# Platinum-Group Element Abundance Patterns in Different Mantle Environments

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Mantle-derived xenoliths from the Cameroon Line and northern Tanzania display differences in their platinum-group element (PGE) abundance patterns. The Cameroon Line lherzolites have uniform PGE patterns indicating a homogeneous upper mantle over several hundreds of kilometers, with approximately chondritic PGE ratios. The PGE patterns of the Tanzanian peridotites are similar to the PGE systematics of ultramafic rocks from ophiolites. The differences can be explained if the northern Tanzanian lithosphere developed in a fluid-rich suprasubduction zone environment, whereas the Cameroon Line lithosphere only experienced melt extraction from anhydrous peridotites.

Earth's upper mantle is characterized by overabundances of the PGEs relative to the concentrations that would be expected if the core formed in metal-silicate equilibrium at near-surface conditions (*1*, *2*). This excess, and the nearly chondritic relative PGE abundances that are observed in many peridotites (*1*, *2*), have been explained by models of heterogeneous accretion that propose that a "late veneer" of chondritic material was added to Earth after segregation of the core (*3*). This interpretation has been questioned on the basis of the results of experiments that indicate that the abundances of moderately siderophile elements (for example, P, Fe, Ni, Co, Mo, and W) and Re in Earth's upper mantle are consistent with metal-silicate equilibration (that is, core segregation) at high temperature and pressure (*4*). Furthermore, a number of recent studies have reported nonchondritic PGE abundance ratios in abyssal peridotites and ultramafic rocks from orogenic lherzolite massifs (*5*–*8*). To further address the question of whether Earth's mantle is characterized by chondritic relative PGE abundances, we analyzed the concentrations of Ru, Pd, Ir, and Pt in 16 upper mantle–derived xenoliths from four localities in the Cameroon Line and two localities in northern Tanzania using isotope-dilution, Carius Tube digestion, and multiple-collector inductively coupled mass spectrometry (*9*).

Seven well-characterized (*10*), basalt-hosted ultramafic xenoliths from the Cameroon Line were analyzed (Table 1 and Fig. 1, A through D). Five of the six lherzolites (except P3) are fertile, with ~2 to 3.5% CaO (Table 1) and 10 to 15% clinopyroxene. Handpicked clinopyroxene separates of these samples display light rare earth element (LREE) depletions (chondrite-normalized $[La/Sm]_N$ = 0.29 to 0.43) that are characteristic of melt residues (*10*). The isotopic compositions and Nd-depleted mantle model ages of the lherzolites suggest that formation of the Cameroon line lithosphere occurred in the late Proterozoic, after the extraction of basaltic melts from an upper mantle similar to the present-day Atlantic mid-ocean ridge basalt (MORB) source (*10*). This interpretation is consistent with the results of geochemical and geochronological studies on northern Cameroon metavolcanics (*11*). The spinel lherzolite P3, with only ~8% clinopyroxene, contains trace amounts of amphibole and is markedly enriched in LREE ($[La/Sm]_N$ = 6.1 in clinopyroxene) and U, attesting to the metasomatic enrichment processes that affected the Cameroon Line mantle lithosphere in the Mesozoic (*10*).

All the spinel lherzolites display nearly flat PGE patterns at ~0.002 to 0.01 × CI-chondrite (Fig. 1, A through D). The observed variation of absolute PGE abundances, despite similar PGE patterns, is attributed to the "nugget effect," which is the inhomogeneous distribution of PGE-carrier phases, probably mainly sulfide minerals, within mantle rocks. P3 displays PGE patterns similar to those of unmetasomatized xenoliths, demonstrating that its PGE inventory was only marginally altered by the metasomatic processes that were associated with the enrichment of incompatible lithophile trace elements. This and the notable freshness of the other Cameroon Line xenoliths analyzed in this study (*10*) argue against the possibility that the nearly flat chondrite-normalized PGE patterns are of late secondary origin (for example, caused by the addition of a primitive sulfide phase) rather than a primary feature of these samples. The harzburgite sample (N12, Table 1 and Fig. 1D) is characterized by approximately chondritic relative abundances of Ir, Ru, and Pt and a depletion of Pd relative to the other PGEs. The latter feature is probably related to the origin of this sample as an ultramafic residue of melt depletion (*10*).

