PETROTECTONIC EVOLUTION OF THE MAKSYUTOV COMPLEX,
SOUTH URAL MOUNTAINS, RUSSIA

A DISSERTATION
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AND ENVIRONMENTAL SCIENCES
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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Thesis Abstract

The high- to ultrahigh-pressure (UHP) Maksyutov subduction complex extends 200 km along-strike in the footwall of the Main Uralian fault in the south Ural Mountains. The complex consists of three main units tectonically juxtaposed in this continental-collision suture zone: an eclogite-bearing gneiss (Unit #1); the intermediate-grade Yumaguzinskaya metasedimentary unit containing no eclogite; and a meta-ophiolite mélange (Unit #2). Field work shows that Unit #1 contains boudins of eclogite, layers of eclogitic gneiss, and rare ultramafic bodies within host metasedimentary mica-schist and quartzite; Unit #2 consists of lenses of serpentinite melange and blocks of metasomatic rock (~rodingite), metabasalt, and Ordovician-to-Silurian marble within mica schist and graphite quartzite host rock.

A structural/petrologic cross-section through the Karayanova area yields new quantitative data for the complex and, regionally, for the south Urals. Structural analysis has identified the major structures; regional folding within the complex is parallel to the dominant foliation trending northeast-southwest. Stereonet data show that, during exhumation, this large-scale folding was refolded about axes trending southeast. Unit #1 and the Yumaguzinskaya unit are tectonically and petrologically distinct units juxtaposed by west-vergent thrusting and recrystallization within the same subduction zone; a shear zone developed later between Unit #2 and the Unit #1/Yumaguzinskaya tectonic package accompanying exhumation. Field relations and petrofabric examination of eclogite- and blueschist-facies assemblages demonstrate that blueschist-facies recrystallization overprinted an earlier eclogite-facies metamorphism. Thermobarometric measurements yield P-T values of 594-637° C, 1.5-1.7 GPa for eclogite, but these possibly reflect annealing conditions during the early-stage exhumation at ~375 Ma. Cuboid graphite aggregates may testify to precursor conditions for Unit #1 within the diamond stability field, if such textures are correctly interpreted.
Measured $^{18}$O/$^{16}$O partitioning between pairs of coexisting phases yield three main recrystallization temperature ranges: (1) $587 \pm 109^\circ$ C, attending Unit #1 eclogite-facies metamorphism; (2) $453 \pm 17^\circ$ C, during transitional blueschist-/greenschist-facies metamorphism for the amalgamated Unit #1/Unit #2 assembly; and (3) $250 \pm 68^\circ$ C, reflecting late-stage hydrothermal alteration and exhumation. Oxygen isotope data for units #1 and #2 indicate that garnet, blue amphibole, and pyroxene crystallized in isotopic equilibrium, validating previous thermobarometric calculations for a Unit #1 retrograde metamorphic event. Variation in $\delta^{18}$O/$^{16}$O values for phengites suggests the possibility of late metamorphic fluid infiltration. Retrograde recrystallization at high-pressure in the presence of fluids and a calculated slow exhumation rate for the Maksyutov accounts for the fact that relict UHP coesite and diamond have not have been preserved during decompression.

Fifteen apatite fission-track samples were taken along a 70 km north-south transect from Maksyutovo to Shubino, from a 5 km east-west traverse at Karayanova, and from the hanging wall of the Main Uralian fault near Novopokrovka. I present apatite fission-track ages that for Unit #1 range from $236 \pm 14$ Ma to $265 \pm 16$ Ma and for $210 \pm 12$ Ma to $311 \pm 45$ Ma for Unit #2; one sample from the Yumaguzinskaya unit yields an age of $261 \pm 17$ Ma. Two hanging wall samples from Ordovician sedimentary rocks give ages of $198 \pm 15$ Ma and $279 \pm 36$ Ma. Confined track length data show unimodal distributions with mean track lengths ranging from 12.2 $\mu$m to 14.0 $\mu$m showing that all samples underwent partial annealing. Modelling results indicate that the Maksyutov Complex was exhumed and cooled below $110^\circ$ C en masse in the Late Carboniferous (~$315$ Ma). The east-west transect at Karayanova shows that there was no inter-unit movement in the Maksyutov Complex after about $315$ Ma indicating that the three units of the Maksyutov Complex must have been tectonically juxtaposed after the Early to Middle Devonian HP-UHP event that effected Unit #1 and before $315$ based on higher temperature thermochronometers; the entire Maksyutov Complex must have been assembled between $335$ Ma and $315$ Ma.
Hanging wall samples from near the southeast contact of the Maksyutov Complex give some evidence for minor movement along the MUF until about 300 Ma. The new fission-track ages presented here limit late-stage exhumation rates to no more than 2.5 mm/yr, much slower than reported exhumation rates for other UHP terranes.

Unusual cuboid graphite aggregates (up to 13 mm edge length) from the eclogitic gneiss unit of the Maksyutov Complex deflect a foliation defined by groundmass graphite and phengite, and pressure shadows have developed around these blocky aggregates. Carbon isotope ratios, $\delta^{13}C/^{12}C$ vs. VPDB, for the cuboid graphite range from about -24 to -42‰, demonstrating that these rocks have retained an original biogenic carbon signature. X-ray diffraction, laser Raman spectroscopy, infrared spectroscopy, and transmission electron microscopy indicate that graphite is well-crystallized with minor defects; no relict organic compounds were detected. Comparisons of these cuboid aggregates with thin sections and scanning electron microscope images of proven graphitized diamonds from the Beni Bousera peridotite massif show that Maksyutov graphite is similar. Laboratory experiments by other workers on graphite demonstrate that this intriguing morphology could not be the result of deformation, because graphite returns to its original shape and size on stress release. Existing experiments on diamond graphitization do not adequately replicate the conditions of natural rocks being exhumed from subduction zones characterized by ultrahigh pressures, and thus cannot be applied with confidence to the Maksyutov Complex. Our spectroscopic and microscopic studies suggest that these cuboid aggregates probably are diamond pseudomorphs.
Preface

This thesis represents five years of work on the Maksyutov Complex, south Ural Mountains, Russia, including field work and data collection, sample preparation and analysis, and manuscript preparation. There are three chapters in this thesis: each chapter was written as independent papers, and each stands alone by addressing particular scientific issues. Chapter 1 is in review for *Lithos* (authors: Mary L. Leech and W. G. Ernst); Chapter 2 has been accepted pending revisions to *Tectonics* (authors: Mary L. Leech and Daniel F. Stockli); and Chapter 3 was published in *Geochimica et Cosmochimica Acta* (authors: Mary L. Leech and W. G. Ernst, *Geochim. Cosmochim. Acta*, 62, 2143-2154, 1998).

The manuscripts that have been or will be published from this thesis have more than one author. Data collection, analysis, interpretation, and manuscript preparation were done by me to a great extent, but fission track counting and measuring was completed by my co-author, Daniel Stockli. Co-authorship is a result of valuable discussions with, and reviews by, the co-authors.
Acknowledgments

I am a product of San José State University and proud of it! I think they did a
damn good job preparing me for my geology career and I think I've proven to a few people
that successful scientists come from schools that aren't Ivy League. I will never forget
something that Richard Sedlock said about me (it wasn't said directly to me but had a big
impact nonetheless); he mentioned to a friend of mine that he thought I was "a natural" at
structural geology. I know it doesn't seem like much, but that statement made me feel
good and confident about myself, even if just for a moment. No one in geology has ever
said anything like that to me again. What a simple thing to do - to praise someone's ability
- that I can look back on and try to convince myself that, yes, I can do it.

When I finished my Bachelor of Science at San José State University, I thought I
would be doing graduate research in structural geology. Before I ever arrived at Stanford,
I was communicating with Louie Liou and Gary Ernst about the possibility of my doing
field work in two ultrahigh-pressure terranes in Kazakhstan and Russia. I didn't know
what ultrahigh-pressure metamorphism was, I had taken one semester of petrology that
included only a few weeks studying metamorphic rocks, and I had never been out of the
country (except for Canada which doesn't count), but I gave it a shot. My learning curve
was very steep. Looking back though, I would not have changed a thing.

This research would not have been possible without the financial, technical, and
moral support from many organizations and individuals. First, I would like to thank the
Department of Geological and Environmental Sciences for supporting me during my first
year at Stanford. For the next three years of my graduate career, my research was
supported by a National Science Foundation Minority Graduate Fellowship (a now extinct
program unfortunately). I was proud to receive a Lieberman Fellowship from Stanford
University for the fifth and last year of my Ph.D. research; it seemed a fitting tribute to my
grandmother who died from ALS during my graduate school application process.
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How can I possibly start to thank the friends I’ve made at Stanford? I can’t begin to try to name them all here, but I must mention Laura Webb, Brad Ritts, and Ben Surpless who helped initiate and perpetuate our regular “afternoon breakie-breaks” that prepared us in such a wonderful way to loosen up our minds for seminar discussions and act as a mental enema for writing. Jeremy Hourigan, Todd Greene, and Betsy Mason were all good (and bad in a good way) influences who helped keep things fun. Even when I started to feel like a crusty, old graduate student, there were folks like Cindy Martinez (in their post-orals not-quite-a-slump) made sure I took a break to relax once in a while.

I have new-found regard for Crustal Geophysics group friends, Norm Sleep and George Thompson, who challenge the petrologist’s views of the way things work, keep the geologists honest, and who we wouldn’t want to do without.

My family has been a constant source of support while I’ve been a graduate student. They worried about me when I travelled to Kazakhstan, Russia, and China; took...
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INTRODUCTION

This thesis presents the first confirmation of ultrahigh-pressure (UHP) metamorphism in the Ural Mountains, and provides the pressure-time-temperature history of the UHP Maksyutov Complex that is necessary to understand the causes and environments of UHP metamorphism.

IMPORTANCE OF UHP METAMORPHISM

Definition

Ultrahigh-pressure (UHP) metamorphism is defined as metamorphism of crustal rocks to pressures great enough to crystallize the index minerals coesite (a high-pressure polymorph of quartz requiring a minimum $P > 2.7$ GPa) and/or diamond. Before 1984, coesite and diamond were thought to occur only in meteorite impact craters and mantle xenoliths.

Occurrences

Thus far, only five terranes subjected to ultrahigh pressure have been recognized worldwide. The Kokchetav Massif in northern Kazakhstan, the Sulu-Dabie belt in east-central China, the Dora Maira Massif in the Italian Alps, and the Western Gneiss Region in coastal Norway are UHP terranes with confirmed coesite, coesite pseudomorphs and, in the case of the Kokchetav occurrence, diamond (Sobolev and Shatsky, 1990). Rare occurrences of microdiamond inclusions have also been described from the Dabie Shan (Xu et al., 1992; Okay, 1993) and from the Western Gneiss Region (Dobrzhinetskaya et al., 1995). Reports of coesite pseudomorphs from the Maksyutov Complex in the south Ural Mountains of Russia (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988) suggest that these rocks, too, have been metamorphosed at ultrahigh pressures. Recently I have shown that cuboid graphite aggregates from Maksyutov are probably
pseudomorphic after diamond (Leech and Ernst, 1998), indicating even higher pressures for this terrane (>3.2 GPa) than previously thought.

**Importance of UHP metamorphism**

The discovery of coesite and diamond in upper-crustal rocks promises to revolutionize our understanding of continental collision zones (e.g. Liou et al., 1994; Coleman and Wang, 1995; Hacker and Liou, 1998). The processes by which buoyant continental crust is subducted to depths exceeding 100 km and later returned to the surface are not yet well known. Ultrahigh pressure terranes record a complete geodynamic path that challenges our beliefs about subduction, exhumation, continental collision and growth, and crust/mantle interactions.

**UHP questions and outstanding problems**

While our knowledge of UHP terranes has vastly improved since the first reports of coesite and coesite pseudomorphs (e.g. Chesnokov and Popov, 1965; Chopin et al., 1984; Smith, 1984; Wang et al., 1989), many questions still need answering:

(1) What tectonic processes can subduct low-density continental rocks into the upper mantle?

(2) What mechanisms are responsible for exhuming UHP rocks? Is this a structural problem or related to buoyancy and the kinetics of metamorphic reactions?

(3) What exhumation rates are required to preserve UHP mineralogy?

(4) Why does UHP metamorphism occur in so few orogens worldwide? Is this limited by the subduction process (creation) or by the exhumation process (preservation)?

One approach to constraining the problems is to study extreme cases. The Urals are apparently unique in having eclogite expanses along strike for 2000 km, thereby forcing us to address 2D mechanics for UHP creation, rather than always appealing to local 3D plate tectonic complexities to explain areally limited UHP occurrences. Exhumation along a long
plate boundary may result from 3D effects when an entire plate edge fails to collide coevally; the slab may pivot in a way that, although there is a net downward movement of high density material, parts of the slab (i.e., a promontory on the East European platform) along with the associated crustal rocks are returned to shallow depth.

**THE URALS AS A NATURAL LABORATORY FOR UHP STUDIES**

**Development of the Ural Mountains**

The Ural Mountains differ from other Paleozoic orogens (e.g. the Variscides, Caledonides, and Appalachians) in their great crustal thickness, up to 55 km, and low mean elevation of no more than 500 m, preserving a collisional structure that lacks large-scale late-orogenic extension (Dewey et al., 1988; Berzin et al., 1996; Echtler and Hetzel, 1997; Knapp et al., 1998). The Urals are a 2000-km long, 400-450 km-wide orogen formed by oblique collision between the East European platform and microcontinental blocks to the east during Late Devonian to Permian time (Zonenshain et al., 1984, 1990; Coleman et al., 1993; Puchkov, 1997). The Uralian collision began in the south in the Late Devonian, possibly pivoting on an East European platform promontory in the central Urals, and finally reaching full-collision in the polar Urals in the Late Permian. The eastern and northern regions of the mountain belt also experienced a Mid-Jurassic deformation. While all west-east tectonic zones from the foreland fold-and-thrust belt to the East Uralian Zone are exposed in the southern Urals, the eastern zones of the north Urals are covered by Mesozoic and Cenozoic sedimentary rocks from the West Siberian basin. The main ophiolitic suture of the Urals is the Main Uralian fault (MUF); rocks to the west have protolith affinities with the East European platform and form the high-pressure (HP) and UHP belt; rocks to the east are low-grade (greenschist) island-arc complexes.
Introduction

South Urals

The UHP Maksyutov Complex extends 200 km north-south in the south Urals on the west side of the MUF (Fig. 1). This region is geophysically well-known as a result of the 200-km-long URSEIS seismic reflection/refraction profile, which provides evidence for the large crustal thickness and probably existence of an eclogitic crustal root (Berzin et al., 1996; Carbonell et al., 1996; Echtler et al., 1996; Juhlin et al., 1996; Knapp et al., 1996). The metasedimentary protolith to the Maksyutov Complex rifted from the East European craton in the Early to Middle Ordovician. Basaltic rocks from 397 ± 20 Ma pre-Uralian oceanic crust (Edwards and Wasserburg, 1985) were incorporated into Maksyutov host metasediments during subduction either by inclusion in the subduction zone or by intrusion of dikes during rifting and oceanic crust formation (Savelieva et al., 1997).

Garnet and clinopyroxene thermobarometry on Maksyutov eclogites yield an equilibrium temperatures ranging from 594° to 637° C and minimum pressure estimates of 1.5 to 1.7 GPa (Beane et al., 1995; Lennykh et al., 1995; Leech and Ernst, 1998), or up to 2.7 GPa if coesite pseudomorphs (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988) are indeed present. These reports of coesite pseudomorphs have not been confirmed; however, my work shows that unusual graphite aggregates may be pseudomorphs after diamond which substantiates the Russian claims of UHP metamorphism (Leech and Ernst, 1998). Thermobarometric estimates on eclogites may represent annealing during slow exhumation during which minerals re-equilibrated at lower P-T conditions, leaving little evidence of UHP metamorphism. Leech and Stockli (in review) report fission-track ages limiting exhumation rates to less than 1.5 mm/yr.

Central Urals

The central Urals are characterized by a major bend in the linear trend of the mountain belt, probably the result of a salient on the East European platform. This region of the Urals is characterized by the greatest amount of shortening and is dominated by

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Figure 1. Tectonostratigraphic map of the Ural Mountains showing the belt of high-pressure/low-temperature complexes (modified after Puchkov, 1989; 1997). URSEIS, ESRU, and QUARTZ-PNE are deep seismic profiles.
Introduction

gneiss complexes (Echtler et al., 1997b). The ESRU seismic profile shows at least a 45-km crustal thickness in this area (Juhlin et al., 1996).

The Ufaley Complex west of the MUF shares the same structural position as the Maksyutov Complex but is characterized by high-pressure/low-temperature (HP-LT) metamorphic assemblages, i.e. a lower metamorphic grade probably representing a shallower fragment of the same subducting slab. Peak metamorphic conditions for East Ufaley have been reported as 950-1200°C and 3.0-3.5 GPa (Belkovski, 1984; 1986, cit. Echtler et al., 1997b) suggesting possible UHP metamorphism but later metasomatism (and presumably recrystallization) at lower P-T conditions. The few radiometric data that exist are K-Ar ages that range between 300-400 Ma (Ovchinnikov, 1963; Harris, 1977, cit. Echtler et al., 1997b).

