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Start of the Wilson Cycle at 3 Ga Shown by Diamonds from Subcontinental Mantle

Steven B. Shirey[1]* and Stephen H. Richardson[2]*

Mineral inclusions encapsulated in diamonds are the oldest, deepest, and most pristine samples of Earth's mantle. They provide age and chemical information over a period of 3.5 billion years—a span that includes continental crustal growth, atmospheric evolution, and the initiation of plate tectonics. We compiled isotopic and bulk chemical data of silicate and sulfide inclusions and found that a compositional change occurred 3.0 billion years ago (Ga). Before 3.2 Ga, only diamonds with peridotitic compositions formed, whereas after 3.0 Ga, eclogitic diamonds became prevalent. We suggest that this resulted from the capture of eclogite and diamond-forming fluids in subcontinental mantle via subduction and continental collision, marking the onset of the Wilson cycle of plate tectonics.

The set of plate tectonic processes whereby continental pieces are dispersed and then reassembled on the surface of Earth, known as the Wilson cycle (*1*–*3*), leads to supercontinents, crustal growth, mountain building, the basic distribution of crustal age provinces, and ore deposits. This fundamental, multistage cycle repeats through geologic time, and its operation from the Precambrian through today is apparent in the geologic record of crustal rocks (*2*–*6*); however, the timing of the start of the Wilson cycle is uncertain.

Mineral inclusions in diamonds, formed within the ancient lithospheric mantle keels of stable continental crustal regions known as cratons, may provide insight into the Wilson cycle from deep within the continental lithosphere. Lithospheric macrodiamonds amenable to geochronological investigation formed in the Precambrian via fluids involved in carbonate reduction or methane oxidation (*7*) and have resided at depths of 125 to 175 km for billions of years (*8*). Mineral inclusions, mainly silicates and sulfides, that formed or equilibrated at the time of diamond growth were encapsulated by diamonds and remained impervious to the widespread metasomatism (*9*, *10*) that affected the lithosphere throughout time. Diamonds, with their protected inclusion cargo, were typically picked up later in Mesozoic to Cenozoic kimberlitic volcanism and were carried to the surface as xenocrysts in kimberlite (*8*).

We analyzed the complete literature data set of 4287 silicate inclusions and 112 sulfide inclusions in diamonds from the nuclei of five ancient continents (Australian, Kaapvaal, Siberian, Slave, and Zimbabwe; fig. S1) (*11*), which were previously studied for their geochronology (*12*–*14*). Each mineral group can be classified according to its composition. Peridotitic inclusions are akin to peridotite from the mantle, whereas eclogitic inclusions resemble metamorphosed basaltic rock from the crust (fig. S2). Peridotitic silicate inclusions can be further subdivided into harzburgitic or lherzolitic, depending on the degree of major element depletion resulting from previous partial melting.

Typically, specific portions of the continental lithosphere are probed by studying groups of diamonds from the same kimberlite pipe. Silicate inclusions are amenable to analysis using the Sm-Nd isotope system only after combining like mineral grains from multiple diamonds, whereas single sulfide inclusions from one diamond are amenable to analysis using the Re-Os isotope system. Therefore, determining the full spread of formation ages for multiple generations of diamonds from a given locality is limited by the necessity of combining inclusions, particularly for eclogitic inclusions and use of the Sm-Nd system (Fig. 1A). The crucial consideration for using diamonds to constrain the Wilson cycle is that they yield the age of isolation, by incorporation into the subcontinental lithospheric mantle (SCLM), of the inclusion components from the convecting mantle. For silicate inclusions, this often can be 500 to 1500 million years older than the diamond crystallization age, whereas for sulfide inclusions it is only

