carboniferous subduction zone. Eclogites have major- and trace-element compositions of tholeiitic basalts with enriched mid-ocean ridge basalt (E-MORB) characteristics, whereas sedimentary gneiss resembles continent-derived shales. The geochemical data combined with field relations and Proterozoic protolith ages suggest the eclogite boudins formed as dikes or sills of basalt in sedimentary continental material of the East European platform during the initial opening of the paleo-Uralian ocean. Portions of the mafic boudins show large-ion lithophile-element (LILE) and light-rare-earth element (LREE) enrichment. Fluid transport of the LILE and LREE in the subduction zone seems to have been channelized (or otherwise spatially organized) on a scale of meters, rather than resulting from pervasive fluid flow. The metasomatizing fluids were most likely dehydration fluids produced during prograde metamorphism of sediments or K-altered basalts that were preserved through peak metamorphism and may have transported additional elements during retrograde metasomatism.

Introduction

ALTHOUGH FLUID-rock interactions in subduction zones are thought to influence the chemistry of volcanic-arc lavas, including primitive island-arc basalts (e.g., Tatsumi and Eggins, 1995), the nature of this influence has been long discussed. A principal line of evidence for fluid-rock interactions is that volcanic rocks from arcs typically display enrichments of large-ion lithophile elements (LILE, e.g., Ba, K, Rb, Cs, Sr) and light-rare-earth elements (LREE), and depletions of high-field strength elements (HFSE; e.g., Nb, Ta, Ti, Th, Hf, and Zr) relative to mid-ocean ridge basalts (MORB); given the depth constraints upon partial melting of basalt, it is difficult to call upon slab melting alone to produce these effects. The principal components of arc volcanic rocks appear to be a depleted mantle wedge (Woodhead et al., 1993), subducted sediment (Plank and Langmuir, 1993) and altered oceanic basalt (Elliott and Plank, 1997). A possible influ-

ence of subducted continental crust (Davidson, 1987) and the processes (relative amounts of fluid-versus melt-metasomatism) and the timing of element mobilization continue to be debated (e.g., Breeding, 2004). Most of these results have depended upon studies of the chemistry of arc volcanic rocks.

To understand fluid-rock interactions in subduction zones, one can also examine the geochemistry of metamorphosed and metasomatized mafic and sedimentary rocks from subduction-zone metamorphic terranes. Subduction-influenced element mobility that has been identified by such studies include: (1) the migration of REE and HFSE on the scale of decimeters to meters (Sorensen, 1989, 1991; Sorensen and Grossman, 1993); (2) the formation of aluminous enclaves within metamorphosed ultramafic mélange rocks through the removal of volatiles from metasedimentary rocks (Bebout and Barton, 1993); (3) K-metasomatism of mafic rocks (Beane and Liou, 1995; Sorensen et al., 1997); (4) the extraction of LILE, U, and Pb from metasedimentary units (Breeding et al., 2004); (5) Cs, Rb,

¹Corresponding author; email: rbeane@bowdoin.edu

and Ba fluid infiltration at 2.0 GPa (Zack et al., 2001); and (6) the formation of high-pressure veins that are enriched in Cs, Rb, Ba, Pb, and K during dehydration of eclogites (Becker et al., 1999).

An exhumed subduction complex with what is interpreted to be its overlying volcanic arc, both exposed in the southern Ural Mountains, is a setting in which to examine both fluid-rock interactions in a subduction complex and the composition of coeval arc magmas. Deeply subducted crust of the Eastern European craton (the Maksyutov Complex), and the forearc and arc volcanic rocks of the Magnitogorsk zone are exposed in this region. Overall, this setting resembles present-day continent-arc collisions along the northern margins of Australia (Brown and Spadea, 1999). Eclogite and paragneiss of the Maksyutov Complex underwent ultrahigh-pressure (UHP) metamorphism at 2.6–3.2 GPa, 650°C (Bostick et al., 2003). In this paper, we show that the bulk-rock geochemistry of metamorphosed mafic and sedimentary rocks from the deeply subducted slab allows the tentative assignment of protoliths, an evaluation of fluid-mediated mass transfer in the paleosubduction zone, and an evaluation of this mass transfer's impact on the overlying arc volcanic rocks.

Geological Setting

The Main Uralian fault (MUF) is the major arc-continent suture of the Paleozoic Uralide orogen, extending 2500 km along the axis of the approximately 400 km-wide orogen (Fig. 1; Zonenshain et al., 1984, 1990). The URSEIS project reflection seismic profile shows that the east-dipping MUF separates the East European platform on the west from the accreted Siberian-Kazakhian terrane assemblage to the east (Fig. 1B; Brown et al., 1998; Hetzel and Romer, 2000; Hamilton, 1970). The footwall beneath the Main Uralian fault in the south Uralide orogen consists of a generally west-vergent thrust stack (Brown et al., 1998; Brown and Spadea, 1999). The Maksyutov Complex, formed during Late Devonian to Early Carboniferous eastward subduction of the East European continental margin, resides in the upper part of this thrust stack (Brown et al., 1998; Beane and Connelly, 2000). The Maksyutov Complex is bounded on its western margin by the Yantyshevo-Yuluk fault that backthrusts greenschist-facies Silurian to Middle Devonian metasediments of the Suvanyak Complex eastward over the Maksyutov Complex (Brown et al., 1998; Chibrikova and Olli, 1994). To the east of the Maksyutov Complex, the

Magnitogorsk island arc is in the hanging wall of the Main Uralian fault (Zonenshain et al., 1984; Hetzel et al., 1998). The basement of the Magnitogorsk island arc complex is ophiolites, overlain by Lower to mid-Devonian island-arc volcanic rocks, and topped by Middle to Upper Devonian forearc basin sediments (Zonenshain et al., 1984; Savelieva and Nesbitt, 1996). East of the Magnitogorsk island-arc complex are the Vendian–Ordovician Mugodzhar and Ilmen microcontinents intruded by Late Carboniferous–Permian granitic plutons (Zonenshain et al., 1990; Bea et al., 2002).

Maksyutov Complex

The Maksyutov Complex is exposed in a 15–20 km wide, 150 km long belt with a structural thickness of 5–10 km (Beane et al., 1995; Lennykh et al., 1995; Dobretsov, 1974; Hetzel et al., 1998; Leech and Willingshofer, 2004). The Maksyutov Complex is subdivided into three lithostratigraphic units (names as first designated in Krinizky and Krinizkaya, 1961). From bottom to top these units are the Kairakli, Yumaguzino, and Karamola (Fig. 1C).

Kairakli unit. The Kairakli unit consists of blocks and boudins of mafic eclogite, talc-enstatite, olivine-enstatite, and jadeite-quartzite in a matrix of metasedimentary rocks (Fig. 2A; Dobretsov et al., 1974, 1996; Beane et al., 1995; Hetzel et al., 1998). The metasedimentary rocks occur as intensely deformed schist and gneiss, including metapelite, metagraywacke, and graphitic quartzite (Fig. 2A; Dobretsov et al., 1996; Hetzel et al., 1998; Leech and Ernst, 1998; Alekseev, 2000). Three stages of metamorphism are observed in mafic eclogite samples: M_1 (eclogite facies) garnet + omphacite + phengite + quartz + rutile; M_2 (blueschist facies) garnet + glaucophane $\pm$ lawsonite $\pm$ titanite; and M_3 (greenschist facies) epidote + chlorite $\pm$ albite $\pm$ actinolite (Fig. 3; Beane et al., 1995; Lennykh et al., 1995; Hetzel, 1999; Schulte and Blümel, 1999). Some eclogite boudins show little or no evidence of retrograde metamorphism; others are partially or completely retrograded (Fig. 2B). In this unit, field evidence for fluid-rock interaction and possible metasomatism includes the presence of garnet-rich veins (Fig. 2B), 1 to 2 m thick zones of muscovitized eclogite (Dobretsov et al., 1996), and a dm thick coarse white mica-filled fracture (east bank of Sakmara River, near the former village of Karyanova). Other petrographic evidence for fluid-rock interaction consists of “fishnet” (term from Spry, 1969) and atoll textured garnets (Figs. 4A and 4B) that may

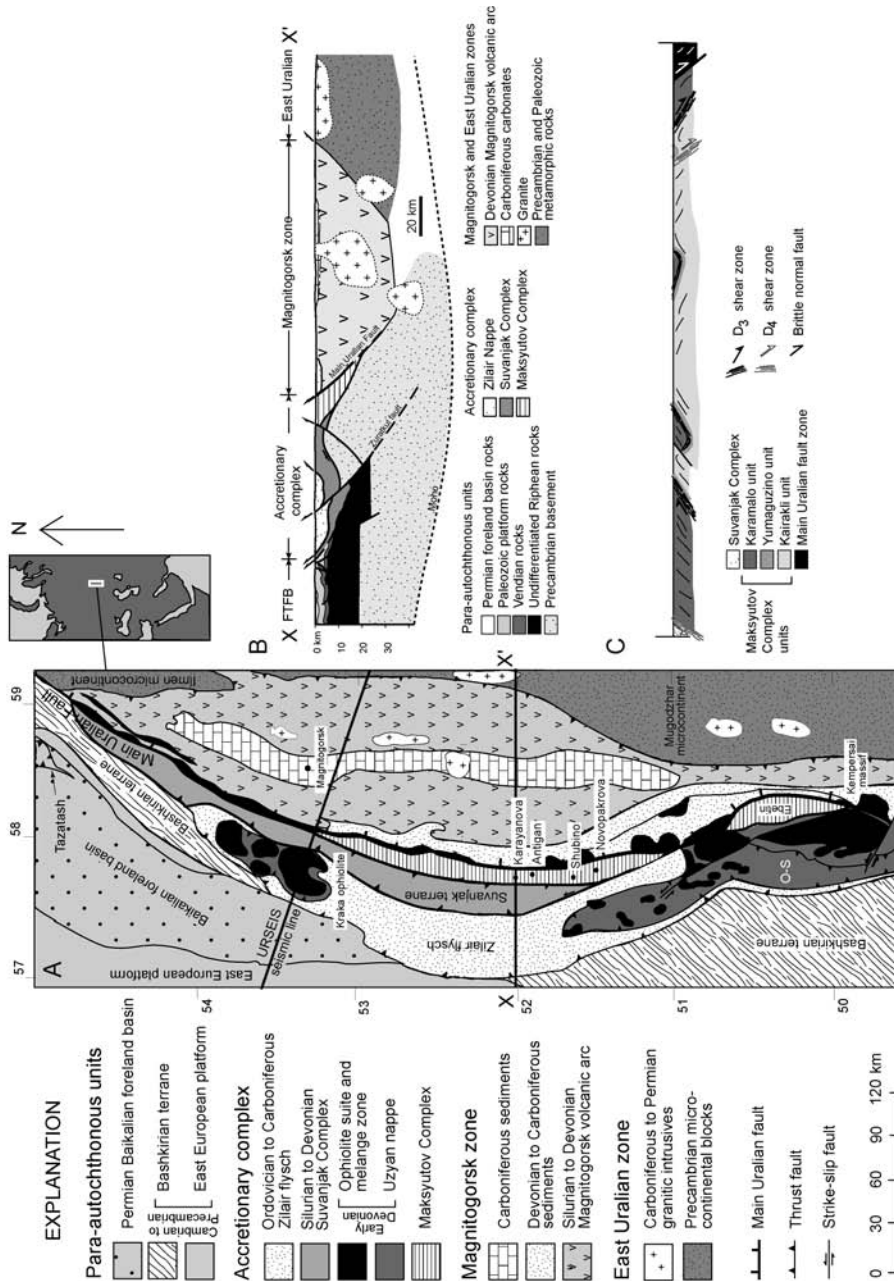


FIG. 1. A. Tectonostratigraphic map of the south Ural Mountains (after Leech and Stockli, 2000; Beane and Leech, 2007) with sampling areas that are mentioned in the text and tables. B. Crustal-scale cross-section X-X' through the south Urals based on Brown et al. (1998). C. E-W cross-section of the Maksyutov Complex at Antigan (modified after Hetzel et al., 1998) showing the structural relationship between the different units.