Fission-track dating in the central Urals shows a regional cooling event occurred between ~280 and 210 Ma; a small temperature increase from about 210 to 110 Ma is interpreted as caused by burial in the Late Jurassic and Cretaceous (Seward et al., 1997). Modelling of fission-track data indicates that denudation began again in the Late Cretaceous. The combination of fission-track ages and K-Ar data suggest that central Urals metamorphic complexes were exhumed very slowly (i.e., >>1mm/yr) like the Maksyutov Complex and probably do not preserve UHP indicator minerals.

Polar Urals

Much remains to be known about the polar Urals. Rocks are classed as Precambrian on Russian maps simply because they are high-grade (Puchkov, 1997). The QUARTZ-PNE refraction profile confirms that the Uralian crustal root extends into the Polar Urals (Schueller, et al., 1997). The Urals remained one of the least accessible areas of the former Soviet Union (FSU) until the early 1990s. Most publications are hidden in obscure Russian journals and lack essential details, for example precise sample locations or details of standards and error analyses for geochronological data. While individual
Introduction

scientists are excellent, many Russian labs use out-dated techniques and instrumentation, for example ages by K-Ar rather than by the more accurate $^{40}\text{Ar}/^{39}\text{Ar}$ method. Although Russian structural interpretations and thermochronologic analyses have been hindered by the Russian bureaucracy and economic problems, their geology maps and petrography are excellent. Thus beyond a basic knowledge, the Urals remain near-virgin territory for scientific exploration.

QUESTIONS TO BE ADDRESSED

The Urals may be unique in that deep-seated rocks (HP and/or UHP) are exposed along the entirety of the mountain belt. In contrast, the western part of the Dabie Shan is metamorphosed only to greenschist facies conditions, and the UHP rocks of the Caledonides are localized in the Western Gneiss Region probably as a result of a different exhumation mechanism acting in those areas. This dissertation research and upcoming postdoctoral work attempts to offer new insight into why we find UHP rocks where we do and why they do not occur in all orogens. The next stage in my research will be to use a combination of petrography, geochemistry, and thermochronology to establish along-strike constraints in the polar Ural Mountains on the following questions related to the Uralian orogen:

(1) What is the timing of collision, metamorphism, and exhumation in the Urals and what was the rate of exhumation of these HP rocks? I will establish P-T-t paths using thermobarometry and radiogenic dating techniques to constrain the exhumation history and rate for polar Urals samples (e.g. Leech and Stockli, in review).

(2) Why do we see evidence for UHP metamorphism in the south and possibly central Urals (Leech and Ernst, 1998, Belkovski, 1984; 1986, cit. Echtler et al., 1997b) but there are no reports from the HP belt in the polar Urals? Is this just an artifact of an as-yet limited study? What are the along-strike variations in the Urals? I will compare P-T-t paths
and thermochronologic data along the orogen and calculate exhumation rates to determine where and why UHP rocks are preserved.

(3) By what mechanism(s) do low-density continental rocks subduct into the upper mantle and what are the tectonic mechanisms responsible for the exhumation of UHP rocks? This problem may be related to slab buoyancy and the kinetics of metamorphic reactions. I will search for prograde and retrograde P-T-t paths in polar Urals samples (though in the south Urals these are overprinted by later metamorphism and deformation), and constrain the exhumation history for the region.

(4) What is the relationship between metamorphism and deformation in the Urals? I will use petrography in conjunction with microstructural studies (e.g. Leech et al., 1996) to relate the metamorphic and structural history in these samples. This data may offer insight into the mechanism for exhumation.
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Chapter 1: Petrotectonic evolution of the Maksyutov Complex

Chapter 1

Petrotectonic evolution of the ultrahigh-pressure Maksyutov Complex, south Ural Mountains: Structural and isotopic constraints

Has been submitted under the same title, by Mary L. Leech and W. G. Ernst, to Lithos

ABSTRACT

The Maksyutov Complex consists of three fault-bounded lithologic units: a quartzofeldspathic gneiss containing mafic eclogite boudins (Unit #1); a metasedimentary blueschist-facies (Yumaguzinskaya) unit; and a meta-ophiolitic mélangé (Unit #2). The geologic history of the putative ultrahigh-pressure (UHP) assembly of the Maksyutov Complex is complicated by several stages of prolonged retrograde metamorphism and deformation. The Sakmara River exposes all three units near the former village of Karayanova. A structural/petrologic cross-section through the area yields new quantitative data for the complex and, regionally, for the south Urals. Analysis of the Karayanova area has identified the major structures; regional folding within the complex is parallel to the dominant foliation trending northeast-southwest. Stereonet data show that, during
exhumation, this large-scale folding was refolded about axes trending southeast. Unit #1 and the Yumaguzinskaya unit are tectonically and petrologically distinct units juxtaposed by west-vergent thrusting and recrystallization within the same subduction zone; a shear zone developed later between Unit #2 and the Unit #1/Yumaguzinskaya tectonic package accompanying exhumation. Field relations and petrofabric examination of eclogite- and blueschist-facies assemblages demonstrate that blueschist-facies recrystallization overprinted an earlier eclogite-facies metamorphism. Thermobarometric measurements yield P-T values of 594-637°C, 1.5-1.7 GPa for eclogite, but these possibly reflect annealing conditions during the early-stage exhumation at -375 Ma. Cuboid graphite aggregates may testify to precursor conditions for Unit #1 within the diamond stability field, if such textures are correctly interpreted. Measured $^{18}$O/$^{16}$O partitioning between pairs of coexisting phases yield three main recrystallization temperature ranges: (1) $587 \pm 109$° C, attending Unit #1 eclogite-facies metamorphism; (2) $453 \pm 17$° C, during transitional blueschist-/greenschist-facies metamorphism for the amalgamated Unit #1/Unit #2 assembly; and (3) $250 \pm 68$° C, reflecting late-stage hydrothermal alteration and exhumation. Oxygen isotope data for units #1 and #2 indicate that garnet, blue amphibole, and pyroxene crystallized in isotopic equilibrium, validating previous thermobarometric calculations for a Unit #1 retrograde metamorphic event. Variation in $\delta^{18}$O/$^{16}$O values for phengites suggests the possibility of late metamorphic fluid infiltration. Retrograde recrystallization at high-pressure in the presence of fluids and a calculated slow exhumation rate for the Maksyutov Complex accounts for the fact that relict UHP coesite and diamond have not have been preserved during decompression.

INTRODUCTION

Most reports on the Maksyutov subduction complex focus on the petrology of the high- to ultrahigh-pressure (HP-UHP) eclogitic unit; this is the lithology from which the first descriptions of coesite pseudomorphs were reported by Chesnokov and Popov.
Chapter 1: PetroTECTonic evolution of the Maksyutov Complex

(1965). Until recently, little was known about the overall structure and deformational history of the complex and its relationship to an exhumation mechanism. In this paper, we combine petrological, geochemical, and structural components of the Maksyutov Complex in order to develop an overall model for the development of the complex within the context of metamorphism and deformation. A complete cross-section through the Maksyutov Complex is exposed near Karayanova, along the Sakmara River, showing the structural relationship between all three units and exposing most rocks types in a small area (Fig. 1). Previously, the only study incorporating significant structural data for the complex concentrated on a transect through Antingan, an area lacking extensive exposure, several kilometers southeast of the Karayanova area (Hetzel et al., 1998). We focus on the eclogitic Unit #1 which preserves the history of the Maksyutov Complex since the HP-UHP metamorphism.

Leech and Ernst (1998) investigated graphite cuboids from metapelites which may represent pseudomorphs after diamond, thus suggesting the possibility of UHP metamorphism for Unit #1; although still problematic, we will refer to the highest-pressure metamorphic event as the UHP event. Most likely, slow exhumation relative to other UHP terranes and the influx of aqueous fluids caused UHP index phases to re-equilibrate at lower P-T conditions, explaining the lack of relict coesite or diamond in the Maksyutov Complex (Hacker and Peacock, 1995; Ernst et al., 1997; Webb et al., in review). Preservation of micro-diamond relics, chiefly as armored micro-inclusions in garnet and zircon which act as pressure vessels, requires an exhumation rate so rapid that the diamond-bearing rocks did not reside at depth long enough to re-equilibrate to graphite (Sobolev and Shatsky, 1990; Sobolev et al., 1994).
Figure 1. Map of Karayanova area geology with structural data superimposed; the cross section shows the large-scale relationship between units (no vertical exaggeration). Equal area stereonets showing structural data for the Karayanova area including (#1) poles to \( S_{UHP} \) foliation in Unit #1 with a \( \pi \)-axis (pole to the great circle) showing trend of \( F_{EF} \) folding; (Sta. 3) poles to \( S_{UHP} \) foliation and a \( \pi \)-axis to small-scale folding at station 3; (Yum) poles to foliation for the Yumaguzinskaya unit; (#2) poles to foliation and \( \pi \)-axis in Unit #2; and (F.A.) fold axes for Units #1 and #2 and their corresponding \( \pi \)-axes for the \( F_{BF} \) folding event.
Chapter 1: PetroTECToNIC evolution of the Maksyutov Complex

GEOLOGIC SETTING

Development of the Ural Mountains

The Urals are an approximately 2,300-km long, 400 km-wide orogen formed by oblique collision between the East European platform and microcontinental and cratonal blocks on the east during the Late Paleozoic (Zonenshain et al., 1984, 1990; Lennykh et al., 1995; Dobretsov et al., 1996; Puchkov, 1997). The Uralian collision began in the south in the Late Devonian, possibly pivoting on an East European platform promontory in the central Urals, and finally reaching full-collision in the polar Urals in the Late Permian. The major suture of the Urals is the ophiolitic Main Uralian fault (MUF); rocks to the west have protolith affinities with the East European platform and form the high-pressure (HP) and UHP subduction belt, whereas rocks to the east are low-grade (greenschist-facies) island-arc complexes that developed on the hanging-wall plate.

The Maksyutov Complex extends more than 120 km north-south in the south Urals in the footwall of the MUF. The metasedimentary protolith of the Maksyutov Complex rifted from the East European platform in the Early to Middle Ordovician. Basaltic rocks of pre-Uralian oceanic crust affinity were incorporated into these host metasediments at around 400 Ma during plate convergence, either by inclusion in the subduction zone or by intrusion of dikes during rifting and oceanic crust formation (Edwards and Wasserburg, 1985; Savelieva et al., 1997). For a detailed examination of the surrounding geology of the mountain belt, see Brown et al. (1996).

Overview of the Maksyutov Complex

The Maksyutov Complex consists of three main fault-bounded units: an eclogite-bearing gneiss, Unit #1; the intermediate metamorphic grade metasedimentary Yumaguzinskaya Unit; and a meta-ophiolite mélange, Unit #2 (Fig. 1). Unit #1 contains boudins of eclogite, layers of eclogitic gneiss, and very rare ultramafic bodies within host metasedimentary garnet gneiss, mica schist, and quartzite. The Yumaguzinskaya contains

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similar rock types to Unit #1, but is metamorphosed to no more than lower blueschist facies and contains no mafic rocks; it apparently represents a higher crustal level than the UHP Unit #1. Unit #2 consists of lenses of serpentinite mélangé and blocks of metasomatic rock (~rodingite), metabasalt, and Ordovician/Silurian marble within mica schist and graphite quartzite host rocks (Dobretsov et al., 1996); peak metamorphism for Unit #2 was transitional greenschist/blueschist facies. Unit #2 and the Yumaguzinskaya, considered to tectonically overlie Unit #1 (Lennykh et al., 1995), were juxtaposed with Unit #1 in the subduction zone after the Early to Middle Devonian UHP metamorphic event that affected only Unit #1 (Matte et al., 1993; Beane et al., 1995; Beane, 1997). All three units subsequently were overprinted by a late, low-pressure, greenschist-facies metamorphism and folded together about NE-SW trending axes.

Fe-Mg exchange geothermometry calculated for garnet and clinopyroxene (Powell, 1985) yields an equilibrium temperature ranging from 594° to 637° C for eclogites from Unit #1. Minimum pressure estimates using the jadeite component of clinopyroxene (Holland, 1980) range from 1.5 to 1.7 GPa (Beane et al., 1995; Hetzel et al., 1998; Leech and Stockli, in review), but may be as high as 3.1 GPa if the graphite aggregates described by Leech and Ernst (1998) are, in fact, pseudomorphs after diamond. It is also possible that these thermobarometric values may represent annealing during exhumation whereby minerals re-equilibrated under lower P-T conditions, leaving little evidence of the earlier UHP metamorphism.

**Occurrence and ages of ultrahigh-pressure(?) metamorphic rocks**

Attempts at a well-constrained age for the highest-pressure metamorphic stage for the Unit #1 eclogites have so far been inconclusive (Leech and Stockli, in review). Rutiles dated using conventional U-Pb TIMS methods give ages ranging from 377 ± 2 Ma to 384 ± 4 Ma (Beane, 1997); however the closure temperature for rutile in this chemical system are not well known, and estimates range from 380° to 650° C (Mezger et al., 1989;
Chapter 1: PetroTECTonic evolution of the Maksyutov Complex

Zaldegui et al., 1996). Preliminary Sm-Nd dating of garnet and pyroxene have yielded widely varying dates ranging from 357 ± 15 Ma to 404 ± 20 Ma (Beane, unpublished data; Shatsky et al., 1997); the mineral separates used by Shatsky et al. probably contained inclusions, because they described eclogite samples with abundant atoll garnets. These Sm-Nd data overlap considerably with lower temperature systems; this overlap could, in part, be explained by mixing between the porphyroblastic garnet and inclusions, thus affecting the apparent ages. Because dated basaltic rocks from other areas in the south Urals that are likely analogues to the eclogitic protolith in the Maksyutov Complex give ages near 400 Ma, the age of UHP metamorphism probably occurred between 400 and 375 Ma, but until more definitive data become available, it is impossible to date the UHP event exactly.

Constraints on exhumation and late-stage evolution

Intermediate-temperature $^{40}$Ar/$^{39}$Ar data from Unit #1 yield ages from 372 ± 3 Ma to 377 ± 3 Ma (Beane, 1997), which reflect equilibration during an early stage in the exhumation history. $^{40}$Ar/$^{39}$Ar analyses for the Yumaguzinskaya unit provide ages from 356 ± 3 Ma to 365 ± 2 Ma; in contrast, Unit #2 rocks range from about 332 ± 3 Ma to 339 ± 3 Ma. Apatite fission-track modelling results obtained by Leech and Stockli (in review) indicate that the Maksyutov Complex was exhumed to upper crustal levels and cooled below 110°C en masse during the Late Carboniferous (~315 Ma). An east-west transect at Karayanova shows that significant inter-unit movement in the Maksyutov Complex ceased after about 315 Ma. The range of $^{40}$Ar/$^{39}$Ar ages, combined with apatite fission-track data, indicates that the three units were juxtaposed between ~330 - 315 Ma.

FIELD RELATIONS AND PETROGRAPHY

Field relations and metamorphic/deformational fabrics for thin sections from Unit #1 in the Karayanova area are summarized below in order to describe the multistage evolution of the Maksyutov Complex. Table 1 lists the mineral assemblages that document
Table 1. Mineral assemblages for Unit #1 samples showing UHP and retrograde mineralogy.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Location</th>
<th>Rock type</th>
<th>Peak metamorphic mineralogy</th>
<th>Retrograde mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-16</td>
<td>Karayanova</td>
<td>Mica schist</td>
<td>Phn+Qtz+Ab+Grt+Rt+Cal+Zrn+Pl</td>
<td>Phn+Qtz</td>
</tr>
<tr>
<td>MC-37</td>
<td>Karayanova</td>
<td>Eclogitic gneiss</td>
<td>Grl+Cpx+Phn+Qtz+Rt</td>
<td>Gln+Phn+Qtz+Pl+Chl</td>
</tr>
<tr>
<td>MC-38</td>
<td>Karayanova</td>
<td>Eclogitic gneiss</td>
<td>Grt+Cpx+Phn+Zrn+Ap</td>
<td>Gln+Lws+Phn+Pl+Qtz+Chl</td>
</tr>
<tr>
<td>MC-98</td>
<td>Karayanova</td>
<td>Eclogite</td>
<td>Grt+Cpx+Phn+Zrn+Ap</td>
<td>Phn+Qtz+Ab+Rt</td>
</tr>
<tr>
<td>MC-109</td>
<td>Karayanova</td>
<td>Eclogite w/Lws</td>
<td>Grt+Cpx+Phn+Qtz+Rt</td>
<td>Gln+Lws+Qtz+Chl</td>
</tr>
<tr>
<td>MC-116</td>
<td>Antingan</td>
<td>Eclogitic gneiss</td>
<td>Grt+Cpx+Phn+Ap</td>
<td>Grt+Lws+Phn+Qtz+Ep</td>
</tr>
<tr>
<td>MC-118</td>
<td>Antingan</td>
<td>Eclogite</td>
<td>Grt+Cpx+Zrn+Ap</td>
<td>Grt+Phn+Qtz</td>
</tr>
<tr>
<td>MC-154</td>
<td>Shubino</td>
<td>Eclogite</td>
<td>Grt+Cpx+Phn+Rt+Zrn+Ap</td>
<td>Phn+Chl+Qtz</td>
</tr>
<tr>
<td>MC-156</td>
<td>Shubino</td>
<td>Eclogite</td>
<td>Grt+Cpx+Phn+Gln+Rt</td>
<td>Phn+Qtz</td>
</tr>
<tr>
<td>MC-161</td>
<td>Shubino</td>
<td>Eclogite</td>
<td>Grt+Cpx+Phn+Zo+Pl+Mag+Rt+Zr+Ap</td>
<td>Gln+Phn+Qtz</td>
</tr>
<tr>
<td>MC-178</td>
<td>Karayanova</td>
<td>Eclogite</td>
<td>Grt+Cpx+Phn+Rt+Ap+Zr</td>
<td>Gln+L.ws+Ab+Qtz</td>
</tr>
</tbody>
</table>
various stages of metamorphic mineral growth for the different rock types; abbreviations are after Kretz (1983). Petrography and microstructures from all three Maksyutov units have been described in detail by other workers (Beane et al., 1995; Lennykh et al., 1995; Beane, 1997; Hetzel et al., 1998). For brevity, we describe only field relations and sample descriptions relevant to the metamorphic and structural evolution of the complex; we concentrate on Unit #1 because the history of this lithotectonic unit tracks the longest-term development of the complex.