All the spinel lherzolites, except sample

**Table 1.** Analytical results for the Cameroon Line and northern Tanzanian xenoliths. Sample location abbreviations: Cam., near Mount Cameroon; Oku, near Oku; Nga., Ngaoundéré Plateau; Biu, Biu Plateau; Las., Lashaine; Olm., Olmani. Lithology abbreviations: sp., spinel; lherz., lherzolite; harz., harzburgite; gt., garnet; chr., chromite.

| Sample | Location | Lithology | CaO (weight %) | Cr* (ppm) | Ir (ppb) | Ru (ppb) | Pt (ppb) | Pd (ppb) |
|---|---|---|---|---|---|---|---|---|
| | | | *Cameroon Line* | | | | | |
| C235A | Cam. | sp. lherz. | 3.32 | 2982 | 0.88 | 1.56 | 2.40 | 1.40 |
| C235D | Cam. | sp. lherz. | 3.38 | 2729 | 3.29 | 5.34 | 6.13 | 2.91 |
| C271I | Oku | sp. lherz | 2.07 | 2484 | 3.19 | 6.24 | 5.63 | 2.92 |
| C273Q | Oku | sp. lherz. | 3.18 | 2283 | 1.15 | 1.90 | 2.17 | 1.19 |
| P3 | Nga. | sp. lherz. | 3.41 | 2484 | 3.93 | 6.50 | 5.44 | 3.92 |
| P13 | Nga. | sp. lherz. | 3.00 | 2443 | 2.33 | 4.20 | 4.25 | 2.56 |
| Sp. lherzolite average | | | 3.06 | 2568 | 2.46 | 4.29 | 4.34 | 2.48 |
| N12 | Biu | harz. | 0.44 | 1874 | 2.85 | 4.11 | 6.99 | 0.88 |
| | | | *Northern Tanzania* | | | | | |
| BD-730 | Las. | gt. lherz. | 0.72 | 2033 | 2.86 | 3.71 | 0.44 | 0.15 |
| BD-771 | Las. | chr. lherz. | 0.41 | 1468 | 0.98 | 5.67 | 0.43 | 0.27 |
| OMX-3 | Olm. | harz. | 0.18 | 1530 | 4.05 | 6.26 | 5.90 | 4.40 |
| OMX-5 | Olm. | dunite | 0.25 | 1205 | 1.15 | 3.19 | 0.64 | 1.00 |
| OMX-8 | Olm. | harz. | 0.29 | 1640 | 1.64 | 2.22 | 0.26 | 0.14 |
| OMX-10 | Olm. | harz. | 0.51 | 2120 | 0.99 | 1.06 | 0.32 | 0.16 |
| OMX-12 | Olm. | dunite | 0.14 | 990 | 1.23 | 1.13 | 0.071 | 0.095 |
| OMX-14 | Olm. | dunite | 0.41 | 1715 | 0.20 | 0.66 | 0.27 | 0.13 |
| OMX-16 | Olm. | dunite | 0.28 | 747 | 0.028 | 0.49 | 0.41 | 0.23 |
| CI chondrites (*32*) | | | | | 455 | 710 | 1010 | 550 |

*CaO and Cr abundances determined by x-ray fluorescence at the University of Edinburgh.