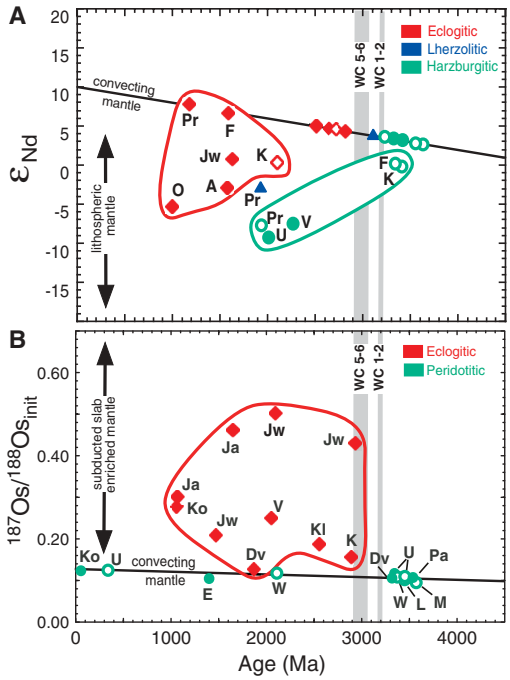

Fig. 1. (**A**) Silicate inclusion initial Nd isotopic composition versus Sm-Nd age for diamonds of peridotitic (circles), lherzolitic (triangles), and eclogitic (diamonds) parageneses. Solid symbols are isochron studies for composites of garnet and clinopyroxene grains; open symbols are model age studies for composites of garnet only. Unlabeled points on convecting mantle curve are mantle extraction ages extrapolated from labeled points (*11*). (**B**) Sulfide inclusion initial Os isotopic composition versus Re-Os age. Solid symbols are isochron studies; open symbols are model age studies for single grains. For isochron studies, mantle extraction ages extrapolated from labeled points are typically <100 million years (one scale division) older than the isochron age (*11*). In (A) and (B), WC 1-2 denotes Wilson cycle rifting (stages 1 and 2) for the Pilbara craton (*6*); WC 5-6 denotes Wilson cycle continental closure (stages 5 and 6) for the Kaapvaal craton. Locality abbreviations are given in table S1.

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10 to 100 million years older than the diamond crystallization age (*11*).

Eclogitic silicate inclusion suites give Sm-Nd isochron ages from 1 to 2 Ga, whereas peridotitic silicate inclusion suites give isochron or model ages from 1.9 to 3.4 Ga (Fig. 1A and table S1). Most eclogitic and all peridotitic silicate inclusion suites form from protoliths enriched in light rare earth elements (LREEs; i.e., low $^{147}Sm/^{144}Nd$) that, at least for peridotitic silicate inclusions, require a two-stage history of depletion followed by strongly LREE-enriched alkali-carbonate metasomatism. Relative to eclogitic silicate inclusions, peridotitic silicates were encapsulated with systematically lower initial Nd isotopic compositions (Fig. 1A); moreover, the mantle extraction age for peridotitic silicate inclusions is much older than for eclogitic silicate inclusions. Most diamonds with eclogitic silicate inclusions formed later than 2.2 Ga, but their protoliths began to separate from the convecting mantle around 3.0 Ga, whereas peridotitic silicate inclusion protoliths date from the Paleoarchean.

Single sulfide inclusions analyzed for Re-Os isochrons or model ages (Fig. 1B and table S1) show that the Archean and the Proterozoic were major eras of diamond formation. Although this is also the case for silicate inclusions, sulfide inclusions can be more specifically linked to geologic events, because there is a direct relationship between the Re/Os ratio of the sulfide and that of the diamond protolith, given that sulfides crystallize from (or equilibrate directly with) diamond-forming C-O-H-S fluids. Eclogitic sulfides, with one exception, form from protoliths that have a systematically higher initial Os isotopic composition than do peridotitic sulfides. The isochron and mantle model ages for the peridotitic sulfides extend to older ages than those of the eclogitic sulfides. Peridotitic sulfide inclusion protoliths typically date from the Paleoarchean; only rarely do peridotitic sulfides form at younger times. More important, the Paleoarchean was an era when diamonds with eclogitic sulfides did not form.

The composition of sulfide inclusions varies with age (Fig. 2). Proterozoic and Archean (<3 Ga) sulfide inclusions show eclogitic or basaltic Re/Os ratios (2 to 30), with some Proterozoic inclusions trending toward lower Re/Os ratios typical of the fertile mantle. Archean (>3 Ga) sulfide inclusions show peridotitic Re/Os ratios (0.01 to 0.03) and plot in a group with higher Os contents and lower Re/Os ratios typical of depleted subcontinental mantle. No Paleoarchean sulfide inclusions with high, eclogitic Re/Os ratios have been found. Paleoarchean sulfides have low Re/Os because they crystallized in mantle peridotite that was residual after melt extraction that lowered its Re concentration to less than 10 parts per trillion. Sulfides younger than 3 Ga have higher Re/Os because they crystallized from basaltic or komatiitic (i.e., eclogitic) melting products of the mantle (Fig. 2).

The type of sulfide inclusion changes with age; peridotitic sulfides occur prominently before 3.2 Ga while eclogitic inclusions are completely absent, whereas eclogitic sulfides are prevalent after 3.0 Ga (Fig. 1B and Fig. 3). The Re/Os of peridotitic sulfide inclusions rises from a $^{187}Re/^{188}Os$ of about 0.02 in the Paleoarchean to an average of around 1 in the Proterozoic to Phanerozoic. The Re/Os ratio of eclogitic sulfide inclusions is consistently higher by one to two orders of magnitude, shows large variability, and does not change substantially from the Mesoarchean through to the Neoproterozoic.