Eclogite mineral chemistry

Mafic eclogite occurs throughout Unit #1 of the Maksyutov Complex as large tectonic blocks (up to tens of meters in length), eclogitic gneissic bands transposed parallel to compositional layering, and boudins (10 cm to 2 m in length) within host phengite schists, garnet gneisses, and quartzites. Schists contain varying amounts of garnet, graphite, and glaucophane; gneisses and quartzites in Unit #1 have compositional banding with different proportions of garnet, phengite, glaucophane, and, in the gneisses, clinopyroxene. The eclogite protolith is probably related to early-formed oceanic crust (associated with rifting of the metasedimentary protolith from the East European platform) that was incorporated into Maksyutov metasedimentary host rocks during subduction, either by tectonic insertion in the subduction zone, or by injection of basaltic dikes (Savelieva et al., 1997).

Most garnets from eclogite boudins are almandine-rich (Alm$_{54-68}$, Prp$_{7.29}$, Gr$_{5-29}$, Sp$_{1-4}$). Garnets from host schists have a much smaller almandine content (Alm$_{36-41}$, Prp$_{28}$, Gr$_{14-19}$, Sp$_{13-17}$); this difference probably represents a later growth stage during retrograde metamorphism or a different bulk rock composition among eclogites and metasediments. Clinopyroxene is omphacite in composition, with jadeite component ranging from Jd$_{47}$ to Jd$_{55}$. White micas are mostly phengite in composition, occurring both as a matrix phase and as inclusions within garnet in eclogite and in graphite in host schists;
Chapter I: PetroTECTonic evolution of the Maksyutov Complex

Phengites have a consistently high Si value, ranging from 3.3 to 3.5 per formula unit (11 oxygens). Mineral compositions were analyzed using the five-spectrometer JEOL 733 electron microprobe at Stanford University; results are precise to 1% for major elements. Representative analyses of minerals from eclogites and metasedimentary host rocks are shown in Table 2. Several samples were chosen for whole-rock chemical analysis; the results are shown in Table 3 for comparison purposes with other subduction complexes.

Garnet and omphacite crystallized during metamorphic stage M_{UHP}, the highest-pressure metamorphism. The UHP phases grew synchronously with the D_{UHP} deformation that probably records synsubduction deformation; on an outcrop scale, M_{UHP} garnet and pyroxene are aligned parallel to the compositional banding, termed the S_{UHP} fabric. First-stage folds are defined by compositional layering, deformed into nearly transposed tight, isoclinal folds with axial planes subparallel to the S_{UHP} foliation. Metamorphic stage M_{EF} pyroxene (eclogite-facies) is deflected around M_{UHP} garnet, giving evidence for a later high-pressure stage of pyroxene growth attending D_{EF} deformation. This later stage of folding, F_{EF}, consists of axial planes perpendicular to S_{UHP} foliation, and refolds F_{UHP} folds. Textural relations (i.e. pressure shadows and alignment in the foliation) for phengite and quartz indicate that these phases crystallized during at least two stages of metamorphism, most likely syn-M_{EF} and during the subsequent HP (M_{BF}).

Retrograde metamorphism and deformation

Blueschist-facies metamorphism, M_{BF}, overprints eclogite and host metasedimentary rocks of Unit #1. Hetzel et al. (1998) suggested that blueschist- and eclogite-facies metamorphism were synchronous; in contrast, we report clear evidence in the field for a late blueschist overprint on eclogite-facies assemblages. The cores of many eclogite blocks and boudins contain no glaucophane or lawsonite, whereas at the rims of these bodies and in the surrounding host rocks, glaucophane replaces clinopyroxene, and phengite textures show a clear blueschist-facies overprint. Localized crenulation cleavages
Table 2. Electron microprobe data for Unit #1 samples from Karayanova; MC-161 collected from Shubino.

<table>
<thead>
<tr>
<th></th>
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<tr>
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<td>Phengite</td>
<td>Phengite</td>
<td>Garnet</td>
<td>Garnet</td>
<td>Garnet</td>
<td>Garnet</td>
<td>Garnet</td>
<td>Garnet</td>
<td>Garnet</td>
</tr>
<tr>
<td>SiO₂ (wt. %)</td>
<td>54.145</td>
<td>51.128</td>
<td>51.151</td>
<td>38.143</td>
<td>37.483</td>
<td>37.910</td>
<td>37.550</td>
<td>56.405</td>
<td>56.049</td>
<td>55.610</td>
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<tr>
<td>TiO₂</td>
<td>0.254</td>
<td>0.750</td>
<td>0.653</td>
<td>0.189</td>
<td>0.160</td>
<td>0.187</td>
<td>0.130</td>
<td>0.236</td>
<td>0.187</td>
<td>0.190</td>
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<tr>
<td>Fe₂O₃(Total)</td>
<td>1.829</td>
<td>2.797</td>
<td>2.540</td>
<td>16.369</td>
<td>29.880</td>
<td>28.700</td>
<td>30.800</td>
<td>5.977</td>
<td>4.311</td>
<td>6.840</td>
</tr>
<tr>
<td>MnO</td>
<td>0.019</td>
<td>0.000</td>
<td>0.000</td>
<td>7.122</td>
<td>1.368</td>
<td>0.302</td>
<td>1.750</td>
<td>0.070</td>
<td>0.000</td>
<td>0.080</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.534</td>
<td>0.427</td>
<td>0.383</td>
<td>0.093</td>
<td>0.017</td>
<td>0.046</td>
<td>0.030</td>
<td>7.788</td>
<td>7.684</td>
<td>7.490</td>
</tr>
<tr>
<td>K₂O</td>
<td>9.492</td>
<td>10.534</td>
<td>10.680</td>
<td>0.000</td>
<td>0.000</td>
<td>0.010</td>
<td>0.010</td>
<td>7.788</td>
<td>7.684</td>
<td>7.490</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.020</td>
<td>0.043</td>
<td>0.058</td>
<td>0.016</td>
<td>0.037</td>
<td>0.049</td>
<td>0.060</td>
<td>7.788</td>
<td>7.684</td>
<td>7.490</td>
</tr>
<tr>
<td>Total</td>
<td>99.996</td>
<td>94.781</td>
<td>94.446</td>
<td>99.996</td>
<td>99.733</td>
<td>99.998</td>
<td>100.990</td>
<td>99.962</td>
<td>100.000</td>
<td>99.930</td>
</tr>
</tbody>
</table>

Using 11 O for phengite

| Si         | 3.398 | 3.446 | 3.459 | 2.959 | 2.974 | 2.963 | 2.964 | 2.012 | 1.990 | 1.991 |
| Ti         | 0.012 | 0.038 | 0.033 | 0.011 | 0.010 | 0.011 | 0.008 | 0.006 | 0.005 | 0.007 |
| Al         | 2.195 | 1.979 | 1.962 | 2.098 | 1.998 | 2.027 | 2.017 | 0.483 | 0.501 | 0.524 |
| Cr         | 0.001 | 0.002 | 0.003 | 0.001 | 0.002 | 0.003 | 0.008 | 0.003 | 0.003 | 0.002 |
| Fe(Total)  | 0.096 | 0.158 | 0.144 | 1.062 | 1.983 | 1.876 | 2.030 | 0.178 | 0.128 | 0.144 |
| Mn         | 0.001 | 0.000 | 0.000 | 0.468 | 0.092 | 0.020 | 0.117 | 0.002 | 0.000 | 0.001 |
| Mg         | 0.370 | 0.421 | 0.439 | 0.410 | 0.548 | 0.716 | 0.466 | 0.359 | 0.398 | 0.374 |
| Ca         | 0.005 | 0.001 | 0.000 | 0.962 | 0.407 | 0.389 | 0.419 | 0.425 | 0.463 | 0.417 |
| Na         | 0.065 | 0.056 | 0.050 | 0.014 | 0.003 | 0.007 | 0.004 | 0.539 | 0.529 | 0.554 |
| K          | 0.760 | 0.906 | 0.921 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| Total      | 6.903 | 7.007 | 7.011 | 7.985 | 8.017 | 8.013 | 8.033 | 4.007 | 4.017 | 4.014 |

Using 12 O for garnet

Using 6 O for clinopyroxene

| Alm       | 35.35 | 65.44 | 62.51 | 66.95 | 50.10 | 50.50 | 53.96 |
| Pyr       | 14.13 | 18.08 | 23.86 | 15.37 | 3.81  | 2.82  | 3.09  |
| Grs       | 33.15 | 13.43 | 12.96 | 13.82 | 44.09 | 46.67 | 42.94 |
| SpS       | 16.13 | 3.04  | 0.67  | 3.86  | 16.13 | 3.04  | 0.67  |
Table 3. Representative X-ray fluorescence data for Unit #1 eclogite and host gneisses from Karayanova; MC-204 from Antingan.

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<td>0.65</td>
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<td>n/d</td>
<td>n/d</td>
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<td>26</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
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<td>76</td>
<td>80</td>
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<td>53</td>
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in blueschist are defined by the subparallel alignment of stage M_{BF} white mica, sodic amphibole, and rarer zoisite; some of those retrograded samples show evidence for three deformational events, as distinguished by cross-cutting crenulation cleavages. The third deformation event, and the corresponding F_{BF} folding is oblique to both D_{UHP-EF} and F_{UHP-EF} fabrics, and is developed locally as small-scale folds and the crenulation cleavage mentioned previously. Three stages of garnet growth, M_{UHP-BF}, can be distinguished in eclogite and blueschist samples. First-metamorphic stage garnet is fractured and pulled apart subperpendicular to S_{UHP} in many samples, probably by the later D_{EF} deformation. A greenschist-facies overprint partially replaces garnet by even later (M_{GF}) chlorite, rare actinolite, and epidote; M_{BF} lawsonite is replaced in most samples by M_{GF} clinozoisite and white mica.

The Yumaguzinskaya Unit may have been subjected to the same HP metamorphism, M_{BS}, as Unit #1; quartzites from the Yumaguzinskaya contain garnet, Na-amphibole, stilpnomelane, and white mica. The Yumaguzinskaya does not contain any mafic rocks and thermobarometry is largely based on the mineral assemblages seen in metasedimentary rocks. Hetzel et al. (1998) associated the Yumaguzinskaya with the upper part of the eclogitic Unit #1. Although Unit #1 and the Yumaguzinakaya probably had similar protoliths (i.e. quartzofeldspathic sedimentary rocks), the mineral assemblages found in the Yumaguzinskaya are significantly different, having a much higher quartzofeldspathic component, and readily distinguished from Unit #1 metasedimentary rocks. Unit #2 contains garnet and lawsonite pseudomorphs in M_{BF} metasomatic rocks, but probably never reached pressures greater than about transitional greenschist/blueschist facies, for Na-amphibole relics are totally lacking.

STRUCTURAL GEOLOGY

Figure 1 presents a simplified geologic map of the Karayanova area, with structural data superimposed; the cross-section shows structural relationships among the three units.
of the Maksyutov Complex in this area. The overall structure of the complex is dominated by NE-SW trending foliation and gentle folding of the three units about asymmetrical $F_{UHP}$ fold axes parallel to the dominant foliation; this large-scale fabric is probably a result of the oblique convergence and SE-directed subduction of the leading edge of the East European platform. The three units of the Maksyutov Complex must have been juxtaposed in the same subduction zone; the eclogitic Unit #1 was overthrust by the Yumaguzinskaya (an inferred contact in the field) and both were later overthrust by Unit #2 in a major shear zone that can be seen along the Sakmara River in the study area.

The large-scale structures are described by the stereonet data shown in Figure 1. Poles to foliation in both units #1 and #2 show that the dominant foliation, $S_{UHP}$, which strikes ENE-WSW has been folded about asymmetrical, shallowly-plunging fold axes, $F_{EF}$, which trend southwest. The large-scale folding affects the entire complex, deforming all three units into a series of asymmetrical syn- and antiformal folds. The complex-wide folding suggests that this phase of deformation occurred during exhumation, perhaps after the three units had been tectonically juxtaposed; based on $^{40}$Ar/$^{39}$Ar dating and apatite fission-track modelling, this folding most likely have been after about 335 to 315 Ma, when the three units were subjected to a common deformational and metamorphic history (Beane, 1997; Leech and Stockli, in review). Foliation data from Station 3 along the Sakmara River shows local minor variations in foliation and fold trends, but differs by no more than 20° dip. Fold axes from throughout the Karayano area show that the trend of the main folding, $F_{EF}$, was refolded about axes trending SSE and correspond to the $F_{BF}$ folding episode.

**STABLE ISOTOPE GEOCHEMISTRY**

*Carbon isotopes*

Carbon isotope analyses ($\delta^{13}C/^{12}C$ vs. VPDB) reveal that graphite occurring throughout the Maksyutov Complex is consistent with sedimentary protoliths (see Leech.
Chapter 1: PetroTECTonic evolution of the Maksyutov Complex

and Ernst, 1998, for a detailed description). Graphite from Unit #1 metasediments and eclogites has a mean near -28%c, retaining the original biogenic carbon signature; graphite $\delta^{13}C_{VPDB}$ from Unit #2 marble averages about -1.0%c, which corresponds to carbon isotope values characteristic of marine carbonates.

**Oxygen isotopes**

Oxygen isotopes may reveal the role of fluids during retrograde metamorphism (e. g., Sharp et al., 1993), and whether mineral assemblages crystallized under equilibrium conditions. New analytical data for the Maksyutov Complex are displayed in Figure 2, which also shows the relative partitioning of oxygen isotopes between different phases. Oxygen was extracted from mineral separates using a CO$_2$ laser in a BrF$_5$ atmosphere at the Geophysical Laboratory, Washington, D.C. Gore Mountain garnet standard ($\delta^{18}O/^{16}O = 5.6\%$ vs. VSMOW) was used to calibrate the unknowns. Standard deviation for all samples was less than $\pm 0.1\%$. The bulk-rock oxygen isotope signature, $\delta^{18}O$, for Unit #1 metasedimentary rocks ranges from about $+7\%$ to $+23\%$; Unit #1 eclogite $\delta^{18}O$ values range from $+8\%$ to $+15\%$. A metabasalt and metasomatite from Unit #2 have $\delta^{18}O$ values similar to Unit #1 eclogites, $+8\%$ and $+11\%$ respectively; similarly, $\delta^{18}O$ for Unit #2 metasediments fall between $+11$ and $+20\%$, comparable to values of Unit #1 metasedimentary rocks. All samples fall within ranges typical of corresponding metasediments and oceanic crust; oxygen isotope values for different minerals exhibit regular partitioning behavior, and reflect the bulk compositions of the host lithologies.

Figure 3 shows the correlation between the $\delta^{18}O$ values of garnet and coexisting phases, demonstrating relatively systematic fractionation; such regular partitioning is consistent with the hypothesis that these phases achieved isotopic equilibrium. The data

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Figure 2. Oxygen isotope data for Unit #1 metasediments and eclogites, and Unit #2 mineral separates from the Maksyutov Complex. Mineral abbreviations are after Kretz (1983).
Figure 3. Garnet and coexisting mineral-pair diagram showing that samples fall on a straight line and evidently crystallized under equilibrium conditions. The dashed line shows that quartz is systematically enriched in $\delta^{18}O$ by about 3.5‰ with respect to eclogitic phases; note also that phengite varies in $\delta^{18}O$ enrichment from 0 to 2‰ $\delta^{18}O$. 

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imply that the different minerals crystallized synchronously during metamorphism; these data, in addition to petrographic evidence, indicate thermobarometric calculations employing these phases are valid. Quartz is systematically enriched in $^{18}O$ by about 3.5‰. With the exception of white mica, garnet-clinopyroxene, -clinoamphibole, and -lawsonite exhibit regular, but extremely small fractionations.

Phengite, in some cases, appears to be enriched in $^{18}O$ by about 1-2‰ relative to coexisting garnet, but other samples lie on the equilibrium line. Textural relations of phengite with respect to eclogitic phases suggest a retrograde recrystallization of the white mica; therefore, its oxygen isotope composition may provide clues regarding the composition of the fluid attending backreaction (Ongley et al., 1987). Retrograde phengite probably grew during the $M_{2,3}$ metamorphic event, which helps constrain the timing of fluid infiltration.