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C235A (Fig. 1A), are characterized by an enrichment of Ru relative to Ir and a small depletion of Pt and Pd relative to Ir and Ru (Fig. 1, A through C). These similarities are reflected in the calculated average spinel lherzolite PGE abundance data (Table 1 and Figs. 1D and 2) that show an enrichment of Ru relative to Ir of ~10%, whereas Pt and Pd, with similar CI-normalized abundance levels, are depleted by ~10 to 15% relative to Ir. The average PGE ratios of the Cameroon Line lherzolite xenoliths have relative standard deviations of between 7% (Ru/Ir) and 20 to 25% (Pd/Ir and Pt/Ir). These values are similar to, or larger than, the reproducibility of PGE ratios for individual samples (9). The data are of particular significance because the samples were collected at four different localities along a ~600-km-long stretch of the Cameroon Line (*10*). Our results therefore suggest that the PGE signature of the lithospheric mantle in the Cameroon Line is homogeneous at the 10 to 25% level, with approximately chondritic relative abundances, on the scale of several hundreds of kilometers.

The possible genetic link between the Cameroon Line lithospheric mantle and the present-day Atlantic MORB source (*10*) warrants a more detailed comparison between the PGE systematics of the Cameroon Line xenoliths, published data for fertile lherzolites from orogenic peridotite massifs that are thought to represent former subcontinental mantle, and the different chondrite meteorite classes (Fig. 2). The Pt/Ir ratio of the Cameroon Line lherzolite average is identical, within error, to the Pt/Ir ratios of chondrites and the Pyrenean peridotite average. In comparison to the meteorite results, the Cameroon Line xenoliths and the orogenic lherzolites are characterized by, on the average, higher Ru/Ir ratios. The differences are, however, smaller than the estimated uncertainties of the averages, except for H-type ordinary chondrites, which lie just outside of the Cameroon Line error bars by ~2%. Positive Ru anomalies of a similar magnitude have also been identified in mantle peridotites from a number of other locations (*7, 8*). The largest variations between the sample groups are visible in the Pd/Ir data. The Pd/Ir ratios of carbonaceous and ordinary chondrites are identical to the Cameroon Line lherzolite average, whereas EH-type enstatite chondrites and alpine peridotites have significantly higher ratios, in spite of the large errors involved in the comparison.

In summary, it is evident that the PGE systematics of the Cameroon Line mantle lithosphere are remarkably similar to carbonaceous and H- and L-type ordinary chondrites but unlike enstatite chondrites. Many orogen-