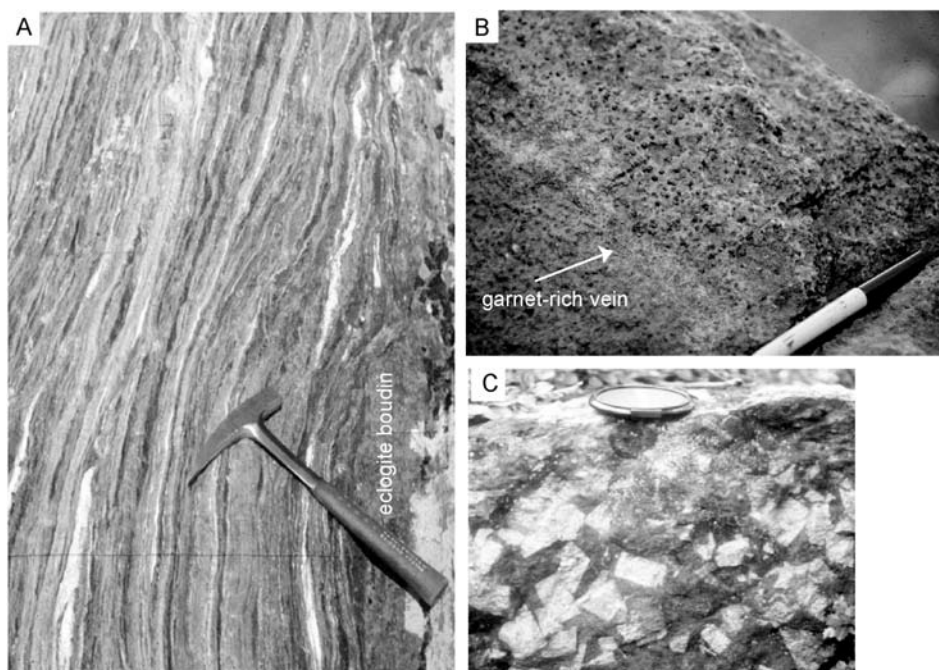


FIG. 2. Photographs showing key field relations. A. Banded gneiss of the Kairakli unit, showing quartz-rich and mica-rich metasedimentary rocks with eclogite boudin. B. Eclogite of Kairakli unit partially retrograded to blueschist facies, and with a pale garnet-rich vein. C. Metasomatized mafic rock of the Karamola unit with large, white pseudomorphs after lawsonite.

reflect the presence of fluid at high-pressure conditions (Hawkins et al., 2005); these textures typically are observed in garnet-bearing metasedimentary rocks or in mica-rich eclogites (Table 1). The presence of late-stage fluids is evidenced by veins of chlorite and the partial retrogression of some garnet to chlorite (4C).

Mineral compositions for this unit have been previously reported in Beane et al., 1995; Dobretsov et al., 1996; Glodny et al., 2002; Hetzel, 1999; and Leech and Ernst, 1998. In eclogite boudins, garnet is almandine rich (Alm_{54-63} , Prp_{7-29} , Grs_{8-29} , Sps_{1-4}), clinopyroxene is omphacitic in composition (Jd_{39-55}), and white mica is present typically as phengite ($\text{Si}_{3.3-3.6}$) and rarely as paragonite. In blueschist, epidote displays Ps_{3-29} and amphibole compositions are glaucophane and barroisite. In metasedimentary rocks, garnet grains display lower almandine components (Alm_{36-41} , Prp_{27-33} , Grs_{14-20} , Sps_{13-17}) than those from eclogites, and white mica again occurs either as phengite ($\text{Si}_{3.3-3.5}$) or rarely, paragonite.

Bostick et al. (2003) calculated a T of 680°C and P of 2.6 GPa from garnet core and omphacite inclu-

sion compositions; these estimates plot adjacent to the quartz-coesite boundary (Fig. 3). Quartz-garnet-omphacite $\delta^{18}\text{O}$ equilibration in both mafic eclogite and graphite-bearing schist yields T estimates of 595° to 711° C (Leech and Ernst, 2000). Omphacite compositions yield minimum P estimates of 1.5 to 2.6 GPa (Beane et al., 1995). Finally, a report of what appears to be relict coesite (Dobretsov and Dobretsova, 1988) and the documentation of microdiamonds (Bostick et al., 2003) indicate UHP peak metamorphic conditions (Fig. 3).

The protolith, peak metamorphic age, timing of deformation, and the age of exhumation have all previously been reported for the Kairakli unit (see Fig. 3). Based on U-Pb SHRIMP data from zircon cores of 1778 ± 27 Ma (Beane and Leech, 2007) and detrital zircon ages of 1800 ± 20 Ma (Krasnobayev et al., 1995), the metasedimentary rocks of the Kairakli unit had Proterozoic protoliths. Additional U-Pb SHRIMP data from zircons yield 550 to 485 Ma (Leech and Willingshofer, 2004; Beane and Leech, 2007). The age of peak metamorphism is approximately 385 Ma (U-Pb rutile ages of Beane and

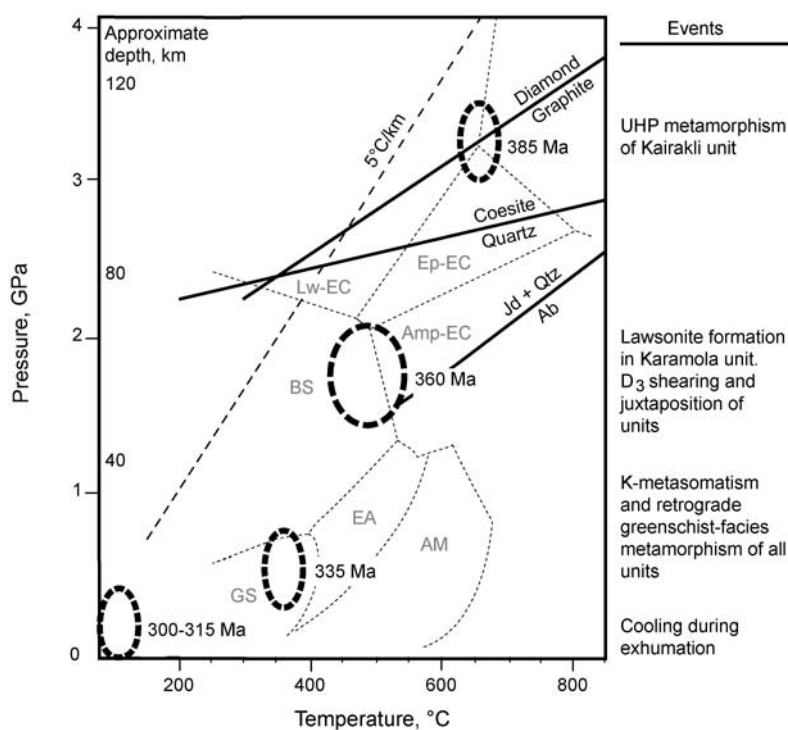


FIG. 3. P-T-t path showing UHP metamorphism of the Kairakli unit ~385 Ma, lawsonite formation in the Karamola unit, and juxtaposition of all three units during blueschist-facies retrograde metamorphism in the Kairakli unit (~360 Ma). K-metasomatism leading to pseudomorphism of lawsonite in the Karamola unit accompanied by greenschist-facies retrograde metamorphism of all units (~335 Ma); and final exhumation (300–315 Ma). Ages are from Table 1. Petrogenetic grid for metabasaltic bulk-rock compositions from Liou et al. (1998). Metamorphic facies abbreviations: AM = amphibolite; Amp-EC = amphibolite-eclogite; BS = blueschist; Ep-EC = epidote eclogite; Lw-EC = lawsonite eclogite. Figure after Beane and Leech (2007).

Connelly, 2000; Rb-Sr ages of Shatsky et al., 1997; SHRIMP zircon ages of Leech and Willingshofer, 2004). The timing of retrograde shear zone development ranges from 370 to 344 Ma, based on $^{40}\text{Ar}/^{39}\text{Ar}$ and Rb-Sr ages (Beane and Connelly, 2000; Hetzel and Romer, 2000). A weighted age estimate for retrograde shear is 360 ± 8 Ma (Hetzel and Romer, 2000). Apatite fission-track data indicate that exhumation and late-stage cooling occurred at 300 ± 25 Ma (Leech and Stockli, 2000).

Yumaguzino unit. The blueschist-facies Yumaguzino unit consists of white quartzite with a structural thickness of 600 m (Lennykh et al., 1995). A ductile shear zone (360 ± 8 Ma; Hetzel and Romer, 2000; Beane and Connelly, 2000) is well developed in this unit, and also juxtaposed the Kairakli and Karamola units during exhumation (Hetzel et al., 1998).

Karamola unit. The Karamola unit consists of transitional blueschist- to greenschist-facies, serpentinite-matrix mélange, volcanic rocks, marble, and graphite-bearing quartzite (Dobretsov et al., 1996; Beane and Liou, 2005). U-Pb SHRIMP data for zircons in the quartzofeldspathic rocks yield Proterozoic core ages (1417 ± 26 Ma and 1098 ± 18 Ma; Beane and Leech, 2007) and younger 520 to 548 Ma ages (Beane and Leech, 2007). Marble lenses within the Karamola unit contain Late Silurian to Early Devonian conodonts (Puchkov, 1993).

The discontinuous serpentinite-matrix mélange has 0.5 m^2 – 10 m^2 blocks of chlorite-rich, lawsonite- and garnet-bearing, metasomatized basalts (Lennykh and Valizer, 1986; Schulte and Sindern, 2002; Beane and Liou, 2005). Field and petrographic evidence for element mobility includes mafic blocks that have Ca-rich phases in the core