**Oxygen isotope geothermometry**

The measured partitioning of oxygen isotopes between coexisting minerals may be utilized to evaluate the temperatures of their last equilibration, provided the phases recrystallized synchronously, under conditions of chemical equilibrium (i.e., no zoning). Furthermore, temperatures are only as accurate as the experimentally determined fractionation factors and mineral coefficients for phases on which the derived $T$ values are based. We employed the fractionation data of Matthews and Schliestedt (1984), Matthews (1994), and Rosenbaum and Mattey (1995) to compute thermal conditions attending recrystallization of various phases listed in Tables 4 and 5. Temperatures calculated using the fractionation factor and mineral coefficients from Rosenbaum and Mattey (1995) yield temperatures on the order of 15°-20° C higher than calculations from Matthews and Schliestedt (1984) and Matthews (1994). The difference in temperature estimates for these thermometers is most likely due to the calibration of the temperature dependence of fractionation (Rumble and Yui, 1998); Rosenbaum and Mattey (1995) determined

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Table 4. δ¹⁸O values used for geothermometry.

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<tr>
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<td>Unit #2</td>
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Table 5. Calculated temperatures using oxygen isotope partitioning†.

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<td>MK-223, Quartzite</td>
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<td>678 ± 83° C</td>
<td>453 ± 17° C</td>
<td>250 ± 68° C</td>
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</table>

†Temperatures calculated using fractionation factors and mineral coefficients from Matthews and Schliestedt (1984) and (1994). *Values calculated from experimentally determined fractionation and coefficients from Rosenbaum and Mattey (1995). ‡Sample not used in average temperature calculation (see text).
fractionation based on a higher temperature system (>900°C) than Maksyutov samples experienced during metamorphism, therefore the slightly lower temperatures calculated for quartz-garnet oxygen isotope partitioning record a temperature closer to the actual isotopic exchange closure temperature (Sharp, 1991). Useful mineral pairs included Qtz-Grt, Qtz-Cpx, Qtz-Pl, Qtz-Phn, and Phn-Pl. Clearly, a wide range of retrograde equilibration values are exhibited in the isotopic data. However, several tentative conclusions seem justified.

(1) Five quartz-garnet-omphacite equilibration values (Table 5) from a mafic eclogite and the graphite-cuboid-bearing garnet schist range broadly from 595° to 711° C, averaging between about 670 ± 75° C and 699 ± 14° C using different fractionation factors Qtz-Grt partitioning (Matthews and Schliestedt, 1984; Matthews, 1994; Rosenbaum and Mattey, 1995). These temperatures are slightly higher, but similar to the thermobarometric values (594 - 637° C) arrived at by Beane et al. (1995), Lennykh et al. (1995), and Hetzel et al. (1998) for Unit #1 assemblages, based on phase equilibria and on Fe-Mg partitioning between Grt and Cpx.

Garnet records the highest closure temperature for the various mineral pairs in eclogite, from 685°-711° C for samples M-16-94 and MC-99-95 (Table 5). Eclogite sample MK-19D records closure to further isotopic exchange about 160°-170° C lower than other eclogite samples suggesting a localized fluid infiltration and re-equilibration during cooling; similar discordant temperatures between samples separated more than one meter are reported for the UHP Sulu terrane (Rumble and Yui, 1998). Peak metamorphic (UHP) oxygen isotope values are probably not represented in the data as retrograde fluid-assisted oxygen diffusion has most likely obscured peak isotopic ratios; thermometers are known to fail to record peak temperatures in other slowly cooled high grade metamorphic terranes (Sharp et al., 1988; Sharp and Jenkin, 1994; Eiler et al., 1992). Clinopyroxene for all eclogite samples appears to close to oxygen diffusion about 100° C lower than for garnet.
Oxygen isotope fractionation in plagioclase and phengite record two lower-temperature recrystallization events that correlate to the blueschist- and greenschist-facies metamorphic events at about 450° and 250° C respectively (Table 5).

(2) For quartz-albite and quartz-phengite pairs, three rocks — the Unit #2 metabasalt and the stilpnomelane quartzite, and the Unit #1 graphite-cuboid-bearing garnet schist — show evidence of having re-equilibrated at approximately 453 ± 17° C. Such a temperature would be appropriate for the transitional blueschist/greenschist facies metamorphism attending shearing and the suturing of Unit #1 to Unit #2 lithotectonic units during early exhumation/decompression deep within the subduction zone.

(3) Apparent temperatures of 250 ± 68° C provided by quartz-phengite pairs for all four metasedimentary lithologies and an phengite-bearing eclogite indicate fluid-induced metasomatism and back-reaction during late-stage uplift of the more fluid-rich rocks, more permeable rock types.

Although these conclusions remain somewhat speculative, it seems likely that the Maksyutov Complex underwent a multistage series of deformational and recrystallization/metasomatism events during its prolonged exhumation to upper crustal levels and ultimate exposure (Leech and Stockli, in review), marking the suture zone between the East European craton and central Asian microcontinental blocks (Dobretsov et al., 1996). Discordant calculated oxygen isotope temperatures are expected for slowly cooled metamorphic rocks with fluids present. Re-equilibration of $^{18}$O/$^{16}$O values is further enhanced with coeval deformation and at elevated pressure (Sharp et al., 1988; Sharp, 1991; Eiler et al., 1992; Sharp and Jenkin, 1994), thus substantiating our interpretations for the overall metamorphic and deformational evolution of the Maksyutov Complex.

**PETROTECTONIC EVOLUTION**

A combination of thermochronologic, fission-track data modelling, and structural, geochemical, and petrologic data constrain the evolution of the Maksyutov Complex in the
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context of the overall geodynamic setting of the south Ural Mountains, as described in previous sections. Here we present a working hypothesis for the evolution of the UHP(?) complex and adjacent lithotectonic bodies (Fig. 4).

Stage 1: Precambrian to ~400Ma

The protolith to Maksyutov metasedimentary rocks (originally part of the East European platform) are Precambrian, based on Russian dating (Dobretsov et al., 1996). During Early to Middle Ordovician time, these strata were rifted apart from the East European platform by the formation of intervening oceanic crust. By about 400 Ma, basaltic rocks were incorporated into the sedimentary protolith either by inclusion of basaltic rocks in subduction zone, or as basaltic dikes related to the rifting and oceanic crust formation (Edwards and Wasserburg, 1985; Savelieva et al. 1997).

Stage 2: UHP metamorphism and early exhumation to 375 Ma

U-Pb and Sm-Nd data indicate that UHP metamorphism probably occurred between about 400 and 375 Ma, but the precise timing is still uncertain. Metamorphic stage M_UHP minerals crystallized and the regional compositional banding and S_UHP foliation (along with F_UHP folding) developed during peak metamorphism. Exhumation was synconvergence and probably accomplished by a combination of west-directed thrusting as described by Berzin et al. (1996), Echtler et al. (1997), and Brown et al. (1998), followed by normal faulting to the east on the MUF (Fig. 4). Early stages of the exhumation probably coincided with eclogite-grade recrystallization of garnet, pyroxene, and phengite (the M_EF event); this recrystallization may account for zoning in garnet and pyroxene (see Hetzel et al., 1998).
STAGE 1: RIFTING AND EARLY PLATE CONVERGENCE
Ordovician to Silurian
Pre-400 Ma

STAGE 2: UHP METAMORPHISM OF THE MAKSYUTOV COMPLEX
Early to Middle Devonian
400 to 375 Ma

STAGE 3: EXHUMATION AND ASSEMBLY OF UNITS
Late Devonian
375 to 315 Ma

STAGE 4: COOLING AND CONTINUED CONVERGENCE
Late Carboniferous to Middle Triassic
315 to 230 Ma

STAGE 5: PRESENT

Figure 4. PetroTECTonic evolution of the Maksyutov Complex based on apatite fission track ages from Leech and Stockli (accepted pending revisions) and modelling from Matte (1998); Stage 5 is adapted from reflection seismic data from Brown et al. (1998).
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Stage 3: Late exhumation and assembly of the Maksyutov Complex, 375 to 315 Ma

Apatite fission-track and $^{40}$Ar/$^{39}$Ar data indicate that Unit #1 cooled from 350°C to 110°C between about 375 and 315 Ma (Beane, 1997; Leech and Stockli, in review). Thermal relaxation roughly coincided with the onset of the Uralian collision between the East European platform and microcontinental blocks starting in the Early Devonian (Brown et al., 1996). Thermochronologic data also indicate that the three units of the Maksyutov Complex must have been tectonically juxtaposed sometime during this interval.

Between 375 and 315 Ma, both blueschist- (MBF) and greenschist-facies (MGF) metamorphic events and at least two stages of coeval fluid infiltration occurred as the three units of the complex were being juxtaposed within the subduction zone. Unit #1 and the Yumaguzinskaya were thrust together early in the exhumation process after about 356 Ma; the shear zone between these two amalgamated units and Unit #2 must have developed between 330 and 315 Ma, after which all three share a common history; Figure 4 indicates that Unit #2 rocks were derived from oceanic crust in the hanging wall of the MUF, conforming to the current understanding of the structural relationship between Unit #2, the Yumaguzinskaya, and Unit #1 (Beane et al., 1995; Lennykh et al., 1995; Hetzel et al., 1998). The regional-scale folding (F_{EF}) that is evident in Figure 1 most likely began during or just after the units were thrust together during continued convergence. $F_{BF}$ folding probably took place late in this period while the rocks were still behaving ductiley.

Stage 4: Cooling and continued convergence to ~230 Ma

After cooling to 100 to 80°C, fission-track modelling indicates minor reheating and, in some cases, a slowed cooling between about 315 to 230 Ma. While modelling cannot resolve this stage in detail, we interpret this reheating as the result of tectonic reburial of the Maksyutov Complex due to thrusting on the MUF during the main phase of Uralian convergence. This is consistent with the Maksyutov Complex forming the footwall to the
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MUF, and being overridden by west-vergent ophiolite thrust sheets (Matte et al., 1993); the fairly straight NS-trending boundaries of the complex at its west and east contacts probably developed as a result of this overriding thrust sheet. Apatite fission track age and track length modelling indicates a common history for footwall and hanging wall samples (i.e., minor to no movement on the MUF) after the Late Carboniferous (300 Ma).

Stage 5: Cooling and final uplift

Cooling (~40° C) at the end of the Uralian orogeny is most simply interpreted as post-collisional erosional degradation of the mountain belt. It is possible that this stage represents post-orogenic unroofing related to extensional reactivation of the MUF, as suggested by several workers (Matte et al. 1993; Echtler and Hetzel, 1997), but thermal modelling cannot resolve significantly different histories for the footwall and hanging wall after about 300 Ma.

Fission-track data show minor but gradual reheating (~20° C), probably related to the transgression in which Jurassic and Cretaceous marine sediments were deposited over the MUF and the foreland fold-and-thrust belt (Brown et al., 1996; Seward et al., 1997). Final erosional denudation of the Maksyutov Complex and gradual exhumation to the present-day surface probably started in the Tertiary.

CONCLUSIONS

Previous thermochronological constraints on the evolution of the Maksyutov eclogite and metasedimentary host rocks have been placed in the context of the metamorphic and deformational evolution for this complex. Specific points made in this paper differ from reports by other workers, and are detailed here to highlight their significance:

1. Oxygen isotope data for the Maksyutov Complex indicate that garnet and clinopyroxene crystallized in isotopic equilibrium; therefore, thermobarometric calculations

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are valid for the metamorphic stage represented by those minerals. Whether these P-T conditions represent the peak metamorphism, or simply a stage in the decompression annealing has yet to be determined. Evidence for a late-stage fluid infiltration (M_{bf} or M_{gf}), manifested as variation in $\delta^{18}O/^{16}O$ values for phengite from the eclogitic Unit #1, probably initiated a high-pressure and later low-pressure retrograde metamorphic event; when considered with data showing a slow exhumation rate for the complex, this fluid helped remove most geochemical evidence of UHP metamorphism. Coesite and diamond that may have once been present in Unit #1 rocks are now only seen as relic quartz and graphite pseudomorphs.

Oxygen isotope thermometry indicates that there were at least three stages of fluid influx during the retrograde metamorphic history of Maksyutov Complex rocks. Calculated temperatures coincide with eclogite-facies (EF), blueschist-facies (BF), and greenschist-facies (GF) metamorphic and deformational events. Peak metamorphic (UHP) oxygen isotope values are probably not represented in the data; fluid-assisted oxygen diffusion has most likely obscured peak isotopic ratios.

(2) Blueschist-facies metamorphism was an early retrograde event that postdated the UHP and eclogite-facies (EF) events as evidenced by rims of glaucophane on eclogite boudins, and was not coeval with the UHP metamorphism. Petrographic examination of fabrics also shows unambiguously that crystallization of glaucophane post-date the highest-pressure metamorphism.

(3) The protoliths of Unit #1 and the Yumaguzinskaya Unit are similar, but these two units have contrasting early recrystallization histories and should be considered as different tectonic entities. Both units were metamorphosed in the same subduction zone and had a common paragenesis after about 356 Ma, but the petrology of each is distinct; in addition, the Yumaguzinskaya completely lacks eclogitic and ultramafic rocks.

(4) Our structural cross-section through the Maksyutov Complex in the Karayanova area shows two large-scale structural trends. The pervasive NE-SW penetrative fabric that
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affects all three units was caused by SE-directed subduction and folding of the complex during or after the units were juxtaposed early in the exhumation history. These structures were later folded about axes trending SSE, causing what may seem locally like more complex structural variation.

Fluid-enhanced retrogression of Maksyutov rocks supports earlier findings that Unit #1 rocks were subjected to UHP metamorphism but that evidence for peak metamorphism is concealed by geochemical re-equilibration and the slow exhumation rate. Our model for the petrotectonic evolution of the Maksyutov Complex considers the most recent thermochronological, structural, and metamorphic data and represents the most accurate picture for the overall history of the complex.

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Chapter 2

The late exhumation history of the ultrahigh-pressure Maksyutov Complex, south Ural Mountains, from new apatite fission track data

Has been accepted pending revisions under the same title, by Mary L. Leech and Daniel F. Stockli, to Tectonics

ABSTRACT

Fifteen apatite fission track samples were collected from the ultrahigh-pressure (UHP) Maksyutov Complex, south Ural Mountains, in the footwall of the Main Uralian fault (MUF) to constrain the low-temperature cooling history and to establish the late-stage exhumation rate for the complex. Fission track samples were taken along a 70 km north-south transect and a 5 km east-west traverse through the Maksyutov Complex, together with two from the hanging wall of the MUF. Apparent fission track ages for Maksyutov samples range from 210 ± 12 Ma to 311 ± 45 Ma, with a weighted mean age of 256 ± 7 Ma. The samples from the hanging wall of the MUF give apparent ages of 198 ± 15 Ma.
and 279 ± 36 Ma. Confined track length data have unimodal, negatively skewed distributions with mean track lengths ranging from 12.2 μm to 14.0 μm, indicating that all samples underwent partial track annealing at elevated temperatures before final exhumation. Modelling results indicate that the Maksyutov Complex was exhumed and cooled below 110°C en masse in the Early Permian (~315 Ma). The east-west transect shows that there was no significant inter-unit movement in the Maksyutov Complex after about 315 Ma; based on higher temperature thermochronometers, the entire Maksyutov Complex must have been assembled between 335 Ma and 315 Ma. Modelling for the north-south transect indicates that exhumation occurred contemporaneously in the north and south regions of the complex with rapid cooling to 110°C between 375 and 315 Ma; this cooling coincides with the onset of the Uralian orogeny. Comparison of modelling for Maksyutov samples and an Ordovician metasediment from the hanging wall of the MUF indicate that late movement on the MUF was minor, and that the footwall and hanging wall had a similar cooling history after the Late Carboniferous (~300 Ma). Exhumation rates range from 0.3 mm/yr to 1.5 mm/yr between the HP metamorphic event at 375 Ma and 315 Ma using current heat flow data. Our calculated exhumation rate for the Maksyutov Complex is consistent with the complex being an UHP terrane, even though coesite and diamond are not preserved. Modelling indicates minor reheating or slow, monotonic cooling between about 315 to 230 Ma probably as a result of tectonic reburial from thrusting on the MUF during the main phase of Uralian convergence. Cooling at the end of the Uralian orogeny (from about 230 Ma) was most likely due to post-collisional erosional degradation of the mountain belt, but may in part be due to minor late- to post-orogenic extensional unroofing related to the extensional reactivation of the MUF. A small temperature increase beginning at about 180 Ma correlates well with the end of tectonism in the Late Permian, followed by erosional degradation (peneplanation) of the Urals, and a well-documented regional marine
transgression in the Jurassic. Final erosional denudation of the Maksyutov Complex and exhumation of the present day surface probably started in the Tertiary.

INTRODUCTION

The Ural Mountains, with a modern crustal thickness of up to 55 km (based on the URSEIS seismic reflection/refraction profile shown in Figure 1) and topography of no more than 1600 m in the south, differ from other Paleozoic orogens (e.g. the Variscides, Caledonides, and Appalachians) by preserving a collisional structure that lacks large-scale late-orogenic extension (Dewey et al., 1988; Berzin et al., 1996; Echtler and Hetzel, 1997; Knapp et al., 1998). One method to constrain the extension history may be to look at the late-stage evolution of the most important suture zone in the Urals, the Main Uralian fault (MUF).