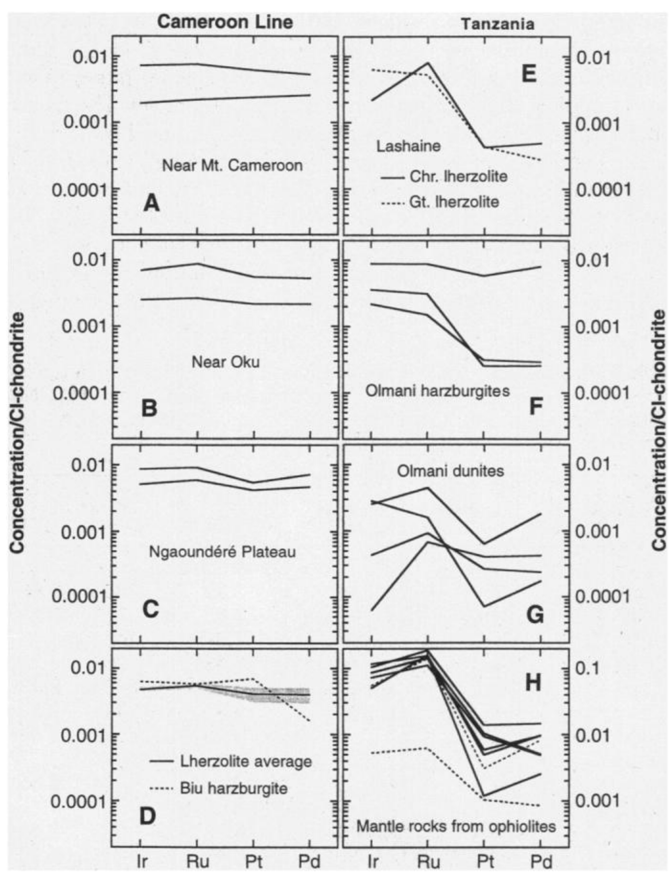


**Fig. 1.** CI-chondrite–normalized PGE abundances of Cameroon Line xenoliths (**A** through **D**); Northern Tanzanian xenoliths (**E** through **G**); and, for comparison, chromitites and dunites from ophiolite complexes (**H**). (A through C) Spinel lherzolites from three localities along an ~600-km stretch of the Cameroon Line are characterized by nearly flat PGE patterns. (D) Harzburgite from the Biu Plateau (dotted line). The average PGE pattern for Cameroon Line spinel lherzolite xenoliths (solid line) displays nearly CI-chrondritc relative concentrations. The gray shading indicates the uncertainty of this average (~7% for Ir and Ru and 20 to 25% for Pt and Pd), as calculated from the relative standard deviation of individual results. For this calculation Ru, Pt, and Pd abundances were normalized to Ir, and Ir concentrations to Ru, to account for the different absolute PGE abundance levels in the samples. (E through G) Lherzolites from Lashaine and Olmani harzburgites and dunites are characterized by strongly fractionated PGE patterns. They are remarkably similar to the PGE patterns of chromitites and dunites from ophiolite complexes shown in (H). In (H), dunites (from Bay of Islands; Twin Sisters, western United States) are shown with dashed lines; chromitites (from New Caledonia; Vourinos, Greece; Outokumpu, Finland; Bati Kef, Turkey; Troodos, Cyprus; and Samail, Oman) with solid lines. The ophiolite data represent average PGE abundances for each location, calculated from published data (*19*). Most of the ophiolites shown in (H) are believed to have formed in suprasubduction-zone environments.

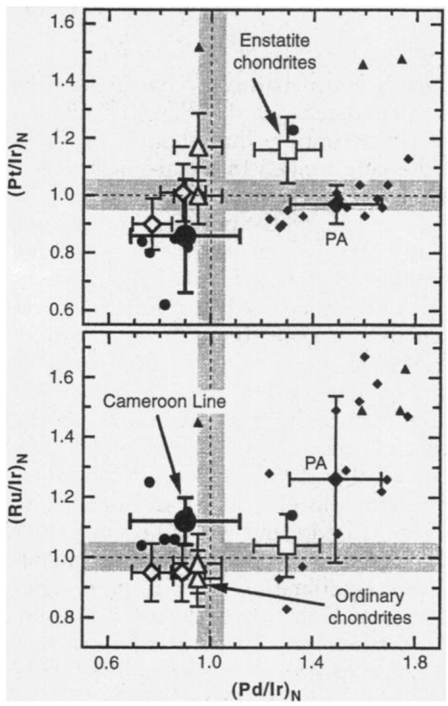


**Fig. 2.** CI-chondrite–normalized (indicated by subscript N) PGE ratio plots of Pt/Ir and Ru/Ir versus Pd/Ir for the Cameroon Line spinel lherzolites (individual data, small dots; average, large dots with error bars), CM- and CV-type carbonaceous chondrites [open diamonds (*29*)], H- and L-type ordinary chondrites [open triangles (*29*)], and EH enstatite chondrites [open squares (*29*)]. The PGE ratios of CO chondrites are within ≤4% of CV values. Also shown are data for fertile lherzolites from orogenic peridotite massifs in the Pyrenees [individual data, small solid diamonds; average (marked PA), large solid diamonds with error bars (*5*)] and the Ronda-Beni Bousera massifs [small solid triangles (*6*)]. Some of the samples in these data sets, particularly for Ronda-Beni Bousera, fall outside of the range of values plotted. The gray shading represents the uncertainty of the CI data [±5% (*30*)]. All other meteorite data were assigned an error of ±10%, based on the variability of Ru/Ir ratios in EH chondrites (*31*). Error bars for the Cameroon Line and Pyrenean lherzolite averages represent the relative standard deviation of PGE ratios for the respective data sets (7 to 24%).