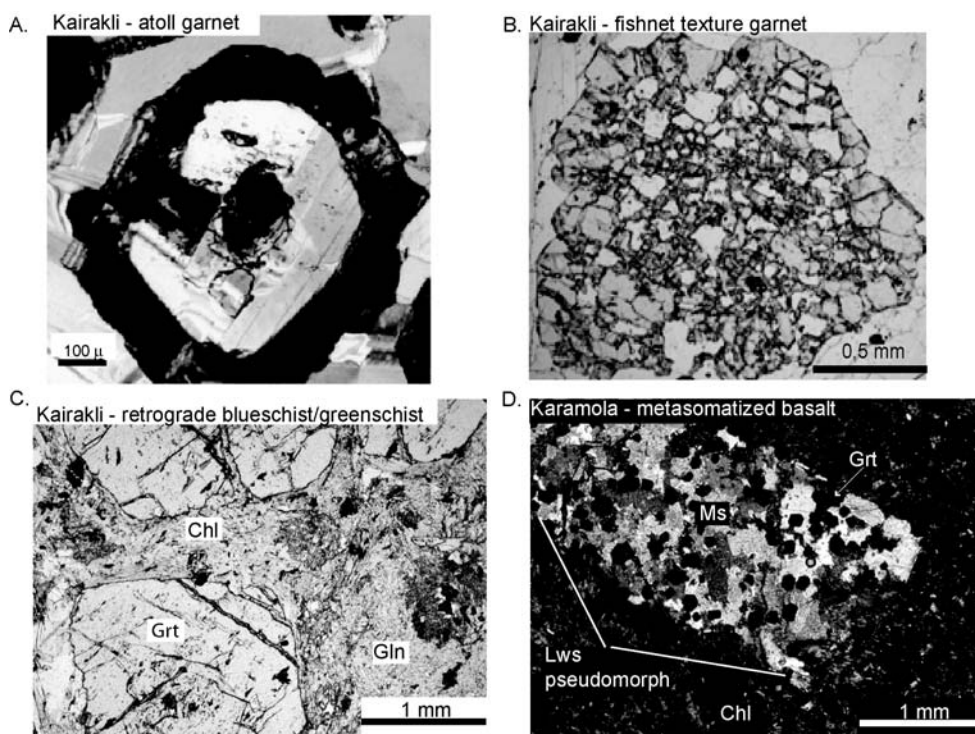


FIG. 4. Photomicrographs taken in cross-polarized light, except for B. A. Fishnet garnet texture in Kairakli eclogite. B. Atoll garnet texture in Kairakli eclogite. C. Retrograde metamorphism of the Kairakli metabasalt, showing Chl filling in fractures and Glc replacing Omp. D. Metasomatized basalt from the Karamola unit showing Lws pseudomorphosed by Ms and Grt within a Chl-rich matrix.

and chlorite-dominated rims. Furthermore, some of the metasomatized blocks include mm to cm sized lawsonite (Figs. 2C and 4D; Beane and Liou, 2005) that was pseudomorphosed by muscovite at conditions around 0.4 GPa and 400°C (Schulte and Sintern, 2002) at 332–339 Ma ($^{40}\text{Ar}/^{39}\text{Ar}_{\text{mica}}$ data; Beane and Connelly, 2000).

Magnitogorsk arc

As noted above, the Magnitogorsk arc is located east (present coordinates) of the Maksyutov Complex, in the hanging wall of the Main Uralian fault (Figs. 1A and 1B; Zonenshain et al., 1984; Hetzel et al., 1998). Arc magmatism began in the Early Devonian (Brown et al., 2001), shifted eastward in the Middle Devonian (Puchkov, 1997), and continued into the Late Carboniferous (Brown et al., 2001). The oldest units of the Magnitogorsk forearc are the Emsian Baimak-Buribai and Tanalyk formations, which consist of lavas and volcanoclastic rocks with boninitic, tholeiitic, and andesitic compositions

(Magnitogorsk age ranges from conodont data of Maslov et al., 1993; Brown and Spadea, 1999; Spadea et al., 2002). The overlying Emsian to Eifelian Irendyk Formation consists of tholeiitic basalt and andesitic to dacitic lavas and pyroclastic rocks interbedded with volcanoclastic rocks (Brown et al., 2001; Spadea et al., 2002). The uppermost Eifelian Karamlytash formation consists of basaltic to rhyolitic composition flows and volcanoclastic rocks (Spadea et al., 2002). East of these formations is the Givetian Ulutau Formation, which consists predominantly of dacitic volcanic rocks, volcanoclastic and conglomeratic sedimentary rocks (Brown and Spadea, 1999; Brown et al., 2001; Spadea et al., 2002).

Geochemistry

Analytical methods

Whole-rock samples of eclogite and metapelite were analyzed for major and trace elements by X-ray

TABLE 1. Information for Samples from Kairakli Unit of the Maksyutov Complex¹

Sample	Locality	Lithology	Mineral assemblages
2c	Karyanova, Sakmara R.	Mica paragneiss	Qtz, Grt (0.15 mm,atoll), Ap, Plag, Phn, Omp, Zrc
3a	Karyanova, Sakmara R.	Banded eclogite	Grt (2.5 mm), Phn, Omp, Rt, Ap
3b	Karyanova, Sakmara R.	Quartzite	Grt (0.2 mm, atoll), Phn, Qtz, Rt
4a	Karyanova, Sakmara R.	Banded eclogite	Grt (5.5 mm), Omp, Phn, Plag, Rt, Ap, Qtz vein
4c	Karyanova, Sakmara R.	Graphite paragneiss	Qtz, Phn, Gr, Ep, Grt (0.5 mm), Zrc
18	Shubino	Mica paragneiss	Qtz, Phn, Grt (5 mm, fishnet), Ap, Zrc, Aln
19b	Shubino	Retrograde eclogite	Grt (7 mm), Glc, Phn, Omp, Plag, Rt (Ttn rims), Ap
19c	Shubino	Massive eclogite	Grt (2.5 mm), Ap, Omp, Ep, Qtz, Plag,Ttn, Rt, Zrc
19e	Shubino	Retrograde eclogite	Grt(4 mm, Chl rims), Omp, Glc, Rt, Ep, Ap, Qtz
35a	Karyanova, Sakmara R.	Banded eclogite	Grt (2 mm, atoll), Omp, Phn, Ep, Rt, Ttn, Cal, Qtz, Ap, minor Chl
35b	Karyanova, Sakmara R.	Banded eclogite	Grt (4.5 mm), Omp, Rt, Ap
35d	Karyanova, Sakmara R.	Retrograde eclogite	Grt (1.75 mm, Chl filled cracks), Omp, Glc, Rt, Ttn, Zrc
42	4 km S. of Novsimbirka	Mica paragneiss	Phn, Plag, Qtz, Grt (0.2 mm), Stp, Ttn, Zrc
43c	4 km S. of Novsimbirka	Blueschist boudin	Grt (Chl rims), Glc, Omph, Ep,Cal, Ttn, Phn, Plag, Rt (Ttn rims)
99	Karyanova, Sakmara R.	Eclogite boudin	Grt (4 mm, atoll), Omp, Phn, Plag, Rutile, Ap
101	Karyanova, Sakmara R.	Enstatite	En, Chl, Wm
102	Karyanova, Sakmara R.	Ultramafic boudin	En, Chl, Wm
103	Karyanova, Sakmara R.	Eclogite	Grt (0.5 mm, atoll), Omp, Wm (coarse, vein), Rt

¹R. = river; lithology modifiers: banded (decimeter-scale width, alternating with paragneiss), massive (km-scale exposure), boudin (less than meter, surrounded by paragneiss). Grt measurements are diameter of largest crystals; fishnet and atoll describe Grt textures. Abbreviations are after Kretz, 1983 where possible: Ap = apatite; Cal = calcite; Chl = chlorite; En = enstatite; Ep = epidote; Glc = glaucophane; Grt = garnet; Omp = omphacite; Phn = phengite; Plag = plagioclase; Qtz = quartz; Rt = rutile; Stp = stilpnomelane; Ttn = titanite; Wm = white mica; Zrc = zircon.

fluorescence (XRF) and instrumental neutron activation analysis (INAA). Sample splits were ground to <100 mesh in an Al-ceramic SPEX shatterbox. The XRF analyses were performed in the Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution (DMS-NMNH). The lower detection limits for SiO₂ is 80 wt%. The INAA analyses were performed at the now-defunct gamma ray spectroscopy facility of the U.S. Geological Survey in Reston, Virginia. The INAA analytical procedures are detailed in Sorensen and Grossman (1989).

Kairakli unit whole rock samples were selected to: (1) represent unaltered mafic protolith composi-

tions (e.g., 4a, 19c, 35b, 99; Table 1); (2) to span an inferred range of metasedimentary rock compositions (e.g., 2c, 3b, 4c, 18, 42; Table 1); (3) evaluate possible element transfer between mafic rocks and their metasedimentary rock matrices at the outcrop scale (3a and b; 4a and c; 18 and 19b, c, and e; 42 and 43c; Table 1); and (4) compare evidence for element mobility between retrograded and non-retrograded samples in the same outcrop (19b, c, and e; 35a, b, and d; Table 1). The XRF and INAA analyses for these samples are reported in Tables 1 and 2. These new data are complemented by analyses of 39 samples from the Karamola unit, reported in Beane and Liou (1995). Five of the Karamola

analyses, shown in Table 3, are used to compare protolith compositions and K-metasomatism in the Kairakli and Karamola units.

Subducted materials

Analyses of Kairakli unit eclogite samples that show little or no evidence of retrograde metamorphism or late mica growth provide the best opportunity to interpret the protolith composition. The SiO_2 contents of these eclogites range from 47 to 55 wt%. The TiO_2 contents range from 1.41 to 1.81 wt%. The MgO contents range from 6.98 to 8.59 wt%. The major-element data (Table 2) suggest that the protoliths of the eclogites were low-K tholeiitic basalts.

Trace-element data (Table 2) elaborate constraints upon the likely protolith. The eclogites show LREE-enriched REE-patterns that resemble those of E-MORB (Fig. 5A). The incompatible-element variation patterns (spider diagrams) of these samples also resemble those of E-MORB (Fig. 5B), except for Cs, Ba, Nb, and Sr values, which vary from sample to sample. Maksyutov eclogite samples show covariations of Nb and Zr—a “discriminant” applied by Becker et al. (2000) to discuss likely protoliths within a suite of Alpine eclogites—that are characteristic of MORB. In the triangular discriminant diagram Zr-Nb-Y (Meschede, 1986), three samples plot in the within-plate tholeiite field, and one sample in the E-MORB field. Taken together, the major- and trace-element data indicate that eclogite protoliths in the Kairakli unit were low-K tholeiitic basalts with E-MORB characteristics. They may have originally erupted at the continental edge of a plate.

Unlike the eclogite samples that show little or no evidence of retrograde metamorphism or late mica growth, most mafic blocks in the serpentinite mélangé of the Karamola unit have undergone variable degrees of Ca-, Mg-, and K-metasomatism (Beane and Liou, 2005). We assume that the least-altered samples of metasomatized mafic blocks provide the best opportunity to discern the protoliths of such blocks (Table 3). Except for Ba, K, and Sr, the incompatible-element variation patterns of the Karamola samples resemble those of both E-MORB and the Kairakli samples (Fig. 6A). The Karamola REE patterns resemble those of the Kairakli samples, except that the former display slightly less LREE enrichment and a greater Eu anomaly (Fig. 6B). The Th-Hf-Ta discriminant diagram of Wood (1980) illustrates that both Kairakli and Karamola show incompatible-element characteristics of E-

MORB, except for Karamola sample 118, which plots as an arc-basalt (Fig. 6C). Overall, the trace-element data suggest the protolith of slightly altered Karamola metabasalt blocks was tholeiitic basalt with E-MORB characteristics. Therefore, the Karamola and Kairakli metabasite blocks could have had a common protolith.

The less mobile elements of metasedimentary gneiss samples of the Kairakli unit resemble the North American Shale Composite (NASC; Fig. 7, Gromet et al., 1984). Two quartz-rich samples display smaller trace-element values than the NASC. This variation could be dilution of the trace element signature by a greater sand content in the protolith, or that incompatible elements were partitioned into metasomatizing fluids or partial melting during metamorphism.