The ultrahigh-pressure (UHP) Maksyutov Complex forms the footwall to the MUF and records a petrologic history since the onset of collision in the Urals. Current thermochronological data for the this complex constrain a high-pressure (HP) stage of its history and cooling through 350° C (e.g. Beane, 1997; Shatsky et al., 1997) but provide little information about the assembly of the complex, its final exhumation along the MUF zone, and the geomorphic evolution of the mountain belt. Apatite fission track (AFT) thermochronology is an effective tool for reconstructing cooling histories, recording information on the timing and rate of late-stage exhumation.

In this paper, AFT data describe the low-temperature cooling history for the Maksyutov Complex and regionally for the south Ural Mountains. In particular, the collection of AFT ages and confined track-length data in conjunction with thermal modelling is a powerful means to obtain a more comprehensive picture of the multi-stage thermal evolution of the rocks currently exposed in the south Ural Mountains and to constrain the timing and magnitude of movement on the MUF. Furthermore, these data
Figure 1. Tectono-stratigraphic map of the south Ural Mountains (after Beane et al., 1995) showing the areas where AFT samples were collected and the location of Figure 3. The 1995 URSEIS seismic line is shown north of the Maksyutov Complex. Cross-section A-B is shown in Figure 2.
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also help us to better understand the crustal mechanics of how ultrahigh-pressure rocks are exhumed to the surface.

Reports of coesite and coesite pseudomorphs (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988) and graphite pseudomorphs after diamond (Leech and Ernst, 1998) from the Maksyutov Complex suggest that these rocks have been metamorphosed at ultrahigh pressures. The processes by which buoyant continental crust is subducted to depths exceeding 100 km and later returned to the surface are not yet well known, but a necessary and often lacking piece of information is the complete pressure-temperature-time path. In particular, the exhumation rate may set important constraints on the mechanism for exhumation. It is clear from this work that extension on the MUF did not play a major role in exhuming Maksyutov eclogites and that the exhumation rate was slow, failing to preserve coesite or diamond. Although UHP metamorphism is only rarely described, it is quite probable that its preservation is limited mainly by the exhumation process; perhaps other high-grade terranes worldwide have experienced UHP metamorphism but exhumation rates were too low to preserve indicator minerals.

TECTONIC SETTING OF THE SOUTH URALS

The Urals are a 2000-km long, 400-450 km-wide orogen formed by oblique collision between the East European platform and microcontinental blocks to the east in Late Devonian to Permian time (Zonenshain et al., 1984, 1990; Coleman et al., 1993). Figure 1 is a tectonostratigraphic map of the southern Urals showing the relative position of the Maksyutov Complex within the orogen. The East European craton is overlain on the east by the Upper Ordovician to Lower Carboniferous Zilair nappe (also known as the Sakmara) clastic wedge sediments. The Zilair nappe is thrust eastward over the strongly deformed Silurian - Lower to Middle Devonian slope-derived sediments and volcanics.
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of the Suwanjak terrane (Brown et al., 1995), forming the western boundary to the Maksyutov Complex (Fig. 1).

The sedimentary protolith to the Maksyutov Complex rifted from the East European craton in the Early to Middle Ordovician. Edwards and Wasserburg (1985) report Sm-Nd whole-rock dates for the Kempersai ophiolite (Fig. 1) in the southernmost Urals of $397 \pm 20$ Ma, and interpret this as the igneous crystallization age for pre-Uralian oceanic crust. These ophiolites may be related to the ophiolites in the hanging wall of the MUF and are represented by the Kraka ophiolite, a remnant kippe of the early westward-directed thrusting on the MUF (Matte et al., 1993). Basaltic rocks related to this early formed crust were incorporated into Maksyutov host metasediments during subduction either by inclusion in the subduction zone or by intrusion of basaltic dikes related to rifting and oceanic crust formation (Savelieva et al., 1997). Figure 2 shows the current cross-sectional relationship between the Maksyutov Complex and the other tectonic units shown in Figure 1 and a cartoon showing the same units in the Early to Middle Devonian.

The MUF is the main suture zone of the Urals and extends over 2000 km along its axis (Fig. 1); it is a diffuse mélangé zone (up to 20 km wide along the length of the Urals) containing ophiolitic rocks and Lower to Middle Devonian blocks derived from the Magnitogorsk arc to the east, all in a serpentinite matrix (Puchkov, 1993; Zakharov and Puchkov, 1994; Brown et al., 1995). The youngest rocks involved in faulting along the MUF are Lower Carboniferous in the southernmost areas; to the north, the MUF is overlain by Jurassic to Lower Cretaceous sediments (Brown et al., 1995).

The Magnitogorsk island-arc complex contains Upper Silurian to Upper Devonian volcanic and volcaniclastic rocks interlayered with Carboniferous inter-arc basin sediments (Zonenshain et al., 1984; Brown et al., 1995). The ophiolites and island-arc assemblages are folded into an open syncline and overprinted by low-grade metamorphism. The
Figure 2. Schematic upper-crustal cross-section A-B (from Fig. 1) across the south Urals through Karayanova showing the structural relationships from the foreland basin in the west to the East Uralian zone (adapted from Brown et al., 1995). An expanded cross-section through the Karayanova area shows the large-scale relationship between the units. Cartoon at the bottom shows the relative position of the tectonic units in the Early to Middle Devonian. No vertical exaggeration.
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Magnitogorsk island-arc complex was thrust eastward over the Vendian to Ordovician Mugodzhar and Ilmen microcontinents (Zonenshain et al., 1990).

The Mugodzhar microcontinent (Fig. 1), now composed of migmatites and granulites, probably rifted from the Russian platform during the Early Ordovician (Zonenshain et al., 1990; Beane et al., 1995). Late Carboniferous to Permian granitic plutons intrude the island-arc complex and microcontinents and may be related to eastward subduction of continental crust beneath the Magnitogorsk island-arc complex (Zonenshain et al., 1990).

GEOLOGIC BACKGROUND

The Maksyutov Complex trends north-south and consists of three main units tectonically juxtaposed: an eclogite-bearing gneiss, called Unit #1; an intermediate-grade Yumaguzinskaya metasedimentary unit lacking eclogite; and a meta-ophiolite mélange, termed Unit #2 (Fig. 2). Unit #1 contains boudins of eclogite, layers of eclogitic gneiss, and rare ultramafic bodies within host metasedimentary mica schist and quartzite; the presence of eclogite and high-pressure/low-temperature assemblages indicates that Unit #1 was involved in a subduction zone. The Yumaguzinskaya contains similar rock types to Unit #1 but is metamorphosed to no more than lower blueschist-facies or upper greenschist-facies, representing a higher crustal level than the UHP Unit #1 rocks. Unit #2 consists of lenses of serpentinite mélange and blocks of metasomatic rock (~rodingite), metabasalt, and Ordovician to Silurian marble within mica schist and graphite quartzite host rock (Dobretsov et al., 1996); peak metamorphism for Unit #2 was blueschist- to upper greenschist-facies.

Unit #2 and the Yumaguzinskaya, considered to tectonically overlie Unit #1 (Lennykh et al., 1995), were juxtaposed with Unit #1 most likely in the subduction zone after the Early to Middle Devonian UHP metamorphic event that affected Unit #1 (Matte et
al., 1993; Beane et al., 1995; Beane, 1997; this study). All three units were overprinted by a late, low-pressure, greenschist-facies metamorphism and subsequently folded together about NE-SW trending axes (Fig. 2).

Fe-Mg exchange geothermometry calculated for garnet and clinopyroxene from eclogite yields an equilibrium temperature ranging from 594° to 637° C (Powell, 1985). Minimum pressure estimates using the jadeite component of clinopyroxene (Holland, 1980) range from 1.5 to 1.7 GPa (Beane et al., 1995; Lennykh et al., 1995; this study) and may be as high as 2.7 GPa (Bohlen and Boettcher, 1982) if coesite pseudomorphs described in eclogite from Shubino (Chesnokov and Popov, 1965) and jadeite quartzite from Karayanova (Dobretsov and Dobretsova, 1988) are interpreted correctly. In addition, graphite phengite schist from near the former village of Karayanova contains unusual cuboid graphite aggregates that deflect a foliation defined by phengite and elongate graphite grains. These graphite aggregates may be pseudomorphs after diamond, which would indicate UHP (Leech and Ernst, 1998). Thermobarometric estimates may represent annealing during exhumation in which minerals re-equilibrated at lower P-T conditions, leaving little evidence of UHP metamorphism.

APATITE FISSION TRACK DATING FOR THE MAKSYUTOV COMPLEX

Fission track thermochronology

Fission tracks are linear damage trails that form in the crystal lattice as the result of spontaneous nuclear fission of trace 238U in minerals such as apatite and zircon (e.g. Fleischer et al., 1975). Spontaneous fission occurs at an essentially constant rate, so the number of tracks may be used to calculate fission track ages. In early studies, fission track ages were commonly interpreted simply as cooling ages, dating when a sample cooled through a mineral-specific closure temperature (Dodson, 1973) during exhumation (e.g. 110° C for apatite).
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In recent years, this technique has been augmented by more sophisticated approaches that use apparent age, single-grain age, and confined track length data to interpret the thermo-tectonic history with modelling techniques. The use of this data for thermochronology relies on the fact that tracks are partially or entirely erased by thermally-induced recrystallization at elevated temperatures. This process, referred to as annealing, causes easily measured reductions in both track lengths and fission track ages (e.g. Naeser, 1979, 1981; Gleadow et al., 1986a,b; Green et al., 1989a,b; Crowley et al., 1991; Corrigan, 1991a, 1992; Tagami et al., 1998). At geologic cooling rates, significant track length and apparent age reduction occurs between about 60° and 110° C, termed the Partial Annealing Zone (PAZ). All apatite fission tracks are completely erased at temperatures greater than about 110° - 135° C, depending in part on apatite composition and the time scale of geologic heating (e.g. Corrigan, 1992). At shallow levels above the PAZ, track-length shortening is minimal due to low ambient temperatures; ages are older and date earlier thermal events or retain detrital provenance ages, depending on the particular circumstances.

Apatite fission track data from rocks that underwent rapid exhumation from structural levels below the PAZ to near-surface levels are characterized by ages that are essentially invariant; track-length distributions are unimodal, narrow, and have long mean lengths (Gleadow et al., 1986b; Green et al., 1989b; Fitzgerald and Gleadow, 1990). However, in the case of slow, protracted cooling and exhumation or later reheating within the PAZ, track lengths are characterized by either bimodal or negatively skewed unimodal distributions with mean track lengths that are significantly shorter than in the case of rapid exhumation (Gleadow et al., 1986b; Green et al., 1989b). Samples that underwent slow cooling, residing within the PAZ at elevated temperatures for geologic time, will yield partially annealed, apparent AFT ages that do not directly date cooling and are usually unrelated to a specific thermal or tectonic event. Modeling methods incorporating age and
track length data can interpret partially annealed data and decipher the thermal histories undergone by such samples.

**Sample preparation and laboratory methods**

Apatites were separated using standard mineral separation techniques (e.g. Dumitru, 1999); apatite yields were low because of the small sample size (< 0.5 to 1.0 kg) but sufficient for dating. While hanging wall sample MC144-95 (Novopokrovka) has a uranium concentration of 19 ppm, uranium concentrations in Maksyutov Complex apatites are low, most ranging from about 3 - 9 ppm U. MK-115 had a small number of induced tracks due to very low uranium content (~0.5 ppm) giving an age of 311 ±45 Ma, which is statistically not significantly different at the 2σ level from the rest of the age population, clustering at about 256 Ma (Table 1).

All apatites were etched for 20 s in 5N nitric acid at room temperature. Grains were dated by external detector method with muscovite detectors. The CN5 dosimetry glass was used as a neutron flux monitor. Samples were irradiated in well thermalized positions at the Oregon State University reactor. External detectors were etched in 48% HF. Tracks were counted with Zeiss Axioskop microscope with 100x air objective, 1.25x tube factor, 10x eyepieces, transmitted light with supplementary reflected light as needed; external detector prints were located with Kinetek automated scanning stage (Dumitru, 1993). Confined, horizontal track lengths were measured only in grains with c-axes subparallel to slide plane (within ±5-10°), following protocols of Laslett et al. (1982). Lengths were measured with computer digitizing tablet and drawing tube, calibrated against stage micrometer (e.g., Dumitru, 1993).
Table 1. Apatite fission track results from the Maksyutov Complex, Urals

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample location and description</th>
<th>Latitude, Longitude</th>
<th>Elevation (m)</th>
<th># of grains</th>
<th>pd (x 10^5)</th>
<th>ps (x 10^5)</th>
<th>pi (x 10^4)</th>
<th>AFT age (Ma)±1σ</th>
<th>P(X^2) %</th>
<th>Mean track length (µm)±1σ (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC29-94</td>
<td>Maksyutovo: Unit #1 mica schist</td>
<td>N52°17.10', E57°46.00'</td>
<td>460</td>
<td>26</td>
<td>1.831</td>
<td>6.499</td>
<td>8.576</td>
<td>236.2±13.8</td>
<td>88</td>
<td>12.25±0.18 (100)</td>
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<tr>
<td>MC33-94</td>
<td>Maksyutovo: Unit #2 quartzite</td>
<td>N52°17.00', E57°46.00'</td>
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<td>29</td>
<td>1.504</td>
<td>6.840</td>
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<td>210.4±12.5</td>
<td>85</td>
<td>13.08±0.17 (100)</td>
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<td>Karayanova: Unit #1 quartzite</td>
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<td>315</td>
<td>30</td>
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<td>242.6±18.7</td>
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<td>20</td>
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<td>4.261</td>
<td>5.211</td>
<td>263.7±20.4</td>
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<td>13.39±0.20 (28)</td>
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<td>MC178-95</td>
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<td>N52°59.48', E57°47.18'</td>
<td>315</td>
<td>30</td>
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<td>2.842</td>
<td>2.832</td>
<td>264.7±16.4</td>
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<td>MC65-95</td>
<td>Karayanova: Yumaguzinskaya graphite mica schist</td>
<td>N52°00.18', E57°47.15'</td>
<td>355</td>
<td>30</td>
<td>1.849</td>
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<td>N52°00.24', E57°47.17'</td>
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<td>MK115</td>
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<td>N51°39.61', E57°55.42'</td>
<td>515</td>
<td>30</td>
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<td>4.384</td>
<td>249.0±15.2</td>
<td>98</td>
<td>13.82±0.10 (150)</td>
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<td>Shubino: Unit #1 eclogite</td>
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<td>1.813</td>
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<td>69</td>
<td>12.84±0.23 (84)</td>
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<td>N51°30.48', E58°59.94'</td>
<td>360</td>
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<td>100</td>
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<td>Near Novopokrovka: quartzite</td>
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<td>360</td>
<td>8</td>
<td>1.469</td>
<td>1.741</td>
<td>2.300</td>
<td>198.4±15.3</td>
<td>52</td>
<td>12.92±0.20 (55)</td>
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</tbody>
</table>

Abbreviations are Elev, sample elevation; ps, spontaneous track density (x 10^6 tracks per square centimeter); Ns, number of spontaneous tracks counted; pi, induced track density in external detector (muscovite) (x 10^4 tracks per square centimeter); Ni, number of induced tracks counted; P(X^2), χ^2 probability [Galbraith, 1981; Green, 1981]; pd, induced track density in external detector adjacent to dosimetry glass (x 10^5 tracks per square centimeter); Nd, number of tracks counted in determining pd. Age is the sample central fission track age; central age given [Galbraith and Laslett, 1993] and calculated using zeta calibration method [Harford and Green, 1983]. Samples were analyzed by D.F. Stockli (zeta value 356±8 for CN5).
Fission track results and discussion

Fifteen AFT samples were analyzed from north-south and east-west transects across the Maksyutov Complex and from Ordovician metasediments in the hanging wall of the MUF to constrain the low-temperature cooling history (Table 1). Apparent ages for all samples from the Maksyutov Complex range from 210.4 ± 12.5 Ma to 311.5 ± 45.4 Ma, whereas two samples from the hanging wall of the MUF are 198.4 ± 15.3 Ma and 279.2 ± 36.3 Ma.

Figure 3 shows apparent ages and confined track length distributions for samples with confined track length data n > 80 (MC143-95 has 57 measure lengths but is included for comparison purposes). Twelve Maksyutov samples intersect the weighted mean age of 256 ± 7 Ma within 1σ. Confined track length data have unimodal distributions with mean track lengths ranging from 12.25 μm to 13.99 μm, suggesting that all samples underwent partial annealing. Track length distributions often show a tail of shorter tracks, indicating some annealing of early formed tracks while residing in the PAZ at elevated temperatures (100° - 80° C). Figure 4 shows a plot of apparent AFT ages versus mean track lengths for samples within the Maksyutov Complex; all samples fall within a fairly small region of ages and mean track lengths.