ic lherzolites, on the other hand, appear to be characterized by less "primitive" PGE ratios. The data furthermore support previous indications of a terrestrial upper mantle that is not characterized by homogeneous PGE ratios throughout but rather by a variety of reservoirs with different PGE systematics (5, 8). It is presently unclear, however, whether these differences are related to original variations in the composition of the late veneer, caused by the addition of differentiated core material to the mantle (5, 8), or are the result of recent geological processes associated with the formation and stabilization of the lithospheric mantle.

The second set of samples, from northern Tanzania, consists of nine ultramafic xenoliths: two lherzolites from Lashaine volcano (Table 1 and Fig. 1E) that were described previously (12) and seven xenoliths from the Olmani Cinder Cone (Table 1 and Fig. 1, F and G). The sample with the highest PGE abundances, OMX-3 (Fig. 1F), displays a nearly flat PGE pattern. All other northern Tanzanian xenoliths are characterized by low concentrations of Pt and Pd, ranging from less than 0.0001 to 0.002 × CI-chondrite.

The Tanzanian peridotites have a wide range of Ru/Ir ratios, but with the exception of two samples (OMX-3 and OMX-16), the nodules display negatively sloping PGE patterns and low ratios of Pd/Ir (range 0.05 to 0.87) and Pt/Ru (range 0.06 to 0.40). The studies of Rudnick and co-workers (13, 14) demonstrated that Olmani xenoliths were pervasively overprinted by carbonatite metasomatism associated with Tertiary to Recent rift volcanism. The similar PGE systematics of Olmani and Lashaine nodules suggest that these late metasomatic reactions had no effect on the PGE patterns of the Olmani samples.

Even though refractory and enstatite-rich cratonic peridotites (such as the Kapvaal and Lashaine garnet lherzolites) have been interpreted as residues following the extraction of komatiitic melts in the Archean (15), petrological studies have demonstrated that such an origin is unlikely for the northern Tanzanian xenoliths (13). An alternative petrogenesis, involving multiple episodes of melt extraction in a subduction zone setting combined with re-enrichment of the refractory residue by silicic melts derived from the subducting slab, has been proposed (13, 16). The location of the Olmani and Lashaine volcanoes within the Usagaran Province, an ~1.9-billion-year-old mobile belt, ~150 km to the east of the Archean Tanzanian Craton would appear to support such an interpretation (13, 15). Similarly, the Pb and Nd isotopic systematics of Lashaine xenoliths record a major chemical fractionation event at ~2.0 billion years ago (17), characterized by melt depletion and concurrent metasomatic enrichment processes involving the addition of a recycled component, ultimately derived from the continental crust, to the lithospheric mantle (13, 17, 18).

The PGE patterns of the Lashaine and Olmani xenoliths with low Pd/Ir and Pt/Ru ratios are similar to the PGE patterns of podiform chromitites and chromite-rich dunites from the mantle sections of ophiolite complexes (19) (Fig. 1H). These rocks display ratios of Pd/Ir (0.03 to 0.23) and Pt/Ru (0.01 to 0.24) that are similar to the ratios measured for the northern Tanzanian xenoliths. All the principal ophiolite complexes are considered to have formed in fluid-rich suprasubduction zone settings (20, 21), and we suggest that the processes causing extremely fractionated PGE patterns may be related to such a fluid-rich tectonic environment. The independent evidence for the formation (or processing) of the northern Tanzanian mantle lithosphere in a subduction zone setting and the similarity of the PGE patterns of the xenoliths to mantle rocks from ophiolites appear to confirm this conclusion. There are two possible mechanisms by which the fluid-rich environment of a suprasubduction zone could cause the fractionated PGE patterns observed in refractory mantle rocks from ophiolites and the northern Tanzanian xenoliths. First, higher degrees of melt depletion are possible as compared with those from anhydrous melting; second, the fractionation may be caused by fluid-phase transport of the more mobile PGEs Pt and Pd.