Geochemical variations

The compositions of samples of eclogite that show evidence for substantial retrograde mineral growth or display abundant, coarse-grained white mica show geochemical contrasts with the apparently unaltered or less altered eclogite samples. In obviously retrogressed samples, SiO_2 contents range from 43 to 49 wt%; TiO_2 , 1.07 to 4.14 wt%; MgO, 5.61 to 8.35 wt%; CaO, 6.82 to 10.35 wt%; K_2O , 0.02 to 0.71 wt%; and Na_2O , 1.45 to 3.63 wt% (Table 2; Fig. 8). The samples that display coarse white mica show overlapping to greater values for some of these components, with SiO_2 contents from 49 to 50 wt%; TiO_2 , 1.09 to 2.21 wt%; MgO, 5.30 to 6.04 wt%; CaO, 6.12 to 9.67 wt%; K_2O , 0.08 to 1.86 wt%; and Na_2O , 3.88 to 6.44 wt% (Table 2; Fig. 8). The retrogressed and coarse mica samples thus contain less MgO and CaO, and more K_2O (coarse-muscovite-bearing samples) and Na_2O . In the same outcrop (19b, c, and e and 35a, b, and d), retrogressed samples are distinctively different in their TiO_2 , CaO, MgO, Na_2O , and K_2O compared to less altered samples.

The trace-element data for some of the retrogressed and coarse-mica-bearing eclogite samples differ significantly from the eclogites that show less evidence for alteration during peak metamorphism or retrogression (Fig. 9). Indeed, four samples from the former group display steeply sloping LREE patterns that contain more LREE than E-MORB. However, two samples exhibit REE patterns that are indistinguishable from the unaltered eclogite samples (Fig. 9B). In addition to REE, at least one member of the LILE is greatly enriched in retro-

TABLE 2. X-Ray Fluorescence and Neutron Activation Analyses
for Metamorphosed Mafic Rocks of the Kairakli Unit

Sample	0.125	4a	19b	19c	19e	35a	35b	35d	43c	103	99
wt%											
SiO ₂	49.13	47.38	47.36	50.67	49.68	49.39	50.89	42.62	48.09	50.22	51.38
TiO ₂	1.09	1.52	4.14	1.81	1.67	1.07	1.41	2.74	1.18	2.21	1.50
Al ₂ O ₃	17.79	15.79	14.13	14.49	15.22	14.09	12.71	17.01	16.27	15.95	14.51
Fe ₂ O ₃	1.18	1.53	3.55	2.18	3.89	1.93	2.54	5.61	2.40	4.77	2.81
FeO	7.7	9.19	10.63	10.55	7.84	9.10	8.77	12.22	11.04	9.50	8.68
MnO	0.23	0.16	0.15	0.25	0.19	0.19	0.15	0.33	0.24	0.26	0.17
MgO	6.04	8.59	7.48	8.14	7.74	8.35	12.72	5.61	7.90	5.30	6.98
CaO	9.67	10.48	8.32	9.57	10.53	6.82	7.05	10.35	7.04	6.12	8.60
Na ₂ O	3.88	2.90	3.20	1.90	1.92	3.63	2.53	1.45	3.35	6.44	5.27
K ₂ O	1.86	0.44	0.71	0.14	0.19	0.64	0.29	0.02	0.40	0.08	0.01
P ₂ O ₅	0.56	0.19	0.32	0.15	0.16	0.15	0.12	0.24	0.14	0.02	0.03
LOI	1.15	2.07	0.46	0.48	0.96	4.29	0.91	1.70	2.53	0.00	0.00
Total	100.28	100.24	100.45	100.33	99.99	99.65	100.09	99.90	100.58	100.87	99.94
ppm											
Rb	48.23	0.00	18.84	0.00	5.68	19.60	5.29	0.00	7.93	6.38	
Sr	317.49	393.44	216.76	281.72	546.92	128.33	122.76	279.12	201.72	40.00	
Y	29	21	36	30	30	22	18	49	28	34	30
Zr	151.08	98.00	237.40	128.00	85.10	100.61	85.86	202.34	129.34	215.18	
Nb	8	2	23	10	9	7	4	16	0	25	6
Ba	541	246	340	31	39	233	66	43	131	51	0
La	18.77	5.95	19.18	7.53	8.41	6.77	5.31	25.14	5.41	18.72	
Ce	47.08	15.52	45.87	18.47	19.73	15.03	13.83	55.26	12.24	49.03	
Nd	29.04	11.47	30.74	13.99	14.06	9.56	9.01	35.35	9.05	21.56	
Sm	6.08	3.59	9.41	4.17	4.67	3.14	3.16	9.56	3.02	5.89	
Eu	1.6	1.32	2.91	1.46	1.65	1.06	1.09	2.81	1.00	1.54	
Gd	5.62	4.44	8.51	6.49	6.04	3.77	3.61	8.80	3.61	7.45	
Tb	0.82	0.64	1.27	0.85	0.86	0.59	0.59	1.22	0.67	1.11	
Yb	2.51	1.82	2.77	2.77	2.97	2.17	1.70	4.47	2.91	3.69	
Lu	0.36	0.24	0.35	0.39	0.38	0.30	0.24	0.66	0.42	0.52	
Hf	3.7	2.07	6.39	2.89	2.83	1.79	2.09	4.66	1.85	6.02	
Ta	0.58	0.31	1.54	0.48	0.46	0.21	0.40	1.06	0.16	1.61	
Th	5.38	0.34	1.52	0.72	0.68	0.74	0.41	2.42	0.39	6.27	
U	1	0.15	0.00	0.23	0.22	0.43	0.18	2.99	0.15	0.90	
Cu	28	102	240	240	114	159	43	69	101	40	56
V	223	271	467	371	353	340	262	351	256	245	347
Sc	21.87	29.74	33.53	43.84	43.49	44.13	30.76	52.81	38.86	45.22	
Tl	11.36	4.38	28.54	12.51	11.91	3.53	11.01	19.58	11.02	16.80	
Cr	60.87	386.51	146.30	129.59	149.33	122.89	661.60	15.79	119.28	267.29	
Co	24.28	45.57	53.91	47.26	45.82	45.21	61.04	53.40	49.54	48.91	
Ni	34.45	162.78	127.95	59.37	79.13	67.27	427.23	56.13	112.77	120.11	
Zn	62.21	61.40	109.25	70.40	63.85	100.16	77.49	121.71	72.46	113.16	
Sb	0	0.15	0.37	0.10	0.00	0.23	0.17	3.35	0.38	0.27	
Cs	1.83	0.49	0.59	0	0	0.6	0.13	0.00	0.33	0.53	

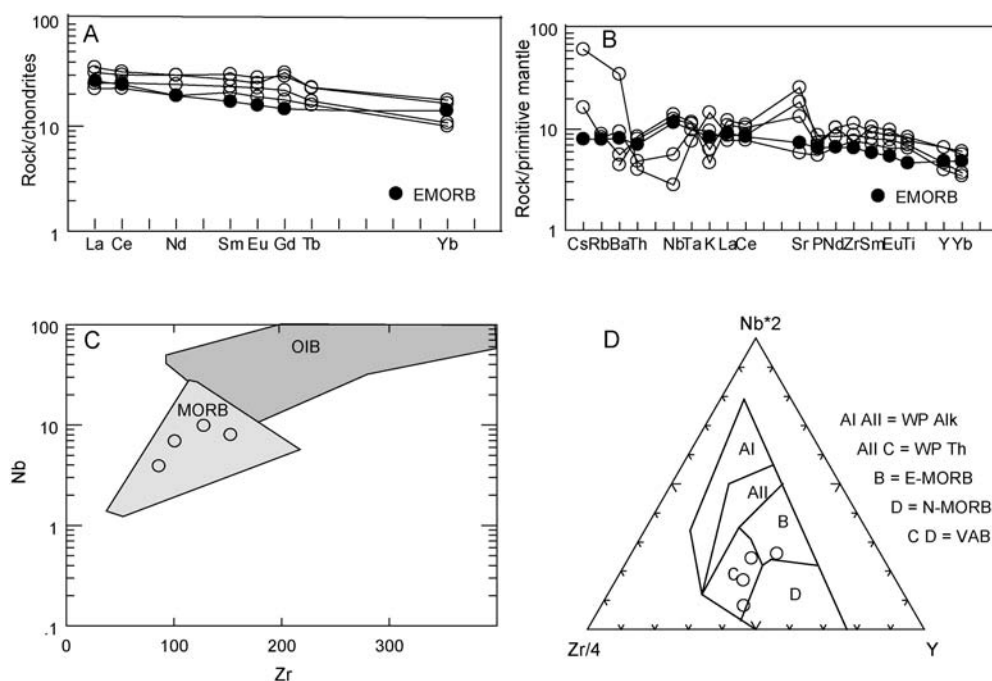


FIG. 5. Composition of least altered eclogite of the Kairakli unit. A. REE patterns are normalized to chondrite values from Sun and McDonough (1989) with EMORB standard for comparison. B. Incompatible element patterns are normalized to primitive mantle values from Sun and McDonough (1989) with EMORB for comparison. C. Nb versus Zr discriminant diagrams after Becker et al. (2000); the two shaded regions delineate fields for mid-ocean ridge basalt (MORB) and ocean island basalt (OIB). D. Zr-Nb-Y discrimination diagram for basalts (after Meschede, 1986).

gressed and micaceous eclogite. The Ba contents of retrogressed and micaceous samples are up to 10 times those of unaltered samples (Fig. 9C). These values are not location dependent; for example, the Ba content of retrograde eclogite sample 19b is 10 times that of sample 19c, which is an unaltered sample from the same outcrop, and the Ba content of coarse mica-bearing sample 35a is nearly four times that of 35b, an unaltered sample from the same outcrop. The coarse muscovite-bearing sample 3a has 10 times or greater the Ba content of the unaltered samples.

A plot of La/Sm vs. Nb/Zr (Fig. 9D) illustrates whole-rock LREE versus high-field-strength element enrichments. In all of the samples, the Nb/Zr ratio is relatively constant at ~0.1, a value typical of E-MORB (as plotted on Fig. 9D). This restricted and apparently "protolith-reflective" Nb/Zr ratio also implies that the ratio of rutile and/or titanite to zircon in the metabasite has been adequately sampled, because the former minerals carry much of the

Ti-Nb-Ta in subduction-zone metabasites, whereas Hf and Zr reside predominantly in zircon (e.g., Sorensen, 1989; Sorensen and Grossman, 1989, 1993). The La/Sm ratio, which is approximately 1.6 for unaltered and some retrogressed samples and increases to approximately 3.1 for the coarse mica samples, suggests that LILE and LREE may have been mobilized together in fluids that metasomatized such rocks. Small-scale heterogeneity of trace-element alteration is again seen in LREE: retrogressed sample 35d displays nearly twice the La/Sm ratio as unaltered sample 35b from the same outcrop.