Fission track modelling

The apparent, partially annealed AFT ages and the confined track length data were used to reconstruct the low-temperature (T < 110° C) evolution of the UHP Maksyutov Complex. Track-length distributions for all samples with sufficient numbers of confined tracks (n > 80, except for MC143-95) were modelled using the modelling program of Gallagher (1995), “Monte Trax”, employing a Monte Carlo-type approach with a genetic algorithm; this stochastic modelling allows us to input FT data and to specify upper and lower limits for both time and temperature during model runs. The T-t boundary
Figure 3. Detailed map of the Maksyutov Complex showing the extent of exposure throughout the complex (adapted from Beane, 1997). Apparent AFT ages are listed for the different sample areas; most samples intersect the weighted mean age of 256 ± 7 Ma within 1σ error. Confined track length distributions are listed for all samples with n > 80 (MC143-95 is included for comparative purposes).
Figure 4. Plot of mean track lengths vs. AFT ages for footwall samples from Maksyutov. Hanging wall sample MC-143-95 is plotted as a rectangle showing no difference from footwall samples.
conditions for model runs were set freely using additional independent geologic data, such as $^{40}$Ar/$^{39}$Ar thermochronologic data from Unit #1, age of deposition, and present-day surface temperature, allowing the model maximum freedom within those bounds. The modelling program, using experimentally-derived annealing data by Laslett et al. (1987), chooses points at random within these bounds which then become the nodes for linear segments adopted for the first run thermal history. Model data obtained from this initial run are compared to the observed FT data; with each succeeding iteration, the model run data tries to improve the fit between predicted and observed AFT data. Despite the infinite number of T-t histories capable of producing the observed age and track length data, generated thermal paths are remarkably reproducible (Fig. 5) and are in good agreement with independent geologic data, such as post-exhumation regional subsidence histories.

**North - south transect** - These samples, collected from five areas along a 70 km north-south transect of the Maksyutov Complex to determine whether there was any differential movement during exhumation along the length of the complex. Modelling indicates that there was no significant difference in the timing or mechanism of late-stage exhumation between the northern and southern regions of the Maksyutov Complex.

**East - west transect** - The largest group of AFT samples were collected along a 5 km transect through all three units of the Maksyutov Complex at Karayanova. Modelling for these samples indicate the three units cooled through 110° C at about 315 Ma; the similarity in thermal histories for the different units rules out major inter-unit movement within the Maksyutov Complex after 315 Ma. The three units of the Maksyutov Complex must have been tectonically juxtaposed after the HP event at 375 Ma that effected Unit #1 and before 315 Ma.
Figure 5. Modelling results for individual samples with confined track lengths n > 80; MC143-95 is shown for comparison with footwall samples.
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**Hanging wall vs. footwall** - Modelling for all samples in the Maksyutov Complex shows that they were exhumed and cooled through 110° C at about 315 Ma. Figure 6 superimposes modelled paths from Unit #1 at Shubino (MC154-95 and MC161-95) onto those of an Ordovician metasediment from the hanging wall of the MUF (MC143-95). While modelling indicates that this sample was never heated to the extent that Maksyutov samples were, there is evidence for minor movement on the MUF until about 300 Ma after which the footwall and hanging wall have a common history.

**THERMO-TECTONIC EVOLUTION**

The fission track data and modelling constrain the following thermo-tectonic episodes for the low-temperature evolution of the Maksyutov Complex in the context of the overall geodynamic setting of the south Ural Mountains:

**375 to 315 Ma**

Apatite fission track and \(^{40}\text{Ar}/^{39}\text{Ar}\) data suggest a relatively “rapid” exhumation of the Maksyutov Complex after undergoing UHP metamorphism and cooling through a temperature of 110° C between 375 and 315 Ma (Fig. 7, stage 1). This “rapid” cooling event roughly coincides with the onset of the Uralian collision between the East European platform and microcontinental blocks starting in the Early Devonian (Brown et al., 1995). The three units of the Maksyutov Complex must have been tectonically juxtaposed sometime during this time interval.

**315 to 230 Ma**

After cooling to 100 to 80° C, fission track modelling indicates minor reheating but in most cases slower monotonic cooling between about 315 to 230 Ma (Fig. 7, stage 2). While modelling cannot resolve this stage in detail, we interpret this reheating event as the
Figure 6. Modelling results for one hanging wall sample (MC143-95) with footwall samples from nearby Shubino (MC154-95 and MC161-95) superimposed to show a probable common history after about 300 Ma.
Figure 7. Summary of modelling for all AFT samples in the Maksyutov Complex showing five stages in the exhumation history since the high-grade metamorphic event. Boxes show the error limits for each inflection point in the exhumation curve.

- ① Exhumation of the Maksyutov Complex to upper-crustal level
- ② Reheating and/or cooling related to Uralian Orogeny
- ③ Post-collisional erosional unroofing (minor extension on the MUF?)
- ④ Jurassic and Cretaceous peneplanation and reburial
- ⑤ Final uplift to present-day position
result of tectonic reburial of the Maksyutov Complex due to thrusting on the MUF during the main phase of Uralian convergence. This is consistent with the Maksyutov Complex forming the footwall to the MUF and being overridden by ophiolite thrust sheets (Matte et al., 1993). Modelling indicates a common history for footwall and hanging wall samples (i.e. minor to no movement on the MUF) after the Late Carboniferous (300 Ma). Reheating or the relative slowing down in cooling rate for different models are both responses to overburden.

230 to 180 Ma

Renewed cooling and/or continued cooling (~ 40° C) at the end of the Uralian orogeny is best interpreted as post-collisional erosional degradation of the mountain belt. It is possible that this stage represents post-orogenic extensional unroofing related to the extensional reactivation of the MUF (Fig. 7, stage 3) as suggested by several workers (Matte et al. 1993; Echtler and Hetzel, 1997), but modelling cannot resolve significantly different histories for the footwall and hanging wall after about 300 Ma.

Post-180 Ma

The small temperature increase (or complete cessation of cooling) beginning about 180 Ma correlates with the end of tectonism in the Late Permian, which is followed by the erosional degradation (peneplanation) of the Urals and a marine transgression in the Jurassic (Brown et al., 1995; Seward et al., 1997). Fission track data show minor but gradual reheating (~20° C) probably related to this transgression in which Jurassic and Cretaceous marine sediments were deposited on the MUF and the foreland fold-and-thrust belt (Fig. 7, stage 4).
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-45 Ma to present

Final erosional denudation of the Maksyutov Complex and exhumation to the present day surface probably started in the Tertiary (Fig. 7, stage 5). Sediments would have been shed to the foreland basin to the west. However, the exact nature of this part of the T-t evolution is only poorly constrained because samples were in the total stability zone for apatite fission tracks.

CORRELATION WITH OTHER FISSION TRACK RESULTS FROM THE URALS

Seward et al. (1997) collected samples for fission track dating along the 200 km west-east URSEIS seismic reflection profiling line (Berzin et al., 1996; Carbonell et al., 1996; Echtler et al., 1996; Knapp et al., 1996) north of the Maksyutov Complex (see Fig. 1). Apparent apatite FT data range from about 180 to 210 Ma (Seward et al., 1997) while zircon fission track ages from near the MUF range from 226 to 288 Ma in both the footwall and hanging wall of the fault (Seward et al., 1997). These fission track data suggest that the Urals have behaved as a single tectonic unit since the Early Triassic.

Combining apparent apatite and zircon age data with modelling, Seward et al. (1997) conclude that a regional cooling event occurred between ~280 and 210 Ma across the south Urals; a small temperature increase (~10 - 30° C) from about 180 to 110 Ma is interpreted as caused by burial in the Late Jurassic and Cretaceous before final denudation starting in the Cretaceous. As described in the previous section, similar events are seen in modelling from Maksyutov data that indicate regional cooling and/or gradual reheating between 300 Ma and 230 Ma and reheating from 180 to 45 Ma.
TECTONIC IMPLICATIONS OF FISSION TRACK DATA

Previous age dating for the ultrahigh-pressure metamorphic event in Maksyutov

Matte et al. (1993) reports a 380 Ma $^{40}$Ar/$^{39}$Ar age from eclogitic white mica and argue that a rapid exhumation rate did not allow phengites to re-equilibrate after the UHP event and thus the 380 Ma represents the age of UHP metamorphism. These data are corroborated by similar $^{40}$Ar/$^{39}$Ar ages from Beane (1997) that range from 372 ± 3 Ma to 377 ± 3 Ma for phengite from eclogite in Unit #1. However, Beane (1997) interprets these data as a cooling age during exhumation, assuming a closure temperature ($T_c$) for white mica of about 350° C ± 50° C (Purdy and Jager, 1976), because thermobarometry for Maksyutov indicates a minimum metamorphic temperature of 594 - 637° C (Leech and Ernst, 1998). Unit #2 $^{40}$Ar/$^{39}$Ar ages indicate cooling from 332 ± 3 Ma to 339 ± 3 Ma; ages from the Yumaguzinskaya unit range from 356 ± 3 Ma to 365 ± 2 Ma (Beane, 1997). The difference in ages for Unit #1, the Yumaguzinskaya, and Unit #2 represents the times the units cooled through 350° C during exhumation. When these cooling ages are viewed in conjunction with AFT data from this study, it is clear that the three units were juxtaposed between about 335 Ma and 315 Ma.

Preliminary $^{206}$Pb/$^{238}$U analyses on rutile from eclogite in Unit #1 give concordant ages of about 377 ± 2 Ma from Shubino and 384 ± 4 Ma from Karayanova which is interpreted as the age of the UHP event (Beane, 1996, 1997). These ages are similar to the 372 ± 3 to 377 ± 3 Ma $^{40}$Ar/$^{39}$Ar dates; the closeness of these ages is interpreted as indicating a rapid exhumation (Beane, 1997). However, the closure temperature for U-Pb in rutile is not well constrained. Zalduegui et al. (1996) reports a $T_c$ for rutile of about 650° C based on similar U-Pb ages from coexisting minerals such as zircon, monazite, and titanite. Mezger et al. (1989) describes the dependency of the $T_c$ on composition, cooling rate, grain size, and the geometry for each phase analyzed before the ages can be interpreted.
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correctly. Mezger et al. (1989) suggests a $T_c$ for U-Pb in rutile of about 420° C for a cooling rate from 0.5° to 1° C/Ma and a grain radius of 0.009 - 0.021 cm and a $T_c$ of 380° C for a grain radius from 0.007 - 0.009 cm.

The $T_c$ for U-Pb in rutile and $^{40}$Ar/$^{39}$Ar in phengite overlap within their error limits; their respective ages probably reflect the same event, a cooling age rather than the age of the UHP event. The ages obtained thus far by $^{40}$Ar/$^{39}$Ar and U-Pb techniques represent cooling through 350° to 380° C, much lower than the 600° C temperature calculated from thermobarometry and do not represent the age of the highest pressure metamorphic event.

Shatsky et al. (1997) report Sm-Nd ages ranging from 357 ± 15 Ma to 378 ± 13 Ma that suggest an event at about 375 ± 3 Ma. The closure temperature in garnets for the Sm-Nd system is about 600 ± 30° C for garnets with a diameter between 0.1 and 5 cm (Mezger et al., 1992). These Sm-Nd data overlap considerably with lower temperature systems, unlike an unpublished Sm-Nd date of 404 ± 20 Ma (Beane, personal communication). Additional high-temperature thermochronology in a well-known chemical system (i.e. U-Pb in zircon) is necessary before we can set additional age constraints on the UHP metamorphic event for Maksyutov.

Heat flow data

The central axis of the Urals is characterized by anomalously low modern heat flow ranging from about 24 to 43 mWm$^{-2}$ with an average of 35 mWm$^{-2}$ for 26 measurements in boreholes typically 1 to 3 km depth (Kukkonen et al., 1997). Periglacial climatic conditions during the last glacial period require a depth dependent correction of +/- 5 mWm$^{-2}$ for heat flow data based on measurements in the area (Kukkonen et al., 1997). Therefore, the range of geothermal gradients for this region is 6° C/km - 16° C/km, using an average conductivity value of 3.0 mWm$^{-1}$K$^{-1}$. 

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It is clear from the fission track samples from both this study and Seward et al. (1997), that U content in both apatite and zircon (the only common U- and Th-bearing minerals) is low, implying low radiogenic heat production. Overall, rocks exposed in the footwall of the MUF have the lowest values of heat production (from U, Th, and K concentrations) across the Urals; these mostly mafic rocks have values between 0.04 and 0.37 μWm⁻³ (Kukkonen et al., 1997). Deep seismic sounding data suggest that the central Urals are characterized by abundant mafic rocks at depth, coinciding with the thick crustal root and a gravity anomaly maximum, thereby explaining at least in part the low heat flow (Kukkonen et al., 1997). Because this low U-Th content presumably dates at least from the Permian Uralian orogeny, we infer heat production, and hence heat flow and thermal gradients, has been low at least since Permian time.

Exhumation rate

Exhumation rates since the onset of the Uralian collision (i.e. after about 375 Ma) are best calculated using modern heat flow data (Kukkonen et al., 1997). Cooling to 110° C using the mean estimated geothermal gradient (11° C/km) implies exhumation at 0.03 mm/yr (Fig. 8). Pre-orogenic exhumation rates are at present impossible to establish, because published high-temperature thermochronology data (Sm-Nd, c. 600° C, 375 ± 3 Ma) overlap with published intermediate-temperature systems (⁴⁰Ar/³⁹Ar, c. 350° C, 374 ± 2 Ma; U/Pb, c. 420° C, 377 ± 3 Ma). However, the existence of a Devonian Sm-Nd age of 404 ± 20 Ma (Beane, unpublished data) suggests either c. 30 Ma of high-temperature isothermal re-equilibration from c. 405 Ma to c. 375 Ma or at least relatively slow cooling. The maximum possible exhumation rate between the 404 ± 20 Ma Sm-Nd age and the 374 ± 2 Ma ⁴⁰Ar/³⁹Ar age is 2.5 mm/yr using a minimal 10° C/km geothermal gradient (Lachenbruch and Sass, 1977); it is important to note that even this rate is the peak rate experienced by the Maksyutov Complex and can only have been sustained for a short time.
Figure 8. Depth-age path for the Maksyutov Complex. Vertical bars show the range of ages for different dating techniques based on closure temperatures for the specific radiogenic systems; the wide range of depths correspond to these closure temperatures and are based on a range of geothermal gradients from 10°C/km for current heat flow data to 20°C/km to correct for possible paleoclimatic effects (Lachenbruch and Sass, 1977). Stages 1 - 5 correspond to those in Fig. 7. Triangle A indicates exhumation rates from the high-grade event to cooling through 110°C. The dashed line shows an exhumation path allowed by higher temperature thermochronology; FT modelling indicates a much steeper slope for stage 1 making this path improbable.
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(no more than ~10 Ma). In contrast, reported exhumation rates for other UHP terranes are much higher at 5 - 25 mm/yr for the Dabie Shan (Webb et al., in review), 6 mm/yr for the Kokchetav Massif (Ernst et al., 1997), and ~3 mm/yr for the Dora Maira Massif (Hacker and Peacock, 1995) elapsed over c. 15 - 35 Ma. (Webb et al., in review). The significantly faster published exhumation rates for other UHP terranes (the Kokchetav Massif and the Dabie Shan) are used to explain the preservation of UHP indicator minerals such as diamond and coesite (e.g. Dobrzhinetskaya et al., 1995; Okay, 1993; Sobolev and Shatsky, 1990). Leech and Ernst (1998) argued that the Maksyutov Complex underwent UHP metamorphism based on possible graphite pseudomorphs after diamond similar to those found in the Beni Bousera and Ronda peridotite massifs (e.g., Pearson et al., 1989; Davies et al., 1993). Triangle A on Fig. 8 indicates the range of depths and ages used for calculating exhumation rates (0.3 to 1.5 mm/yr) from the high-grade event to cooling through 110° C; although a faster rate is possible based on higher temperature chronometers (see the dashed line on Fig. 8), fission track modelling indicates a steeper slope for stage 1 and supports our slower calculated rates.

Diamond is preserved in the Kokchetav Massif under only very special conditions, chiefly as armored micro-inclusions in garnet and zircon, which acted as pressure vessels (Sobolev and Shatsky, 1990; Sobolev et al., 1994) and with a high exhumation rate that did not allow the diamond-bearing rocks to reside at depth long enough to re-equilibrate to graphite. Our calculated exhumation rates for the Maksyutov Complex (0.3 mm/yr to 1.5 mm/yr) support the findings of Leech and Ernst (1998) that even coarse-grained diamond could not be preserved.

CONCLUSIONS

The AFT data for the Maksyutov Complex describe the low-temperature evolution of Maksyutov rocks which is consistent with the geodynamic post-collisional evolution for
the south Urals. The fission track data indicate that UHP eclogites and metasediments underwent a period of exhumation between about 375 and 315 Ma; exhumation rates for this stage in the evolution of the complex range from 0.3 mm/yr to 1.5 mm/yr, using mean current heat flow data. These exhumation rates are slow compared to other UHP terranes and support the earlier finding of Leech and Ernst (1998), based on graphite pseudomorphs after diamond, that relict UHP coesite or diamond should not have been preserved in the Maksyutov Complex. If slow exhumation rates remove most evidence for UHP metamorphism, perhaps it is more widespread than has been appreciated?

This period of exhumation was followed by a slower rate of cooling or reheating perhaps due to thrusting along the MUF and subsequent tectonic reburial of the Maksyutov Complex while remaining within the PAZ. At the end of the Uralian orogeny (about 230 Ma), the rocks underwent an episode of cooling (~40°C) interpreted as erosional degradation of the orogen. This stage may indicate possible minor post-orogenic extension and reactivation of the MUF as a normal fault, but modelling cannot resolve significantly different histories between the footwall and hanging wall after about 300 Ma. This cooling episode was followed by an extended period of time during which the samples resided at ~60°C which is consistent with a regional marine transgression reported by Seward et al. (1997) for fission track samples along the URSEIS seismic profile. This marine transgression buried the area in the Jurassic and Cretaceous starting at about 180 Ma and was followed by a regional peneplanation and final exhumation to the surface at about 45 Ma.