It has been suggested that PGE patterns of mantle rocks can be fractionated during partial melting or crystal fractionation because of the compatibility of Ir and Ru in spinels, whereas Pt and Pd are inferred to be incompatible (22). This explanation, however, is inconsistent with a number of petrological and geochemical studies (23). Furthermore, the northern Tanzanian xenoliths show no correlation between Cr contents and PGE concentrations (Table 1), demonstrating that PGE abundances and patterns of the rocks are not controlled by partitioning into chromite during melt depletion. Presently available PGE concentration data for ultrarefractory mantle peridotites appear to rule out fractionation of PGE ratios in residual mantle rocks from originally chondritic relative abundances to ratios of 0.1 × CI-chondrite and less, solely as the result of melt depletion in a dry environment. Abyssal harzburgites and ultrarefractory alpine peridotites considered to be residues of anhydrous melting are generally characterized by PGE patterns that are less fractionated than those of the northern Tanzanian xenoliths, at similar levels of major element depletion (24). The presence of water in the mantle above subduction zones permits greater degrees of partial melting as compared with those under anhydrous conditions (20, 25). Because melt depletion is generally associated with the loss of Pt and Pd relative to Ir and Ru, this provides one possible explanation for the highly fractionated PGE patterns of residual suprasubduction zone rocks.

The mobilization of the PGEs by magmatic fluids presents an additional mechanism for fractionation. Several studies have identified volatile- and Cl-rich fluid inclusions in chromitites from ophiolite complexes (26), and the mobility of the PGEs in such fluids has been confirmed by theoretical and experimental studies (27). This conclusion is supported by geochemical investigations of natural systems that demonstrate mobility of the PGEs in fluid-rich environments (28). Furthermore, most of these studies suggest a greater transport efficiency for Pt and Pd relative to Ir, Ru, and Os. Selective mobilization of Pt and Pd by fluids released from subducting slabs could thus account for the low Pd/Ir and Pt/Ru ratios observed in mantle rocks from suprasubduction zones.

It appears that the variable but generally fractionated PGE patterns of the Tanzanian xenoliths are most likely the result of a complex petrogenetic history in a suprasubduction zone environment. The fluid-phase transport processes and multiple episodes of melt depletion that dominate petrogenesis in such a tectonic regime provide suitable mechanisms for the fractionation of PGE ratios and can account for the unusual PGE systematics of the refractory Tanzanian nodules.

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9. Before being crushed, the disagregated samples were inspected under a binocular microscope, and pieces showing surface alteration were discarded. The samples were then cleaned with deionized water and crushed in a precontaminated alumina shatterbox. After the 5- to 10-g samples were spiked with tracer solutions of $^{99}$Ru, $^{105}$Pd, $^{191}$Ir, and $^{198}$Pt and desilicificated with HF/HCl, they were further digested in sealed Carius

Tubes [S. B. Shirey and R. J. Walker, *Anal. Chem.* **67**, 2136 (1995)] for ~48 hours at 230°C. After dissolution, the PGEs were isolated from one another and the bulk-rock matrix by anion-exchange chromatography [M. Rehkämper and A. N. Halliday, *Talanta* **44**, 663 (1997)]. The pure PGE fractions were then analyzed with a Plasma 54 multiple-collector inductively coupled plasma mass spectrometer [A. N. Halliday *et al.*, *Int. J. Mass Spectrom. Ion Processes* **146/147**, 21 (1995)]. Multiple analysis of Iceland basalt sample BTHO and Alexo komatiite sample KAL-1 demonstrate that our techniques achieve external reproducibilities of ~1.5 to 9% for the PGEs in the concentration range from parts per billion to parts per trillion. Duplicate analysis of two peridotite samples (OMX-8 and C235A) indicate a somewhat lower reproducibility (≤15%), probably owing to the heterogeneity of the coarse-grained rocks. The PGE ratios of the duplicates, however, were identical to within 1 to 8%. Blanks for the Cameroon Line samples, digested with conventional Carius Tubes, were <10 pg/g for Ru, Pd, and Ir and 100 to 200 pg/g for Pt. Northern Tanzanian xenoliths were digested with the use of a modified Carius Tube design, and this technique achieves blanks of <15 pg/g for all analyzed PGEs (M. Rehkämper, A. N. Halliday, R. F. Wentz, *Fres. J. Anal. Chem.*, in press).