The Mesoarchean assembly of the Kaapvaal craton, which hosts the majority of the diamonds reported here, resulted from the collision of two separate continental blocks—the Witwatersrand and Kimberley blocks—at 3.1 to 2.9 Ga (*15*, *16*). This collision of two blocks of continental lithosphere via the closure of an ocean basin, evident from the separate tectonothermal history of each block (*16*), is a good example of the latter stages (i.e., stages 5 and 6) of Wilson's original definition. Small percentages of Mesoarchean eclogite are widespread in the SCLM of the Kaapvaal craton (*17*), as are eclogitic silicate and sulfide inclusions in diamonds (Fig. 1) (*17*, *18*). This provides compelling evidence that capture and incorporation of eclogite in the SCLM occurs via subduction and continental collision, and is linked to the deep subduction of fluids necessary for diamond formation. If the assembly of the Kaapvaal craton is taken as an example of stages 5 and 6 of the Wilson cycle, then we suggest in principle that the cratonic mantle keels involved in the continental collisional stages of the Wilson cycle, if deep enough, should record the process. They should display eclogites of the closure age in their mantle xenolith sample suites (*17*) and eclogitic sulfide inclusions of the closure age in their diamond populations (*18*). We argue that the preservation of eclogitic materials deep within the SCLM after continental collision is the continental mantle hallmark of the Wilson cycle.

The absence of eclogitic inclusions in the Paleoarchean diamond populations from all cratons studied to date (Figs. 1 and 3) is arguably more important than their abundance at any younger age. This observation is also supported by whole-rock eclogitic xenolith ages of less than 3 Ga from the three cratons where diamonds and eclogites have both been dated (table S1). Only one such study by any isotopic system (e.g., Re-Os, Sm-Nd, or Pb-Pb) has yielded eclogite ages older than 3.2 Ga. Diamonds have not been dated from the latter craton, however, and the large uncertainty on the age (3.4 ± 0.8 Ga) overlaps 3 Ga by a wide margin.

Paleoarchean sulfide and silicate inclusions in diamonds are all peridotitic and of an especially

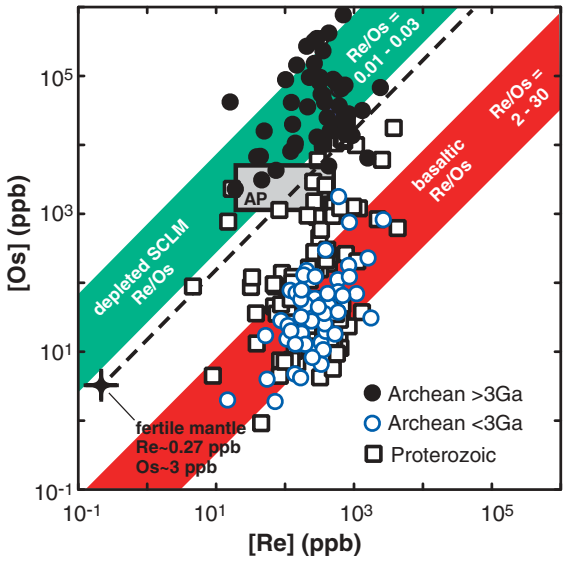

Fig. 2. Sulfide inclusions compared using measured Re and Os abundance in parts per billion (ppb) and grouped by age. Fertile mantle abundances from (*34*) are for whole-rock peridotites. Field labeled AP encloses data for sulfides in present-day abyssal peridotites (*35*).

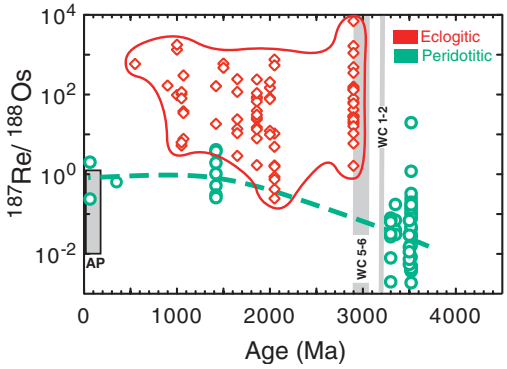

Fig. 3. Peridotitic (circles) and eclogitic (diamonds) sulfide inclusion $^{187}Re/^{188}Os$ (divide by ~3.9 to convert to Re/Os) versus age. Field labeled AP encloses data for sulfides in present-day abyssal peridotites (*35*). WC 1-2 and WC 5-6 are as defined in Fig. 1.