Apatite fission track results suggest that inter-unit thrusting was complete before about 315 Ma. Because $^{40}$Ar/$^{39}$Ar cooling ages are different for the three units of the Maksyutov Complex, they must have been tectonically juxtaposed between the youngest $^{40}$Ar/$^{39}$Ar ages for Unit #2 at about 335 Ma (Beane, 1997) and 315 Ma. The north-south transect through Maksyutov indicates that exhumation was concurrent throughout the
complex and that there was no differential movement between the north and south regions. Comparing AFT modelling results for Maksyutov samples and an Ordovician metasediment from the hanging wall of the MUF, it is clear that movement on the MUF was minor and that the footwall and hanging wall had a common cooling history after about the Late Carboniferous (300 Ma).

Modelling results indicate cooling at the end of collision in the Uralian orogeny; the MUF was probably reactivated as an extensional structure until about 300 Ma. A combination of thrusting to the west and normal faulting on the MUF probably resulted in the final exhumation of the Maksyutov Complex, corresponding to exhumation mechanisms for other UHP terranes (Ernst et al., 1997) and evidence from reflection seismics (Echtler and Hetzel, 1997). There is no evidence in the fission track data to show that there was major extension on the MUF, and because the Urals are characterized by very low heat flow, this may explain in part the lack of large-scale post-orogenic collapse. This new data on the evolution of the Maksyutov Complex allows age constraints on major events during the formation of the south Ural Mountains that were missing in previous tectonic evolution models (e.g. Matte et al., 1993; Matte, 1995; Chemenda et al., 1997).

ACKNOWLEDGMENTS

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Chapter 2: Late exhumation history from apatite fission track data

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Chapter 2: Late exhumation history from apatite fission track data


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Chapter 3

Graphite pseudomorphs after diamond? A carbon isotope and spectroscopic study of graphite cuboids from the Maksyutov Complex, south Ural Mountains, Russia.

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ABSTRACT

Unusual cuboid graphite aggregates (up to 13 mm edge length) from the eclogitic gneiss unit of the Maksyutov Complex deflect a foliation defined by groundmass graphite and phengite, and pressure shadows have developed around these blocky aggregates. Carbon isotope ratios, $\delta^{13}C/^{12}C$, for the cuboid graphite range from about -24 to -42‰, demonstrating that these rocks have retained an original biogenic carbon signature. X-ray diffraction, laser Raman spectroscopy, infrared spectroscopy, and transmission electron microscopy indicate that graphite is well-crystallized with minor defects; no relict organic compounds were detected. Comparisons of these cuboid aggregates with thin sections and scanning electron microscope images of proven graphitized diamonds from the Beni
Bougera peridotite massif show that Maksyutov graphite is similar. Laboratory experiments by other workers on graphite demonstrate that this intriguing morphology could not be the result of deformation, because graphite returns to its original shape and size on stress release. Existing experiments on diamond graphitization do not adequately replicate the conditions of natural rocks being exhumed from subduction zones characterized by ultrahigh pressures, and thus cannot be applied with confidence to the Maksyutov Complex. Our spectroscopic and microscopic studies suggest that these cuboid aggregates probably are diamond pseudomorphs.

INTRODUCTION

Graphite pseudomorphs after diamond have been recognized in the Beni Bougera peridotite massif in northern Morocco and the Ronda peridotite massif in southern Spain (e.g. Pearson et al., 1989; Davies et al., 1993). Scanning electron microscope (SEM) imagery of graphite from these massifs revealed octahedral and cubic faces with corresponding depressions within graphite, and showed that thin coatings of differently-oriented graphite surround the pseudomorphs.

Thus far, only a few crustal terranes subjected to ultrahigh pressure (UHP) have been recognized worldwide: the Kokchetav Massif in northern Kazakhstan, the Sulu-Dabie belt in east-central China, the Dora Maira Massif in the Italian Alps, and the Western Gneiss Region in coastal Norway are examples of well-studied UHP continental terranes with confirmed coesite, coesite pseudomorphs and, in the case of the Kokchetav occurrence, diamond. Rare occurrences of microdiamond inclusions have also been described from the Dabie Shan (Xu et al., 1992; Okay, 1993) and from the Western Gneiss region (Dobrzhinetskaya et al., 1995). Reports of coesite pseudomorphs in the eclogitic unit of the Maksyutov Complex (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988) suggest that these rocks, too, may have been metamorphosed at ultrahigh pressures. Although thermobarometric calculations have demonstrated minimum conditions of about
600 °C, 1.5 GPa for the Maksyutov Complex (Beane et al., 1995; Lennykh et al., 1995; Dobretsov et al., 1996; Beane, 1997), cuboid graphite aggregates from host mica schist support the earlier suggestion of UHP metamorphism proposed by Chesnokov and Popov (1965) and Dobretsov and Dobretsova (1988).

Reports of coesite have not been independently confirmed, but if the cuboid graphite is pseudomorphic after diamond, it would indicate even higher pressures than previously thought. Graphite aggregates pseudomorphic after diamond may occur unrecognized elsewhere in continental collision zones; if our speculations about the Maksyutov paragenesis are correct, this example could encourage further study of carbonaceous matter.

GEOLOGIC SETTING

The Maksyutov Complex trends north-south in the south Ural Mountains of central Russia (Fig. 1). The complex consists of two main units tectonically juxtaposed in this continental collision suture zone (Zonenshain et al., 1990): an eclogite-bearing gneiss, called Unit #1; and a meta-ophiolite, termed Unit #2. Unit #1 contains boudins of eclogite, layers of eclogitic gneiss, and rare ultramafic bodies within host metasedimentary mica schist and quartzite; Unit #2 consists of lenses of serpentinite melange and blocks of metasomatic rock (~rodingite), metabasalt, and marble within mica schist and graphite quartzite host rock (Fig. 2). Unit #1 protoliths are Middle to Late Proterozoic; Unit #2 is Late Proterozoic with blocks of Ordovician to Silurian marble (Dobretsov et al., 1996). Unit #2, considered to tectonically overlie Unit #1 (Lennykh et al., 1995), was probably thrust over Unit #1 after the Middle Devonian HP-UHP metamorphic event that affected Unit #1 and the Early Carboniferous retrograde blueschist- to high-pressure greenschist-facies metamorphism that affected Unit #2 (Matte et al., 1993; Beane, 1997; Beane et al, 1995). Both units were overprinted by a late, low-pressure, greenschist-facies metamorphism and subsequently folded together about NE-SW trending axes.

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Figure 1. Tectonic map of the south Ural Mountains, Russia, the collisional zone between the East European platform and the Siberian craton. The inset map shows the location of the figure. After Beane et al. (1995).
Figure 2. Geologic map of the Maksyutov Complex showing exposure of Units #1 and #2 along the Sakmara River near Karayanova (see Fig. 1). Sample M-16-94 indicates where cuboid aggregates occur. After Lennykh et al. (1995).
Fe-Mg exchange geothermometry calculated for garnet and clinopyroxene (after Powell, 1985) yields an equilibrium temperature ranging from 594° to 637°C. Minimum pressure estimates using the jadeite component of clinopyroxene (after Holland, 1980) range from 1.5 to 1.7 GPa (Beane et al., 1995; Lennykh et al., 1995; this study), but may be as high as 2.7 GPa if coesite pseudomorphs described in eclogite (Chesnokov and Popov, 1965) and jadeite quartzite (Dobretsov and Dobretsova, 1988) are present (Bohlen and Boettcher, 1982). Thermobarometric estimates may represent annealing during exhumation in which minerals re-equilibrated at lower P-T conditions, leaving little evidence of UHP metamorphism (Fig. 3).

CUBOID GRAPHITE, PSEUDOMORPHS AFTER DIAMOND?

Petrography

Graphite-phengite schist (sample M-16-94) from near the former village of Karayanova contains 40% phengite, 38% graphite, 19% quartz, 1% rutile, <1% zircon, and <1% iron oxide minerals. A single cleavage is defined by oriented phengite and graphite flakes. The flakes wrap around large, sub-angular, blocky graphite aggregates; pressure shadows containing quartz and coarse-grained phengite have developed around the aggregates, suggesting that during deformation, the aggregates behaved as coherent, rigid blocks within a more ductile matrix (Fig. 4a). Aligned inclusions of phengite and rutile in the graphite aggregates are subparallel to the foliation. Graphite aggregates have an angular to sub-rounded cross-sectional morphology (Fig. 4b); this is significant because these aggregates may be pseudomorphs after diamond indicating ultrahigh-pressure metamorphism at a minimum pressure of about 3.2 GPa (Kennedy and Kennedy, 1976).

Graphite is abundant throughout the Maksyutov Complex, with volumetric modes in the mica schists locally ranging up to 38% graphite. Disseminated tabular graphite occurs parallel to the dominant foliation in quartzites of both Units #1 and #2, and in metasomatic rocks of Unit #2. Cuboid graphite aggregates (most <5 mm long, but up to
Figure 3. Possible retrograde P-T paths for the Maksyutov Complex: The solid curve is based on Russian reports of coesite (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988) and possible graphite pseudomorphs after diamond (this study); a second possible P-T path is shown as a dashed curve in accordance with the thermobarometric calculations and petrographic studies conducted on eclogites and related rocks from Unit #1 (Beane et al., 1995). The dotted line shows the probable path for Unit #2 rocks. After Lennykh et al. (1995).
Figure 4. Thin sections (in unpolarized light) of graphite schist from Unit #1 cut perpendicular to the foliation: (a) sub-angular graphite aggregate (13 x 10 mm) with phengite and rutile inclusions. The foliation is defined by graphite and phengite flakes that wrap around the graphite aggregate. Note the pressure shadows of quartz and coarse-grained phengite that have formed around the aggregate. Vertical black lines and rings of dots in lower right- and upper left-hand corners are from marking thin section for electron microprobe analysis; (b) cuboid graphite aggregate (about 6 mm long) typical of those in graphite schist in Unit #1.
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13 x 10 mm), made up of flakes ranging in size from about 4 to 100 μm, are found in mica schist near Karayanova, and occur with graphite flakes aligned in the foliation. Scanning electron microscope images show cubic forms of the graphite aggregates (Fig. 5). Graphite is also found as inclusions in garnet in eclogitic gneisses near Antingan village.

**Graphite deformation**

Are these cuboid graphite aggregates a result of a specific deformation mechanism acting on graphite? Indeed, how does graphite deform under the P-T conditions and differential stress these rocks experienced? Edmond and Paterson (1971) described stress-strain experiments for graphite samples (10 x 20 mm) under confining pressures up to 0.8 or 1.0 GPa and room temperature. Under these conditions, they found that graphite specimens returned almost to their original dimensions when both the differential stress and confining pressure were released, even after 20 percent shortening at 0.4 GPa; other samples were shortened 20 percent under confining pressures of 0.2 to 0.8 GPa, and gave similar recoveries. Later experiments by Edmond and Paterson (1972) showed that, in addition to an almost complete recovery of volume, the initial shape of the graphite was retained as well, with most of the recovery occurring below 0.05 GPa; graphite specimens appeared to be undeformed.

Kretz (1996) described graphite in high-grade marble (T = 650° - 700 °C; P = 0.65 - 0.70 GPa) occurring as both undeformed and deformed tabular grains, and suggested that the deformational behavior of graphite is similar to that of biotite. Graphite deforms by cleavage separation, kink-band formation, and folding; breaking across the (0001) basal plane of strong carbon bonds occurred only in mylonitic marble where strain rates were very high.
Figure 5. SEM images showing the external morphology of graphite aggregates that display rough or perhaps slightly deformed cubic forms; dashed white lines trace the edges of cubes on the right side of the figure. These images are similar to those described by Pearson and Nixon (1996) for aggregates from the Beni Bousera massif. Aggregates have about a 4 mm edge length.
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Graphitization of organic matter

Is this poorly crystallized graphite? Graphitization of organic matter is primarily dependent on metamorphic temperature, but the process is facilitated at lower temperatures by shear strain in combination with elevated pressure (Landis, 1971; Teichmuller, 1987; Ross and Bustin, 1990; Ross et al., 1991). Temperatures and pressures suggested for the formation of true, well-ordered graphite in nature range from about 350° to 700 °C and 0.2 to 0.6 GPa (Landis, 1971; Grew, 1974; Diessel et al., 1978; Tagiri and Oba, 1986).

Well-ordered graphite develops over a wide range of metamorphic conditions. Moderately high temperatures (sillimanite zone or amphibolite-facies) are required for near complete graphitization (Grew, 1974; Armstrong, 1982), although Buseck and Huang (1985) described well-ordered graphite in the chlorite zone (greenschist-facies). It is clear that increasing crystallinity is roughly proportional to metamorphic grade within a specific terrane, but not necessarily between terranes. However, higher pressures such as those calculated for the Maksyutov Complex may retard the graphitization process (Dalla Torre et al., 1996, 1997) even if metamorphic temperatures are above those required for complete graphitization at low pressures. With continued progressive metamorphism, the long-range order increases, the carbon layers lengthen and become more planar, interlayer spacing decreases, and the number of defects decreases (Grew, 1974; Buseck and Huang, 1985; Teichmuller, 1987).

Diamond pseudomorphs from the Beni Bousera and Ronda peridotite massifs

An octahedral or cubic morphology of graphite is the most convincing evidence for graphitized diamond. Graphite pseudomorphs after diamond have been recognized in the Beni Bousera peridotite massif in northern Morocco and the Ronda peridotite massif in southern Spain (e.g., Pearson et al., 1989; Davies et al., 1993). Most graphite from both locations has cubic symmetry, but more than 30% of the graphite occurs as aggregates with
no obvious external morphology. Graphite cubes and octahedra are commonly 2 to 8 mm in diameter, but can be up to 12 to 20 mm (Pearson et al., 1989; Davies et al., 1991, 1993; Pearson and Nixon, 1996). Dissolution of silicates surrounding the graphite with hydrofluoric acid reveals graphite cubes and octahedra, but more commonly, graphite with an ovoid form which is due to a 0.01 to 3 mm thick “fibrous” graphite shell that coats most of the octahedra; crushing samples separates some of the graphite cubes and octahedra from the shell graphite (Pearson et al., 1989). Pearson and Nixon (1996) described graphite aggregates occurring as octahedra and other forms of cubic symmetry in the Beni Bousera massif. The rounded, coated graphite aggregates shown in thin section in their figure 10a and 10b and in an SEM image in their figure 11a are strikingly similar to graphite aggregates from the Maksyutov Complex.

Diamond crystal morphology is largely controlled by the temperature and pressure conditions and/or oxygen fugacity at the time of crystallization. Octahedral diamonds result from crystallization at either lower relative temperatures and/or higher pressures, or an oxygen fugacity near magnetite-wustite (Robinson et al., 1978; Taylor, 1985; Sobolev and Shatsky, 1990; Deines et al., 1993). The morphology of the resulting graphite aggregates is most likely dictated by the original crystal form of the diamond (Pearson and Nixon, 1996).

Octahedral forms of diamond predominate in most localities worldwide (Taylor, 1985), but the entire range of morphologies from cubic to octahedral is represented in peridotite massifs (e.g. Beni Bousera), kimberlites and associated mantle xenoliths (e.g. Orapa, Botswana; Roberts Victor, South Africa; and Yakutia, Siberia), and ultrahigh-pressure metamorphic terranes (e.g. the Kokchetav Massif, Kazakhstan; the Western Gneiss region, Norway; and the Dabie Shan, China) (Sobolev and Shatsky, 1990; Shatsky et al., 1991; Viljoen et al., 1991; Xu et al., 1992; Deines et al., 1993; Jerde et al., 1993; Okay, 1993; Dobrzhinetskaya et al., 1994, 1995). Most diamonds with a cubic
morphology are found in rocks with an eclogitic affinity (Spetius, 1995), as is the case for the Maksyutov Complex.

**SAMPLE SEPARATION**

Three techniques were used to separate graphite from Maksyutov rock samples for both isotopic analyses and spectroscopic studies: flotation of graphite from crushed rock samples, acid dissolution of silicates surrounding graphite, and hand-picking graphite directly from the samples. For finely disseminated graphite, manual separation from dry, crushed rock was tedious, so graphite was floated in water; because of the hydrophobic character of graphite, other phases settled out and left a film of graphite on the surface of the water to be skimmed off.

Several samples, including cuboid aggregates, were dissolved in a solution of hydrofluoric and hydrochloric acid to separate graphite from the silicates, in an attempt to preserve any relict cubes or octahedra (shown in Fig. 5). A 1:1 solution of 48.8 - 49.2% HF and 36.5 - 38.0% HCl was used to dissolve the silicates surrounding the graphite aggregates in cm-sized samples. About half of the mixture was decanted every 48 hr and refreshed with another 1:1 solution; this process was repeated at least five times. The procedure left some insoluble fluorides, but did not interfere with the final graphite separation by hand.

For carbon isotope analyses, graphite was hand-picked from several samples of the graphite schist. Aggregate graphite was readily separated by hand from the graphite occurring in the foliation to allow analyses of both forms.