The discriminant plot of Th vs Th/La shows that all unaltered and two retrogressed samples display the HFSE and LREE characteristics of EMORB (Fig. 9E). This said, two retrogressed samples, 19b and 35d, display Th/La ratios of 0.1, consistent with the other samples, but also show greater Th contents than the other metabasites. The two coarse-grained white mica-bearing samples (3a and 103) display

TABLE 3. X-Ray Fluorescence and Neutron Activation Analyses
for Metamorphosed Sedimentary Rocks of the Kairakli Unit

Sample	2c	3b	4c	18	42
wt%					
SiO ₂	79.53	92.16	88.29	73.88	70.66
TiO ₂	0.37	0.16	0.18	0.29	0.30
Al ₂ O ₃	8.66	3.42	3.96	15.11	14.88
Fe ₂ O ₃	1.67	0.30	0.48	0.84	1.53
FeO	1.68	1.26	0.54	1.77	1.45
MnO	0.24	0.14	0.04	0.04	0.08
MgO	1.87	0.65	0.57	0.53	1.27
CaO	1.84	0.46	1.82	2.18	1.07
Na ₂ O	0.91	0.10	0.23	1.22	4.38
K ₂ O	2.11	0.85	0.65	2.18	2.90
P ₂ O ₅	0.08	0.04	0.27	0.09	0.08
LOI	1.61	0.51	2.91	1.84	1.38
Total	100.57	100.05	99.94	99.97	99.98
ppm					
Rb	67.59	28.54	20.23	59.47	59.61
Sr	89.75	30.88	155.75	676.04	100.93
Y	13	7	13	66	37
Zr	81.75	48.77	40.84	218.27	159.28
Nb	7	<2	4	34	14
Ba	583.07	239.85	1040.50	399.77	907.17
La	5.79	4.77	9.58	16.75	24.79
Ce	7.08	9.8	16.72	36.84	47.55
Nd	5.33	4.66	9.11	17.72	23.94
Sm	1.38	1.36	2.15	6.50	5.62
Eu	0.37	0.30	0.42	0.88	0.80
Gd	2.24	4.05	2.53	7.85	5.35
Tb	0.40	0.24	0.30	1.48	0.88
Yb	1.59	0.70	1.70	10.21	5.23
Lu	0.22	0.09	0.26	1.44	0.77
Hf	2.30	0.77	0.94	8.86	4.63
Ta	0.60	0.28	0.27	2.34	0.86
Th	4.61	3.59	4.16	5.53	5.50
U	1.05	0.74	2.49	1.96	0.82
Cu	42	<3	35	3	10
V	79	15	90	39	56
Sc	9.10	4.38	4.00	5.39	9.47
Tl	4423	785	0	3454	0
Cr	43.66	10.90	26.24	10.83	13.26
Co	9.69	1.41	7.27	1.45	4.24
Ni	22	6	32	7	11
Zn	52.36	28.08	38.54	52.48	41.52
Cs	1.88	0.86	0.66	3.05	1.40

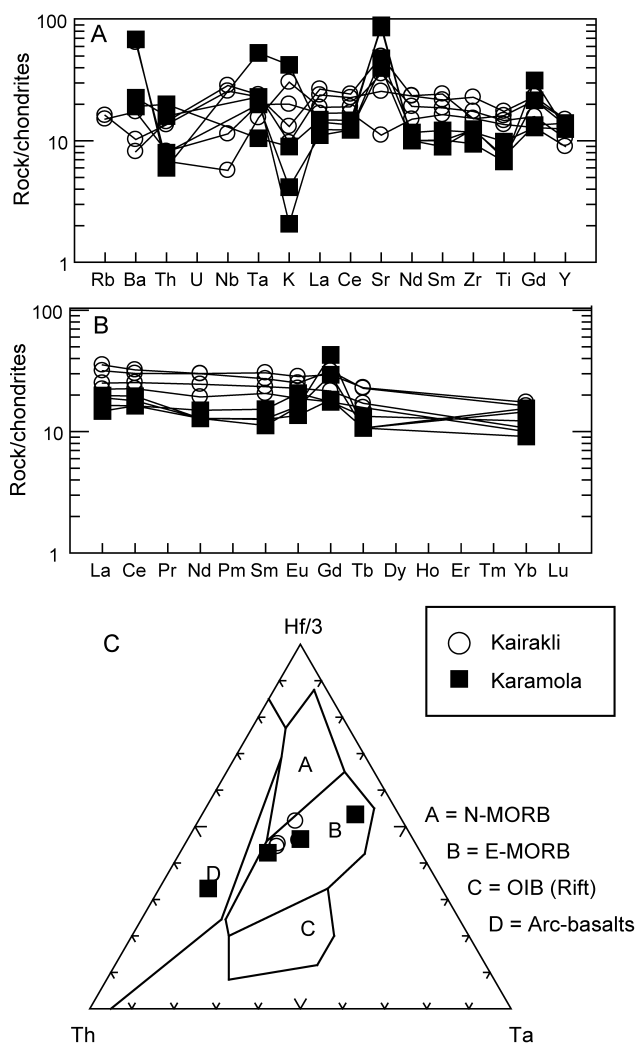


FIG. 6. Comparison of least altered metabasalt of the Kairakli and Karamola units. A. Incompatible element patterns are normalized to chondrite values of Sun (1980). B. REE patterns are normalized to chondrite values from Sun and McDonough (1989). C. Th-Hf-Ta discrimination diagram after Wood (1980).

both greater Th and Th/La ratios. The Th/La ratios for these samples are slightly greater than the average Th/La values of bulk continental crust, subducted sediment, and arc basalts (i.e., 0.24 to 0.27) as reported by Plank (2005). Indeed, these Th/La ratios trend toward the composition of the North American Shale Composite (NASC; Gromet et al., 1984; see Fig. 9F).

Like their counterparts in the Kairakli unit, samples of metabasite from the Karamola unit vary in their Ba and K_2O contents (Fig. 10). As might be expected of even an E-MORB protolith, the least

altered samples have low amounts of both components. However, Sample 11, which is notable for its 0.5 to 1.5 mm-long muscovite pseudomorphs after lawsonite, contains 2.98 wt% K_2O and 1540 ppm Ba (Table 4; Beane and Liou, 2005).

Discussion

Likely protoliths of Kairakli metabasites

Multiple lines of evidence show that eclogites of the Maksyutov Complex are derived from tholeiitic basalts with E-MORB characteristics. Eclogite

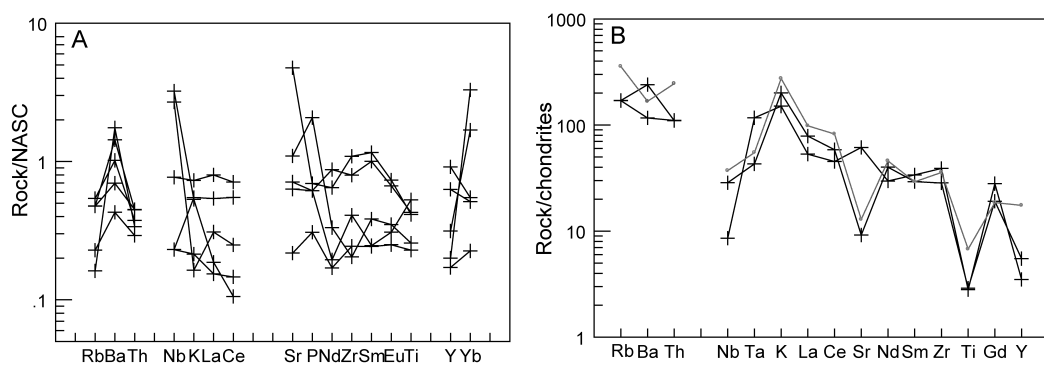


FIG. 7. Composition of sedimentary gneiss of the Kairakli unit. A. Incompatible-element pattern normalized to North American Shale Composite (NASC). B. Incompatible element pattern normalized to chondrite for two samples (+) and NASC (grey); chondrite values of Sun (1980).

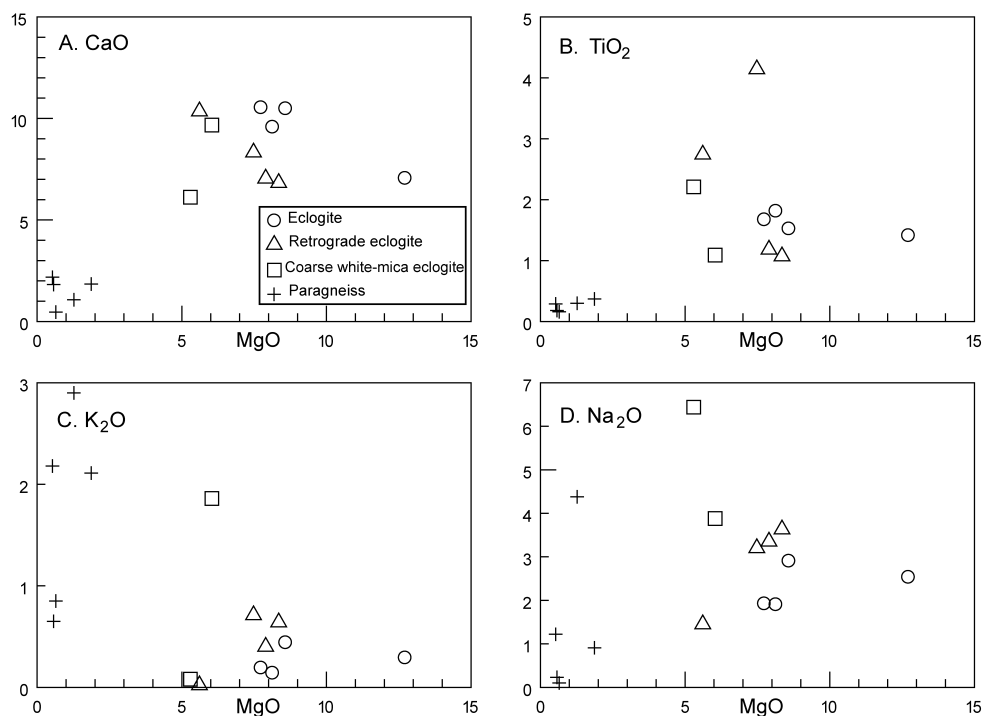


FIG. 8. Major-element variations for retrograde and coarse white mica-bearing eclogite and metamorphosed sedimentary rocks of the Kairakli unit.

samples that show no evidence for retrogression display major-element whole-rock compositions comparable to that of low-K tholeiitic basalts. Their REE patterns are LREE enriched to a degree found in E-MORB. In a Th-Hf-Ta discrimination diagram, these

samples plot in the field of E-MORB. In addition, the Th/La ratios of both unaltered and retrogressed samples are consistent with E-MORB, and the Zr-Nb-Y diagram illustrates that the samples plot in fields defined as E-MORB and within-plate tholeiite.