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23. Spinels from fertile western Australian lherzolites, for example, are characterized by superchondritic Pd/Ir ratios (2), as are chromitites from stratiform chromite deposits [C. McLaren and J. P. R. De Villiers, *Econ. Geol.* **77**, 1348 (1982); S. J. Perry, *Chem. Geol.* **43**, 115 (1984)]. Furthermore, a large proportion of the PGE budget of fertile peridotite xenoliths appears to be contained in acid-leachable, intergranular sulfide phases, whereas spinel is only a minor host for the PGEs (2) [S. R. Hart and G. E. Ravizza, in *Earth Processes: Reading the Isotopic Code*, A. Basu and S. R. Hart, Eds. (American Geophysical Union, Washington, DC, 1996), pp. 123–134]. Although chromitites from ophiolite complexes are characterized by high PGE abundances, a number of detailed studies demonstrate that the PGEs are not incorporated into the lattice of the chromites but are concentrated in sulfide and alloy inclusions; the chromites themselves have no bearing on the fractionation of the PGEs [for example, H. W. Stockmann and P. F. Hlava, *Econ. Geol.* **79**, 491 (1984); R. W. Talkington, D. H. Watkinson, P. J. Whittaker, P. C. Jones, *Tschermaks Mineral. Petrogr. Mitt.* **32**, 285 (1984); R. J. Walker, E. Hanski, J. Vuollo, J. Liipo, *Earth Planet. Sci. Lett.* **141**, 161 (1996)].
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# Transitions Between Blocked and Zonal Flows in a Rotating Annulus with Topography

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The mid-latitude atmosphere is dominated by westerly, nearly zonal flow. Occasionally, this flow is deflected poleward by blocking anticyclones that persist for 10 days or longer. Experiments in a rotating annulus used radial pumping to generate a zonal jet under the action of the Coriolis force. In the presence of two symmetric ridges at the bottom of the annulus, the resulting flows were nearly zonal at high forcing or blocked at low forcing. Intermittent switching between blocked and zonal patterns occurs because of the jet's interaction with the topography. These results shed further light on previous atmospheric observations and numerical simulations.

On short time scales (1 to 10 days), weather evolution is largely driven by three-dimensional, baroclinic instabilities of the prevailing westerlies (*1*) that convert the potential energy in the atmosphere's pole-to-equator temperature difference into the kinetic energy of storms (*2*). One to three times each Northern Hemisphere winter—and occasionally during other seasons—large high-pressure anticyclones form and persist for at least 10 days and sometimes longer than a month (*3–5*). These anticyclones block the nearly zonal flow and deflect it poleward (Fig. 1B). The prediction of blocking events has become central to improving extended-range weather prediction (*6, 7*).

Low-frequency atmospheric variability on the time scale of 10 to 100 days, such as persistent blocking anomalies, is predominantly barotropic, that is, nearly two-dimensional (*5, 8, 9*). Analytic and numerical models have shown that blocked and zonal flow patterns can arise through the interaction of large-scale eastward zonal flow with idealized Northern Hemisphere topography (*7, 8, 10–12*), and recent numerical simulations using a general circulation model (*13*) support these results. Zonal and blocked flows appear as two stable equilibria (*8, 10, 11*) or two separate chaotic flow regimes (*12, 14–16*) in simple and intermediate models.

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