**CARBON ISOTOPE GEOCHEMISTRY**

Carbon isotope measurements were performed at the University of California, Davis, and the Geophysical Laboratory, Carnegie Institution in Washington, D. C. to establish $\delta^{13}C$ vs. PDB for graphite from the Maksyutov Complex. An elemental analyzer
was used at UC Davis and samples were compared to the USGS graphite standard #24 (-16.0‰ vs. PDB), while at the Geophysical Laboratory, samples were analyzed on a mass spectrometer and compared to NBS-21 standard (-28.1‰ vs. PDB); several samples were analyzed at both facilities to provide an interlaboratory calibration. The isotopic composition of carbon is expressed in terms of delta notation (Hoefs, 1987):

$$\delta^{13}C(\%) = \left( \frac{({^{13}}C/^{12}C)_{sp} - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}} \right) \times 10^3.$$  

The reference standard is CO₂ gas released from belemnites of the Peedee Formation (PDB).

Comparison of these values with carbon isotope compositions for diamonds in other continent-continent collision zones, kimberlites, and peridotites with graphite pseudomorphs after diamond establishes the source of carbon in these high-grade rocks and perhaps will lead to a fuller understanding regarding carbon cycling and the geochemistry of the mantle.

Carbon isotope ratios for Unit #1 mica schist range from about -21 to -42‰, with a pronounced frequency peak around -28‰ (Fig. 6). The range of carbon isotope values for the Maksyutov Complex is comparable to that in microdiamonds from the UHP Kokchetav Massif, Kazakhstan (Sobolev et al., 1979; Sobolev and Shatsky, 1990), diamonds with eclogitic inclusions in kimberlitic rocks and associated mantle xenoliths (e.g. Milledge et al., 1983; Galimov, 1988), and graphite pseudomorphs after diamond in the Beni Bousera peridotite massif, Morocco (Slodkevich, 1983; Pearson et al., 1989, 1995). However, kimberlitic and peridotitic diamonds have a wider range of carbon isotope values, from about +2 to -34‰, and a large frequency peak at -5 to -6‰ (Milledge, 1983; Kirkley and Gurney, 1991; Kirkley et al., 1991) indicating a mantle source for the carbon (see Mattey, 1987; Galimov, 1988).

Very negative carbon isotope values might represent carbon from a deep mantle source, perhaps a primitive mantle carbon reservoir (Javoy et al., 1986; Deines et al., 1987, 1993; Galimov, 1988), but more likely these rocks have retained their original
Figure 6. Carbon isotope composition of graphite-bearing rocks and marble from the Maksyutov Complex (Table 1 contains more detailed information). Ranges of typical carbon isotope values for marine carbonates, mantle carbon, and biogenic carbon from Javoy et al. (1986).
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biogenic carbon signature (Milledge et al., 1983; Kirkley et al., 1991). Javoy et al. (1986) and Mattey (1987) give ranges for various carbon sources: Organic carbon has a $\delta^{13}C$ signature ranging from about -15 to -30‰ (mean $\delta^{13}C = -25‰$), whereas marine carbonates have a mean value around 0‰, and mantle carbon ranges from -5 to -8‰. Intermediate values in kimberlites and associated rocks probably result from the mixing of subducted biogenic carbon and mantle carbon in the uppermost mantle (Javoy et al., 1986).

In the Maksyutov Complex, there are no apparent differences in isotopic signature according to the type of graphite sampled: blocky aggregates, graphite aligned in the foliation, and inclusions in other minerals all occupy the same general isotopic range for both tectonic units. Marble is found only rarely as small blocks in Unit #2 and has a mean carbon isotope value of about -1‰ vs. PDB, which corresponds to typical marine carbonates (Table 1). Nitrogen analyses for graphite yield values which indicate atmospheric contamination.

**SPECTROSCOPIC AND MICROSCOPIC STUDIES**

Transmission electron microscopy (TEM), x-ray diffraction (XRD), and both infrared and laser Raman spectroscopic techniques were used to investigate the structure of the graphite aggregates in order to gain insight into their origin and subsequent history. Infrared spectroscopy shows whether or not relict organic compounds remain within the cuboid aggregates. X-ray diffraction characterizes a bulk sample (up to a cm-size area) which is thought to be useful in the determination of graphite crystallization state, although heterogeneity within the sample may be missed because of the scale and nature of the analysis. Sample preparation for XRD is destructive and may change the character of the graphite. Transmission electron microscope analyses are on the scale of a few Å and serve as an excellent tool for investigating the structure of the crystallites, but do not easily allow characterization of a sample as a whole. Laser Raman microspectroscopy allows an
Table 1. Representative carbon isotope data for graphite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>Mass*</th>
<th>Peak size</th>
<th>δ(^{13})C/(^{12})C</th>
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<td><strong>Whole-rock graphite, Unit #1</strong></td>
<td></td>
<td></td>
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</table>

δ\(^{13}\)C/\(^{12}\)C in units of per mil.
* Samples analyzed using an elemental analyzer have mass listed in µg; samples analyzed in multi-port are listed in mg.
† Graphite found as inclusions within garnet and in the matrix.
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intermediate-scale analysis of graphite crystallization in the cuboid aggregates, with a beam size on the order of about 100 μm; it is possible to run a profile across individual graphite aggregates to check for localized differences in crystallization state within a single sample.

Transmission electron microscopy

Transmission electron microscopy samples were prepared by epoxying a copper sample holder ring directly onto graphite aggregates, removing and mounting the aggregate into a TEM sample holder, then ion milling through the center of the aggregate. Imagery of the graphite aggregates from Maksyutov show that the graphite contains minor defects such as dislocations, causing lattice-fringe terminations (Fig. 7). Study of one graphite aggregate shows fairly straight, uniformly spaced lattice fringes containing defects such as lattice-fringe terminations and crystallites that have an anastamosing character, showing a lower degree of structural order.

Selected-area diffraction (SAD) patterns are diffuse and lack rings, which probably result from the defects seen in TEM imaging (Buseck and Huang, 1985). Low-magnification TEM images show that graphite crystals have a very roughly aligned orientation; graphite grains in reflected light appear to be aligned in two preferred directions sub-parallel to the external morphology of the aggregates. Induced effects from the ion milling process may explain some of the apparent defects, but are probably not responsible for all those seen in TEM images because the alleged milling effects continue into the thicker portions of the milled thin section.

X-ray diffraction

Samples were run employing CuKα radiation and a Philips x-ray diffractometer. X-ray diffraction spectra were used to determine the degree of crystallinity in powdered graphite aggregates after obtaining the results of the TEM. Graphite samples were prepared for XRD analysis by mixing powder in distilled water, followed by drying, in order to
Figure 7. TEM images of a graphite aggregate. (a) shows fairly straight lattice fringes; graphite contains many lattice fringe terminations. The inset box is a selected area diffraction pattern for the graphite. (b) shows the anastamosing character of some crystallites.
orient graphite flakes with the (002) planes coincident with the specimen holder; other analyses were performed on dry, powdered graphite. The samples were scanned from 5 to 45° 2θ, scanning 0.05° 2θ every second. Sharp peaks on x-ray diffraction spectra from powdered and oriented samples for the aggregates indicate that the graphite is well crystallized; no broad peaks were obtained, and all 2θ angles correspond with graphite d-spacings. Interplanar d₀₀₂ spacing for the aggregates is ~3.36 Å, which is the d-spacing for fully-ordered graphite according to Warneke and Ernst (1984) and Tagiri and Oba (1986); peak width at half-height (in °2θ) is about 0.324.

**Laser Raman microspectroscopy**

First-order spectra were analyzed from 1200 to 1700 cm⁻¹ and second-order spectra from 2350 to 3350 cm⁻¹ on a LabRam spectrometer; these scans analyzed for the first-order single band at about 1582 cm⁻¹ that is characteristic of well-crystallized graphite as well as two overlapping bands near 2700 cm⁻¹ in second-order wave numbers (Pasteris and Wopenka, 1991). Disorder in graphite appears as a broadening of the 1582 cm⁻¹ band and its shift toward higher wavenumbers as a result of the development of an additional band near 1360 cm⁻¹; second-order spectra exhibit a broadening of the band at 2700 cm⁻¹, the loss of resolution of the two overlapping bands that create that peak, and the suppression of a peak at about 2450 cm⁻¹ (Pasteris and Wopenka, 1991).

Most analyses of Maksyutov graphite aggregates show two large peaks, at about 1582 cm⁻¹ and 1360 cm⁻¹, and a smaller, broad peak at about 2700 cm⁻¹. Figure 8 shows a peak at about 1360 cm⁻¹, a shoulder developed on the high wavenumber side of the 1582 cm⁻¹ peak, and a suppressed peak at about 2450 cm⁻¹ which indicate minor disorder in the graphite probably resulting from the dislocations found in TEM imaging. The Raman spectra for these aggregates are similar to those shown for graphite in the chlorite to biotite
Figure 8. Laser Raman spectra of graphite aggregates showing two large peaks, with the first-order peak at about 1582 cm\(^{-1}\) (O-peak), a peak at 1360 cm\(^{-1}\) showing disorder (D-peak), and a smaller, broad second-order peak at about 2700 cm\(^{-1}\) (S-peak). Note the high wavenumber shoulder on the O-peak and a suppressed peak at about 2450 cm\(^{-1}\).
zone of Barrovian metamorphism for metapelites, according to Wopenka and Pasteris (1993).

**Infrared spectroscopy**

If organic C-H or C-O bonds exist, it would follow that these graphite aggregates could never have been diamond, for organic bonds would certainly have been broken during transformation to diamond. Graphite aggregates separated by acid dissolution were analyzed with an infrared spectrometer to search for organic compounds. Graphite was powdered and mixed with KBr in the ratios 1:100 and 1:20. Each sample was scanned 500 times in addition to the standard KBr for background analyses; background KBr scans were subtracted from the graphite scans to isolate graphite peaks. The spectra show a broad hump between 2900 and 3700 cm\(^{-1}\) (Fig. 9); this adsorptance represents O-H bonds probably from water adsorbed by the sample. Two small peaks between 2300 and 2400 cm\(^{-1}\) result from atmospheric CO\(_2\). The large, broad, composite peak between 400 and 800 cm\(^{-1}\) is from silicates that were not dissolved during the acid dissolution process and/or from inclusions in the graphite. Two low-intensity absorption bands were isolated in the graphite, one at about 1425 cm\(^{-1}\) and another at about 1633 cm\(^{-1}\).

The wavenumbers associated with the two peaks described above might represent C-C bonds or C-O or C-H bonds (Robin and Rouxhet, 1978; Tissot and Welte, 1978). A USGS graphite standard (NBS-21) was run subsequent to the aggregate sample; two noisy peaks representing C-C bonds are located at approximately the same wavenumber positions as the aggregate. It is more probable that the two similar peaks are C-C bonds and not organic-group bonds.
Figure 9. Infrared spectra of acid-separated graphite aggregates. Peaks are at about 1425 cm$^{-1}$ and about 1633 cm$^{-1}$, both probably representing C-C bonds.
RATE OF GRAPHITIZATION OF DIAMOND

Experiments on rates of transformation from $C_{\text{Diamond}} \rightarrow C_{\text{Graphite}}$ show that graphitization per unit time can be estimated by:

$$\frac{dx}{dt} = C \exp^{-\left(\frac{\Delta E + P\Delta V}{RT}\right)},$$

where $C$ is a constant proportional to graphitization rate, $\Delta E$ is the activation energy, and $\Delta V$ is the activation volume (Davies and Evans, 1972). The low activation volume for graphitization ($\sim 10 \text{ cm}^3\text{mol}^{-1}$) indicates that the influence of pressure is small; thus the rate of graphitization is largely dependent on temperature (Pearson et al., 1995). Experimentally determined activation energies for graphitization of diamond are lowest for {110} faces of octahedra ($760 \text{ kJmol}^{-1}$) and highest for {111} faces ($1060 \text{ kJmol}^{-1}$) under anhydrous conditions (Pearson and Nixon, 1996). Using the activation energy for the graphitization of {110} faces, Pearson et al. (1995) calculated that the complete conversion of a diamond octahedron ($\sim 10 \text{ mm edge length}$) to graphite would require about 1 m.y. at 1200 °C or 1 b.y. at 1000 °C.

Rate studies for diamond graphitization require a much slower exhumation rate and higher temperature than is thought to have occurred in the evolution of the Maksyutov Complex. However, these dry graphitization experiments do not take into account the presence of fluids and other rate-enhancing constituents (Tagiri and Oba, 1986) that increase the kinetics of graphitization during return to the Earth’s surface. Re-equilibration that occurred during the exhumation history of the Maksyutov Complex evidently was sufficient for complete graphitization of any diamond that had been present. Diamond is preserved in the Kokchetav Massif under only very special conditions, chiefly as armored micro-inclusions in garnet and zircon, which acted as pressure vessels (Sobolev and Shatsky, 1990; Sobolev et al., 1994).

The rate of transformation for silicates is faster than for diamond $\rightarrow$ graphite. According to Poirier (1981), the activation energy for the olivine $\rightarrow$ spinel transition is
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259 kJmol⁻¹, which is similar to the coesite → quartz reaction (Mosenfelder and Bohlen, 1997). The correspondence of these activation energies probably reflects the reactions being controlled by diffusion of Si across an interface, which is likely to be analogous in many silicate structures (J. L. Mosenfelder, personal communication, 1997). Therefore, if diamond has been completely back-reacted to graphite, the possibility that coesite has survived becomes very unlikely.

DISCUSSION

According to the results of graphite deformation experiments, deformation would be incapable of producing the cuboid morphologies seen in Maksyutov graphite aggregates. Cross-sections of graphite aggregates from Maksyutov in thin sections taken perpendicular to the foliation show a sub-angular, cubic morphology (Fig. 4), and display prominent pressure shadows — indicative of significant strength during deformation and recrystallization. Although SEM imagery was limited by the large size of the aggregates, rounded, or perhaps slightly deformed cubic forms seem probable (Fig. 5). These images are very similar to thin sections and SEM images described by Pearson and Nixon (1996) of graphite pseudomorphs from the Beni Bousera massif. However, Maksyutov graphite has undergone a far more complex history of metamorphism and deformation than Beni Bousera, which probably affected the cuboid graphite morphology: Maksyutov graphite therefore only preserves cubic to rounded morphologies with no apparent difference between the form of the core and coating graphite. Graphitization of the inferred diamond precursor occurred syn- or post-deformation because of the pressure shadows that formed around some aggregates (Fig. 4a). In fact, the rounded graphite shape probably results more from the original diamond form than the deformational history that these rocks underwent.

Grew (1974) noted that XRD analysis provides no evidence for the presence of more than one type of carbonaceous material in a sample; TEM images commonly show

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considerable structural variability within a single grain and between different graphite grains in a single sample (Buseck and Huang, 1985). X-ray diffraction, laser Raman microspectroscopy, and TEM should all be in fairly good agreement in determining the structural order of graphite; apparent discrepancies between different techniques are simply a result of the nature of the analyses. With respect to all three techniques, graphite aggregates from the Maksyutov Complex are composed of well-crystallized graphite, with minor disorder probably brought on by crystallographic defects such as dislocations.

There is no evidence for the survival of relict diamond at Maksyutov using any of these techniques. Graphite that is not pseudomorphic after diamond occurs with diamond in kimberlites and associated eclogite xenoliths, and in several other UHP terranes. If metamorphism took place near the equilibrium P-T field boundary between graphite and diamond, not all graphite may have initially transformed to diamond.

Existing experimental data on graphitization of diamond do not adequately replicate the conditions of natural rocks being exhumed from great depth and thus cannot be applied realistically to the Maksyutov Complex. Experiments using diamond in conditions duplicating those of the natural rock and under appropriate P-T and fluid-present conditions are certainly necessary to address the rate problem.

CONCLUSIONS

Carbon isotope ratios for graphite in Units #1 and #2 of the Maksyutov Complex indicate that it is biogenic carbon, except for graphite in marble which retains a marine carbonate signature. The morphology of the cuboid graphite aggregates is probably an original growth feature; it is not a result of deformation, as indicated by the results of graphite deformation experiments of other workers. Spectroscopic studies including TEM imaging and XRD and laser Raman microspectroscopy demonstrate that the graphite is well-crystallized with only minor dislocation defects; infrared spectroscopy shows an absence of relict organic compounds in the aggregates. Comparison of thin sections
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through cuboid graphite aggregates and SEM imagery of Maksyutov graphite aggregates with diamond pseudomorphs from the Beni Bousera peridotite massif shows many similarities. Maksyutov rocks have undergone a far more complicated metamorphic and deformational history and therefore preserve only deformed cubic to rounded forms and not the core/coating graphite relationship found in the unambiguous diamond pseudomorphs from Beni Bousera. Experimental data on diamond graphitization rates do not bear on the possibility that cuboid graphite aggregates represent pseudomorphs after diamond.

The problem of identifying the origin of these oddly shaped graphite aggregates may be unsolvable. We have tried several analytical techniques to explain the unusual character of graphite in the Maksyutov rocks, but nothing can be proven conclusively. A more thorough search of thick sections of Maksyutov eclogite and host rocks that may reveal coesite, coesite pseudomorphs, or diamond relicts is underway, but so far none has been found to substantiate earlier claims by Russian workers. This study of cuboid graphite aggregates from the Maksyutov Complex has yielded suggestive though nondefinitive results, but we believe that the preponderance of evidence supports the possibility that they are diamond pseudomorphs.

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