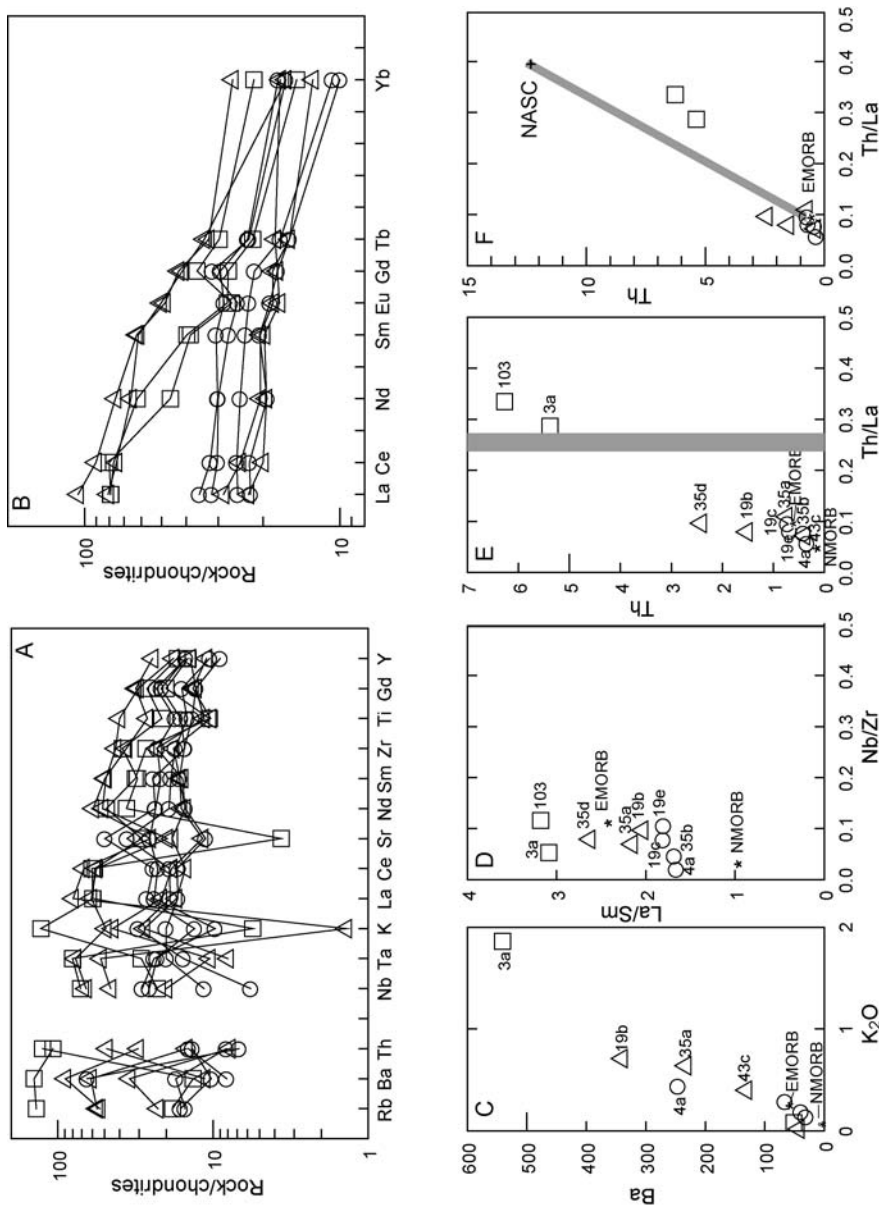


FIG. 9. Trace-element variations from retrograde and coarse white mica-bearing eclogite of the Kairakli unit; symbols are the same as in Figure 8. A. Incompatible element patterns are normalized to chondrite values of Sun (1980). B. REE patterns are normalized to chondrite values from Sun and McDonough (1989). C–F. Trace-element ratios with NMORB (*) and EMORB (*) values of Sun and McDonough (1989) are plotted for comparison. E. Shaded line represents the average Th/La values (0.24–0.27) for bulk continental crust, subducted sediment and arc basalts as reported in Plank (2005). F. Shaded line represents possible element exchange between North American Shale Composite (+) (NASC; Gromet et al., 1984) and EMORB (*).

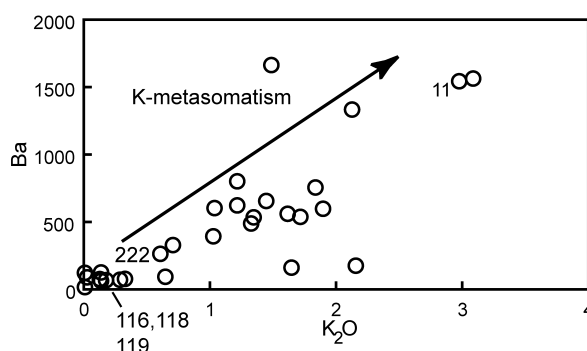


FIG. 10. Element variations from K-metasomatized metabasalt of the Karamola unit. Samples included in Table 4 are labeled; other sample data from Beane and Liou (2005).

Volkova et al. (2004) reported a geochemical study of 40 samples from a single eclogite and blueschist boudin (5 m × 30 m) of the Kairakli unit located 2.5 km south of the village of Karayanova village along the bank of the Sakmara River. These authors concluded that the geochemical signatures of their samples indicate that the protolith of the boudin was “quartz-bearing hypersthene basalts” resembling E-MORB tholeiite. Variations in the compositions of the samples were attributed to fractional crystallization processes of the protolith. Volkova et al. (2004) separated the samples into three clusters with distinct chemical signatures. One group has cumulate characteristics, such as negative Eu anomalies, “decreased contents of Al_2O_3 , K_2O , P_2O_5 , Rb, Cs, Sr, and higher contents of MgO , Co, Cr” (Volkova et al., 2004, p. 752) compared to rocks in the other clusters from the same boudin. However, cumulate processes are less common in large basalt flows, and more typical of sills or dikes emplaced at shallow depths. This, combined with the nature of the sedimentary host rocks, led Volkova et al. (2004) to concur with Leech and Ernst (2000) that the eclogite protoliths were initially dikes and sills of tholeiitic basalt in continental crust.

This study, which examined eclogites from multiple boudins in the Kairakli unit, comes to a similar conclusion as did Volkova et al. (2004) and Leech and Ernst (2000). Eclogites occur as variably sized boudins within sedimentary gneiss, with chemical characteristics similar to those of the NASC, which suggests the original emplacement of the metabasite protolith into a continental crust setting. Furthermore, the consistent E-MORB and within-plate tholeiite geochemical signatures of the metabasites

attests to their origin as dikes and sills in a continental-rift or passive-continental-margin setting; such compositions are far more common at these locations than at spreading ridges. However, an alternate interpretation to our interpretation was proposed by Dobretsov (1974) and Dobretsov et al. (1996). These authors concluded that the Kairakli unit was originally a metasedimentary mélange of microcontinental fragments. This interpretation is supported by one outcrop along the Sakmara River, where ultramafic and enstatite-rich blocks (Samples 101 and 102) are present in mélange in addition to eclogite (Sample 103) and mica-rich gneiss. It is possible to support the mélange interpretation through the field relations of such portions of the Kairakli unit, but most other occurrences of eclogite boudins in gneiss suggest that the Kairakli unit initiated as continental crust (Hetzel, 1999; Leech and Ernst, 2000; Volkova et al., 2004).

Metasedimentary rocks of both the Kairakli (1778 ± 27 , U-Pb SHRIMP on zircon; Leech and Willingshofer, 2004) and Karamola (1417 ± 26 , U-Pb SHRIMP on zircon; Beane and Leech, 2007) units yield Proterozoic protolith ages that suggest affinities with the East European platform (Beane and Leech, 2007). The Middle Cambrian to Early Ordovician (514–548 Ma) U-Pb SHRIMP zircon ages (Leech and Willingshofer, 2004; Beane and Leech, 2007) for eclogites and related rocks from the Kairakli unit overlap with the Early Ordovician age (based on conodont data of Ivanov et al., 1989) for the first magmatic event associated with rifting of the East European platform and opening of the paleo-Uralian ocean. The protolith ages combined with the compositions of the eclogites and paragneiss indicate that the eclogite boudins formed as

dikes or sills of basalt in sedimentary continental materials during the initial opening of the paleo-Uralian ocean.

Element mobility

In many cases, eclogite-facies metamorphism does not seem to have significantly affected the major- and trace-element signatures imparted by basaltic protoliths, as indicated by the compositions of unretrogressed eclogite samples that lack coarse-grained white mica. In contrast, however, retrogressed eclogite and coarse mica-bearing eclogite samples show geochemical variations that can be interpreted as variations in protolith compositions, contamination during intrusion of protolith basalt into the crust, or elemental mobility in fluids or melt during metamorphism. However, selecting among these sources of variability is generally problematic. For example, one might be tempted to attribute the much steeper LREE profiles for four of the samples to protolith differences—and, while this might work for the coarse white mica samples, the other two samples are from the same boudins as samples with less steep LREE profiles, and would presumably have the same protolith as those. Crustal contamination could explain the higher alkali-element contents of most of the retrogressed and coarse-grained, white mica-bearing samples. However, crustal contamination of the protolith magma does not explain the evidence for LILE enrichment in retrogressed samples, or the presence of meter-thick zones of mica-rich eclogites or white mica-filled fractures. These observations are more readily accounted for by fluid-induced element mobility. An aqueous fluid-mediated retrogression would not only explain the development of blueschist- and greenschist-facies phases and textures in the Kairakli eclogites, but it could have mobilized LILE and other elements to account for the mica-filled fractures.

Retrogressed and coarse-grained, white mica-bearing eclogite samples in the Kairakli unit are relatively enriched in LILE (such as K, Ba, and Rb) and LREE, but show little variation in HFSE (such as Nb, Zr, Th) or HREE. The LILE are thought to be more readily mobilized by fluids (e.g., Breeding et al., 2004; Sorensen et al., 1997; Catlos and Sorensen, 2003). Some samples of metasedimentary rock show depletions in LILE and LREE compared to the other two samples and to the NASC. Previous authors have shown that subduction-zone fluids can infiltrate metamorphosing sedimentary rock, break down its phengite, and thus mobilize LILE into the

TABLE 4. X-Ray Fluorescence and Neutron Activation Analyses for Representative Mafic Rocks of the Karamola Unit

Location:	Karyanova				
Sample:	116	118	119	222	11
	wt%				
SiO ₂	36.4	37.6	50.20	50.90	37.5
TiO ₂	0.74	0.77	1.02	0.70	0.72
Al ₂ O ₃	20.8	19.90	15.50	18.50	29.20
Fe ₂ O ₃ (T)	11.3	11.70	10.60	9.05	6.59
MnO	0.22	0.22	0.14	0.15	2.69
MgO	6.14	6.50	6.19	5.74	2.11
CaO	17.6	16.90	8.47	4.49	12.70
Na ₂ O	0.35	0.50	4.20	5.51	0.20
K ₂ O	0.03	0.13	0.06	0.61	2.98
P ₂ O ₅	0.07	0.07	0.10	0.16	0.02
Cr ₂ O ₃	0.03	0.03	0.00	0.01	0.02
LOI	4.6	4.10	2.00	3.20	3.75
Total	98.28	98.42	98.48	99.02	98.48
	ppm				
Rb	n.d.	n.d.	n.d.	n.d.	43
Sr	984	943	526	438	1880
Y	27	28	25	25	56
Zr	70	69	66	53	145
Nb	n.d.	n.d.	n.d.	n.d.	16
Ba	86	73	n.d.	260	1540
La	4.5	4.7	3.5	3.9	44.2
Ce	11	12	10	10	88
Nd	6	6	7	6	40
Sm	1.72	1.93	2.34	1.95	8.29
Eu	0.93	0.79	1.2	0.94	3.02
Tb	0.4	0.4	0.5	0.4	1.1
Yb	2.48	2.64	2.08	1.55	3.67
Lu	0.39	0.42	0.32	0.21	0.54
Th	0.8	1	0.4	0.3	8.9
U	0.5	0.6	0.3	0.3	2.6

¹Samples 116 and 118 underwent Ca-metasomatism; sample 11 underwent Ca- and K- metasomatism. Data selected from 39 analyses reported in Beane and Liou, 2005.

fluids (e.g., Catlos and Sorensen, 2003; Breeding et al., 2004). Furthermore, meters-scale fluid mobility and infiltration of LILE from metamorphosed sedimentary rocks into eclogite were documented by the observations and analyses of Zack et al. (2001) for eclogites from the Central Alps. In the Maksyutov Complex, LILE-bearing fluids appear to have partially infiltrated eclogite boudins, promoting retrogression and enriching the portion of the boudin adjacent to metasedimentary rocks in LILE. The fluid that first infiltrates the more porous metamorphosed sediments and then the eclogite boudins could have been produced during dehydration reactions during prograde to peak metamorphic conditions (basalt to eclogite transformation) (e.g., Dixon and Ridley, 1987; Sorensen and Grossman, 1989; Bebout and Barton, 1993; Ernst et al., 1998; Leech, 2001). Thus, it seems possible that metasomatic fluids could have introduced LILE and LREE from metasedimentary rocks proximal to metabasites during the long prograde and retrograde subduction zone history.

Evidence for fluid-induced metasomatism is also abundant in the mafic blocks of the Karamola unit of the Maksyutov Complex. Petrologic and geochemical evidence suggests that Mg-metasomatism of the blocks followed rodingitization, and continued during serpentinization of the surrounding peridotites, leading to chloritization of igneous plagioclase and prevalent Mg-rich rims around the mafic blocks (Beane and Liou, 2005). Extensive pseudomorphism of lawsonite by muscovite resulted from an influx of K-bearing fluid (Schulte and Sindern, 2002; Beane and Liou, 2005). The increase in Ba accompanying K-metasomatism presented in this study suggests that the source is the metamorphosed sedimentary rocks in the Karamola, Yumaguzino, or Kairakli units; fluids rich in Ba and K are documented as evolving from the metamorphism of sediments in subduction zones (e.g., Catlos and Sorensen, 2003; Sorensen et al., 1997). The K-metasomatism in the Karamola unit and the mica filled fracture in the Kairakli unit suggest at least meter-scale, and possibly kilometer-scale, fluid effects.

Overall, fluid-rock interactions may have been long-lasting, polythermal, and polybaric. One line of evidence for the amount of time fluids were present is mica ages from the Yumaguzino and Karamola units, which reflect fluid influx through mica crystallization. White mica ages from Yumaguzino samples and from a retrograde sample of the Kairakli unit range from 355 to 365 Ma (Beane and Connelly,

2000). These ages are interpreted to reflect development of a shear zone during lower blueschist-facies conditions (Beane and Connelly, 2000; Hetzel and Romer, 2000; Leech and Ernst, 2000). The many documented fractures in this shear zone (Hetzel et al., 1998) would have facilitated fluid flow between the three units of the Maksyutov Complex. Oxygen isotope studies for graphite schist from the Kairakli unit, stilpnomelane-bearing quartzite from the Yumaguzino unit, and metasomatized basalt from the Karamola unit all show equilibration at approximately $453 \pm 17^\circ\text{C}$ (Leech and Ernst, 2000), consistent with temperature estimates for the formation of the shear zone. Furthermore, the influx of K-bearing fluid for replacement of lawsonite by muscovite in the Karamola unit is estimated to have taken place at P-T conditions around 0.4 GPa and 400°C (Schulte and Sindern, 2002) at 332 to 339 Ma (Beane and Connelly, 2000). Evidence for low-temperature fluid flow comes from apparent $\delta^{18}\text{O}$ temperatures of $\sim 250 \pm 68^\circ\text{C}$ calculated for quartz-phengite pairs in metasedimentary rocks and a phengite-bearing eclogite that have been interpreted as resulting from fluid-induced metasomatism (Leech and Ernst, 2000).

Magnitogorsk Island-Arc Volcanics

The LILEs mobilized by fluids in the subducted slab of the Maksyutov Complex may have influenced the composition of the volcanics of the overlying Magnitogorsk island arc. The presence of boninitic and tholeiitic lavas and the absence of terrigenous sediments in the Emsian Baimak-Burabai Formation of the Magnitogorsk volcanic sequence are attributed to initiation of a volcanic arc above an oceanic subduction zone (Spadea et al., 1998). The arc evolved to form tholeiitic to calc-alkaline lavas and volcanoclastics in the overlying Emsian to Eifelian Irendyk Formation (Brown et al., 2001; Spadea et al., 2002). A compositional change toward dacitic to rhyolitic flows in the Eifelian Karamalytash and Givetian Ulutau formations has been interpreted to reflect a continental source, possibly the subduction of the East European continental crust (Brown and Spadea, 1999). This is further supported by Pb isotope ratios of sulfide deposits in the Karamalytash Formation that indicate an old continental crust source (Sunblad et al., 1996). Some Karamalytash volcanics show increased LILE (Cs, Rb, Ba, and K) and increased LREE (La/Sm ratios) compared to

earlier eruptions of the Magnitogorsk island arc (Brown and Spadea, 1999; Spadea et al., 2002).

LILE and LREE are interpreted in this study to have been mobilized by fluids in the underlying subducted slab of the Maksyutov Complex. These fluids are a plausible source of the compositional variations recorded in the Middle Devonian volcanics of the Magnitogorsk arc. Geochemical data from the Maksyutov Complex and Magnitogorsk arc seem to support a model where elements are mobilized in fluids, and where subducted continental crust, in addition to the better documented subducted oceanic sediment, influenced arc magmatism.

Conclusions

1. Eclogite boudins formed as dikes or sills of tholeiitic basalt with E-MORB characteristics in Proterozoic continent-derived shales of the East European platform during the Middle Cambrian to Early Ordovician opening of the paleo-Uralian ocean.

2. The protolith geochemical signatures of tholeiitic basalt and E-MORB are preserved in portions of some blocks, despite eclogite metamorphism at or near UHP conditions.

3. Other portions of the same blocks show significant LILE and light-REE enrichment. This documents for the first time that fluid transport of LILE and REE in metasediment-hosted eclogite-bearing subduction-zone metamorphic terranes may be spatially organized or channelized on a small scale, similar to aspects of hydrothermal veining systems in ore deposits, rather than resulting from pervasive fluid flow.

4. The source of the LILE and LREE-bearing fluids may be more distal than the sedimentary rocks that immediately surround the eclogite boudins. Adjacent sedimentary gneiss preserves signatures of continental shales. These proximal sediments may have allowed fluids to pass through without significant alteration themselves, inasmuch as mafic rocks more readily accepted the LILE and LREE via phengite crystallization. This created a broadly interface-controlled fluid-rock system at margins and in some portions of the mafic boudins.

5. The metasomatizing fluids were most likely dehydration fluids produced during prograde metamorphism, but some low-T metasomatic effects were evidently preserved through peak metamorphism. These "relict" metasomatic effects may have facili-

tated additional element transport during retrograde metasomatism.

Acknowledgments

This paper is dedicated to J. G. Liou, RB's graduate advisor, who encouraged her to begin studies of the Maksyutov Complex. This research was partially supported by a Bowdoin College Faculty Leave Supplement, NSF Graduate Fellowship, NSF Grant 93-04480, and sabbatical visits at the Smithsonian Institution and Boston University (RB). SSS would like to acknowledge the financial support of the Sprague Fund of the Smithsonian Institution for this project. The XRF analyses were performed by V. Avery, Smithsonian Institution, and the INAA data were reduced by J. Grossman, USGS. M. Leech provided constructive feedback during the review.

REFERENCES

- Alekseev, A. A., 2000, Graphite eclogite from the Maksyutovo metamorphic complex, Southern Urals: *Doklady Earth Sciences*, v. 372, p. 669–671.
- Bea, F., Fershtater, G. B., and Montero, P., 2002, Granitoids of the Uralides: Implications for the evolution of the orogen: American Geophysical Union, *Geophysical Monograph*, v. 132, p. 211–232.
- Beane, R. J., and Connelly, J. N., 2000, $^{40}\text{Ar}/^{39}\text{Ar}$, U-Pb, and Sm-Nd constraints on the timing of metamorphic events in the Maksyutov Complex, southern Ural Mountains: *Journal of the Geological Society, London*, v. 157, p. 811–822.
- Beane, R., and Leech, M., 2007, The Maksyutov Complex: The first UHP terrane 40 years later, in Cloos, M., Carlson, W. D., Gilbert, M. C., Liou, J. G., and Sorensen, S. S., eds., *Convergent margin terranes and associated regions: Boulder, CO, Geological Society of America Paper*, v. 419 (forthcoming).
- Beane, R. J. and Liou, J. G., 2005, Metasomatism in serpentinite mélange rocks from the high-pressure Maksyutov Complex, Southern Ural Mountains, Russia: *International Geology Review*, v. 47, p. 24–40.
- Beane, R. J., Liou, J. G., Coleman, R. G., and Leech, M. L., 1995, Petrology and retrograde P-T path for eclogite of the Maksyutov Complex, Southern Ural Mountains, Russia: *The Island Arc*, v. 4, p. 254–266.
- Bebout, G. E., and Barton, M., 1993, Metasomatism during subduction: Products and possible paths in the Catalina Schist, California: *Chemical Geology*, v. 108, p. 61–92.
- Becker, H., Jochum, K. P., and Carlson, R. W., 1999, Constraints from high-pressure veins in eclogites on the

- composition of hydrous fluids in subduction zones: *Chemical Geology*, v. 160, p. 291–308.
- Becker, H., Jochum, K. P., and Carlson, R. W., 2000, Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones: *Chemical Geology*, v. 163, p. 65–99.
- Bostick, B., Jones, R. E., Ernst, W. G., Chen, C., Leech, M. L., and Beane, R. J., 2003, Low-temperature microdiamond aggregates in the Maksyutov metamorphic complex, south Ural Mountains, Russia: *American Mineralogist*, v. 88, p. 1709–1717.
- Breeding, C. M., Ague, J. J., and Bröcker, M., 2004, Fluid-metasedimentary rock interactions in subduction-zone melange: Implications for the chemical composition of arc magmas: *Geology*, v. 32, p. 1041–1044.
- Brown, D., J. Alvarez-Marron, Perez-Estaun, A., Puchkov, V., Ayarza, P., and Gorozhanina, Y., 2001, Structure and evolution of the Magnitogorsk forearc basin: Identifying upper crustal processes during arc-continent collision in the Southern Urals: *Tectonics*, v. 20, p. 364–375.
- Brown, D., Juhlin, C., Alvarez-Marron, J., Perez-Estaun, A., and Oslinski, A., 1998, Crustal-scale structure and evolution of an arc-continent collision zone in the Southern Urals, Russia: *Tectonics*, v. 17, p. 158–171.
- Brown, D., and Spadea, P., 1999, Processes of forearc and accretionary complex formation during arc-continent collision in the Southern Ural Mountains: *Geology*, v. 27, p. 649–652.
- Catlos, E. J., and Sorensen, S. S., 2003, Phengite-based chronology of K- and Ba-rich fluid flow in two paleo-subduction zones: *Science*, v. 299, p. 92–95.
- Chibrikova, Y. V., and Olli, V., 1994, The finds of acritarchs from the metamorphic complex of the Ural-Tau range: A way to better knowledge and use the Bashkortostan interior: Ufa, Bashkortostan, Bashkortostan Academy of Science, 51 p. (in Russian).
- Davidson, J. P., 1987, Crustal contamination versus subduction zone enrichment: Examples from the Lesser Antilles and implications for mantle source compositions of island arc volcanic rocks: *Geochimica et Cosmochimica Acta*, v. 51, p. 2185–2198.
- Dixon, J. E., and Ridley, J. R., 1987, Syros, in Helgeson, H. C., ed., *Chemical transport in metasomatic processes*: Boston, MA, Reidel Publishing Company, p. 489–501.
- Dobretsov, N. L., 1974, Glaucofane schists and eclogite glaucofane-schist complexes in the USSR: Novosibirsk, USSR, Nauka Press, 429 p. (in Russian).
- Dobretsov, N. L., and Dobretsova, L. V., 1988, New mineralogic data on the Maksyutov eclogite-glaucophane schist complex, Southern Urals: *Transactions of the USSR Academy of Sciences: Earth Science Section*, v. 300, p. 111–116.
- Dobretsov, N. L., Shatsky, V. S., Coleman, R. G., Lennykh, V. I., Valizer, P. M., Liou, J. G., Zhang, R., and Beane, R. J., 1996, Tectonic setting and petrology of ultrahigh-pressure metamorphic rocks in the Maksyutov complex, Ural Mountains, Russia: *International Geology Review*, v. 38, p. 136–160.
- Elliott, T., and Plank, T., 1997, Subduction zone processing of oceanic crust: Houston, TX, Lunar and Planetary Institution, Contribution 921, p. 67.
- Ernst, W. G., Mosenfelder, J. L., Leech, M. L., and Liu, J., 1998, H₂O evolution during continental collision and ultrahigh-pressure metamorphism: Phase-equilibrium considerations: *EOS (Transactions, American Geophysical Union)*, v. 79, p. 355.
- Glodny, J., Bingen, B., Austrheim, H., Molina, J. F., and Rusin, A., 2002, Precise eclogitization ages deduced from Rb/Sr mineral systematics: The Maksyutov complex, Southern Urals, Russia: *Geochimica et Cosmochimica Acta*, v. 66, p. 1221–1235.
- Gromet, L. P., Dymek, R. F., Haskin, L. A., and Korotev, R. L., 1984, The “North American shale composite”: Its compilation, major and trace element characteristics: *Geochimica et Cosmochimica Acta*, v. 48, p. 2469–2482.
- Hamilton, W., 1970, The Uralides and the motion of the Russian and Siberian platforms: *Geological Society of America Bulletin*, v. 81, p. 2553–2576.
- Hawkins, A., Selverstone, J., Brearley, A., and Beane, R., 2005, Fishnet and atoll garnets from the Tauern Window, Eastern Alps: Conditions and mechanisms of formation [abs.]: *Geological Society of America, Abstracts with Programs*, v. 37, p. 226.
- Hetzel, R., 1999, Geology and geodynamic evolution of the high-P/low-T Maksyutov Complex, southern Urals, Russia: *Geologisches Rundschau*, v. 87, p. 577–588.
- Hetzel, R., Echter, H. P., Seifert, W., Schulte, B. A., and Ivanov, K. S., 1998, Subduction- and exhumation-related fabrics in the Paleozoic high-pressure-low-temperature Maksyutov Complex, Anting area, Southern Urals, Russia: *Geological Society of America Bulletin*, v. 110, p. 916–930.
- Hetzel, R., and Romer, R. L., 2000, A moderate exhumation rate for the high-pressure Maksyutov Complex, southern Urals, Russia: *Geological Journal*, v. 35, p. 327–344.
- Ivanov, K. S., Puchkov, V. N., Nadedkina, V. A., and Pelevin, L. A., 1989, First results on revised stratigraphy of the Polyakovka Formation based on conodonts, in *Yearbook-88: Sverdlovsk, USSR, Institute of Geology and Geochemistry, Uralian Department, USSR Academy of Sciences*, p. 12–13 (in Russian).
- Krasnobaev, A. A., Davudov, B. A., Lennykh, V. I., Tsherednitschenko, N. B., and Kosolov, W. J., 1995, The ages of zircons and rutiles from the Maksyutov Complex (preliminary data), in *Yearbook 1995: Yekaterinburg, Russia, Uralian Branch, Russian Academy of Sciences*, p. 13–16 (in Russian).
- Kretz, R., 1983, Symbols for rock-forming minerals: *American Mineralogist*, v. 68, p. 277–279.

- Krinizky, D. D., and Krinizkaya, W. M., 1961, Stratigraphy of metamorphic sequences along the middle part of the Sakmara River: *Materialy po geologii Yuznogo Urala*, v. 67, p. 167–174 (in Russian).
- Leech, M. L., 2001, Arrested orogenic development; eclogitization, delamination, and tectonic collapse: *Earth and Planetary Science Letters*, v. 185, p. 149–159.
- Leech, M. L., and Ernst, W. G., 1998, Graphite pseudomorphs after diamond? A carbon isotope and spectroscopic study of graphite cuboids from the Maksyutov Complex, south Ural Mountains, Russia: *Geochimica et Cosmochimica Acta*, v. 62, p. 2143–2154.
- Leech, M. L., and Ernst, W. G., 2000, Petrotectonic evolution of the high- to ultrahigh-pressure Maksyutov Complex, Karayanova area, south Ural Mountains, Russia: Structural and oxygen isotopic constraints: *Lithos*, v. 52, p. 235–252.
- Leech, M. L., and Stockli, D. F., 2000, The late exhumation history of the ultrahigh-pressure Maksyutov Complex, south Ural Mountains, from new apatite fission track data: *Tectonics*, v. 19, p. 153–167.
- Leech, M. L., and Willingshofer, E., 2004, Thermal modeling of an ultrahigh-pressure complex in the south Urals: *Earth and Planetary Science Letters*, v. 226, p. 85–99.
- Lennykh, V. I., and Valizer, P. M., 1986, Lawsonite rodingite of the Maksyutov eclogite-glaucophane schist complex: *Geologia i Geokhimiya*, p. 73–76.
- Lennykh, V. I., Valizer, P. M., Beane, R. J., Leech, M. L., and Ernst, W. G., 1995, Petrotectonic evolution of the Maksyutov Complex, south Urals, Russia: Implications for ultrahigh-pressure metamorphism: *International Geology Review*, v. 37, p. 584–600.
- Liou, J. G., Zhang, R. Y., Ernst, W. G., Rumble, D., and Maruyama, S., 1998, High-pressure minerals from deeply subducted metamorphic rocks: *Reviews in Mineralogy and Geochemistry*, v. 37, p. 33–96.
- Maslov, V. A., Cherkasov, V. L., Tischenko, V. T., Smirnova, A. I., Artyushkova, O. V., and Pavlov, V. V., 1993, On the stratigraphy and correlation of the Middle Paleozoic complexes of the main copper-pyritic areas of the southern Urals: Ufa, Russia, Ufa Scientific Center (in Russian).
- Meschede, M., 1986, A method of discriminating between different types of mid-ocean ridge basalts and continental tholeiites with the Nb-Zr-Y diagram: *Chemical Geology*, v. 56, p. 207–218.
- Plank, T., 2005, Constraints from thorium/lanthanum on sediment recycling at subduction zones and the evolution of the continents: *Journal of Petrology*, v. 46, p. 921–944.
- Plank, T., and Langmuir, C. H., 1993, Tracing trace elements from sediment input to volcanic output at subduction zones: *Nature*, v. 362, p. 739–742.
- Puchkov, V. N., 1993, The paleo-oceanic structures of the Ural Mountains: *Geotectonics*, v. 27, p. 184–196.
- Puchkov, V. N., 1997, Structure and geodynamics of the Uralian orogen, in Burg, J. P., and Ford, M., eds., *Orogen through time: Geological Society Special Publications*, v. 121, p. 201–236.
- Savelieva, G. N., and Nesbitt, R. W., 1996, A synthesis of the stratigraphic and tectonic setting of the Uralian ophiolites: *Journal of the Geological Society of London*, v. 153, p. 525–537.
- Schulte, B. A., and Blumel, P., 1999, Metamorphic evolution of eclogite and associated garnet-mica schist in the high-pressure metamorphic Maksyutov Complex, Ural, Russia: *Geologisches Rundschau*, v. 87, p. 561–576.
- Schulte, B., and Sindern, S., 2002, K-rich fluid metasomatism at high-pressure metamorphic conditions: Lawsonite decomposition in rodingitized ultramafite of the Maksyutov Complex, Southern Urals (Russia): *Journal of Metamorphic Geology*, v. 20, p. 529–541.
- Shatsky, V. S., Jagoutz, E., and Koz'menko, O. A., 1997, Sm-Nd dating of the high-pressure metamorphism of the Maksyutov Complex, southern Urals: *Transactions of the Russian Academy of Sciences, Earth Science Section*, v. 353, p. 285–288.
- Sorensen, S. S., 1989, Petrology of amphibolite-facies mafic and ultramafic rocks from the Catalina Schist, southern California: Metasomatism and migmatization in a subduction zone metamorphic setting: *Journal of Metamorphic Geology*, v. 6, p. 405–435.
- Sorensen, S. S., 1991, Petrogenetic significance of zoned allanite in garnet amphibolites from a paleo-subduction zone: Catalina Schist, southern California: *American Mineralogist*, v. 76, p. 589–601.
- Sorensen, S. S., and Grossman, J. N., 1989, Enrichment of trace elements in garnet amphibolites from a paleo-subduction zone: Catalina Schist, Southern California: *Geochimica et Cosmochimica Acta*, v. 53, p. 3155–3177.
- Sorensen, S. S., and Grossman, J. N., 1993, Accessory minerals and subduction zone metasomatism: A geochemical comparison of two mélanges (Washington and California, U.S.A.): *Chemical Geology*, v. 110, p. 269–297.
- Sorensen, S. S., Grossman, J. N., and Perfit, M. R., 1997, Phengite-hosted LILE enrichment in eclogite and related rocks: Implications for fluid-mediated mass transfer in subduction zones and arc magma genesis: *Journal of Petrology*, v. 38, p. 3–34.
- Spadea, P., D'Antonio, M., Kosarev, A., Gorozhanina, Y., and Brown, D., 2002, Arc-continent collision in the Southern Urals: Petrogenetic aspects of the forearc-arc complex: *Geophysical Monograph*, v. 132, p. 101–134.
- Spadea, P., Kabanova, L. Y., and Scarrow, J. H., 1998, Petrology, geochemistry and geodynamic significance of Mid-Devonian boninitic rocks from the Baimak-Buribai area (Magnitogorsk zone, southern Urals): *Ophioliti*, v. 23, p. 17–36.

- Spry, A., 1969, *Metamorphic textures*: Oxford, UK: Oxford University Press, 350 p.
- Sun, S. S., 1980, Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands, and island arcs: *Philosophical Transactions of the Royal Society of London, Series A: Mathematical and Physical Sciences*, v. 297(1431), p. 409–445.
- Sun, S. S., and McDonough, W. F., 1989, Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes: *Geological Society, London, Special Publications*, v. 42, p. 313–345.
- Sunblad, K., Bibikova, E., Kontar, E., Neymark, L., Bechkolmen, M., and Prokin, V. A., 1996, Source of lead in sulphide ores in the Urals [abs.]: *EUROPROBE Uralides Workshop, Granada, Programme with Abstracts*, p. 12.
- Tatsumi, Y., and Eggins, S., 1995, *Subduction zone magmatism*: Cambridge, MA, Blackwell Scientific, *Frontiers in Earth Sciences Series*, 205 p.
- Volkova, N. I., Frenkel, A. E., Budanov, V. I., and Lepezin, G. G., 2004, Geochemical signatures for eclogite protoliths from the Maksyutov Complex, South Urals: *Journal of Asian Earth Sciences*, v. 23, p. 745–759.
- Wood, D. A., 1980, The application of a Th-Hf-Ta diagram to problems of tectonomagmatic classification and to establishing the nature of crustal contamination of basaltic lavas of the British Tertiary volcanic province: *Earth and Planetary Science Letters*, v. 50, p. 11–30.
- Woodhead, J., Eggins, S., and Gamble, J., 1993, High field strength and transition element systematics in island arc and back-arc basin basalts: Evidence for multiphase melt extraction and a depleted mantle wedge: *Earth and Planetary Science Letters*, v. 114, p. 491–504.
- Zack, T., Rivers, T., and Foley, S. F., 2001, Cs-Rb-Ba systematics in phengite and amphibole: An assessment of fluid mobility at 2.0 GPa in eclogites from Trescolmen, Central Alps: *Contributions to Mineralogy and Petrology*, v. 140, p. 651–669.
- Zonenshain, L. P., Korinevsky, V. G., Kazmin, V. G., Pecherskiy, D. M., Khain, V. V., and Matveyenkov, V. V., 1984, Plate tectonic model of the South Urals development: *Tectonophysics*, v. 109, p. 95–135.
- Zonenshain, L. P., Kuzmin, M. I., and Natapov, L. M., 1990, *Geology of the USSR: A plate-tectonic synthesis*, in Page, B. M., ed., *American Geophysical Union Geodynamics Series*, v. 21, 242 p.