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depleted character (*8*, *19*) (Figs. 2 and 3). Even though three of five cratons (Australia, Kaapvaal, and Siberia) are each represented by only one such sulfide inclusion, these are nonetheless consistent with the data for reasonably large suites of diamonds from the Slave craton. Among 59 sulfide-bearing diamonds from two well-studied kimberlite pipes, Panda (Ekati) and Diavik, 13 are eclogitic and 46 are peridotitic (table S1). All the eclogitic specimens lie on a single data array with an age of 1.8 to 2.1 Ga (*20*), and all have initial Os isotopic ratios suggesting that eclogite was a recent addition to the lithosphere at that time (Fig. 1B). Conversely, all the peridotitic sulfide inclusions fall on older isochrons or data arrays with ages of 3.3 to 3.5 Ga (*19*, *21*) and much lower initial Os isotopic compositions supporting these ages (Fig. 1B). The Slave craton has crustal elements that range in age from 4.0 Ga to as young as 2.7 Ga (*2*, *22*). If the Wilson cycle had operated in the Paleoarchean to assemble this craton, we would expect it to have left clear evidence of this in the form of Paleoarchean eclogitic sulfides, which should have been sampled along with the Paleoarchean peridotitic sulfides and the Proterozoic eclogitic sulfides.

The differences in sulfide inclusion suites from the Kaapvaal and Slave cratons reveal various eras in Earth's geodynamic evolution, analogous to the way in which Wilson (*1*) used different ocean basins in various stages of development to reveal the entire Wilson cycle. The geology of continental crust younger than 3 Ga can be understood as a product of the Wilson cycle. However, for continental crust older than 3.2 Ga, our study suggests that the Wilson cycle is not appropriate because eclogitic materials from the subducting slab that should have been incorporated into the continental lithosphere are missing. The absence of Paleoarchean eclogite xenoliths and eclogitic sulfides in diamonds from the lithospheric mantle of the Slave and other cratons suggests that their continental nuclei formed by non–Wilson cycle processes.

In the Paleoarchean, the absence of a true Wilson cycle does not rule out the presence of some form of recycling or even shallow plate subduction. Indeed, geochemical signatures of subduction from this time have been suggested in continental crust (*23*, *24*), ancient continental sediments (*25*), putative ophiolite complexes (*26*), and Earth's oldest mafic crust (*27*). Slave craton peridotitic sulfide inclusions in diamonds from the Panda kimberlite pipe and their associated harzburgites (*19*) have elevated initial Os isotopic compositions that are best explained by some form of recycling, whereas subsequent studies of other Slave craton peridotitic sulfide inclusions have argued for a deeper, plume-related origin (*21*). This suggests that enriched compositions previously ascribed to plate tectonic subduction (*19*) may have been created by small-scale, local processes that restricted these diamonds to a shallow layer in the lithosphere (*19*) known to have experienced greater oxidation (*28*). We envision oceanic crust that was too buoyant to permit deep subduction and continental crustal fragments that were too small for their mantle keels to capture eclogite. Furthermore, mechanisms such as oceanic plateau accumulation, extensive hydrothermal alteration of growing volcanic piles (*27*), vertical tectonics (*29*), delamination (*30*, *31*), or flow around plume-like mantle instabilities (*32*, *33*) provided less conventional ways of making and recycling crust. In this situation, recycling—coexisting with these other processes—would perhaps have been restricted to slab-free, locally induced downwellings that dragged fluid-bearing lithologies to appropriate depths for remelting driven by density or by convective counterflow. The onset of the Wilson cycle at 3 Ga would have marked the end of crustal growth dominated by such processes.

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Figs. S1 to S3
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Supramolecular Archimedean Cages Assembled with 72 Hydrogen Bonds

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Self-assembly of multiple components into well-defined and predictable structures remains one of the foremost challenges in chemistry. Here, we report on the rational design of a supramolecular cage assembled from 20 ions of three distinct species through 72 hydrogen bonds. The cage is constructed from two kinds of hexagonal molecular tiles, a tris(guanidinium)nitrate cluster and a hexa(4-sulfonatophenyl)benzene, joined at their edges through complementary and metrically matched N-H•••O-S hydrogen bonds to form a truncated octahedron, one of the Archimedean polyhedra. The truncated octahedron, with an interior volume of 2200 cubic angstroms, serves as the composite building unit of a body-centered cubic zeolite-like framework, which exhibits an ability to encapsulate a wide range of differently charged species, including organic molecules, transition metal complexes, and "ship-in-a-bottle" nanoclusters not observed otherwise.

Supramolecular cages assembled from molecular building blocks have captivated the attention of many investigators owing to their elegant structures as well as their ability to encapsulate guest molecules, serving as molecular flasks for confined chemical reactions (*1*), stabilization of reactive molecules (*2*), chiral separations (*3*), and catalysis (*4*). A virus capsid—the outer shell of a virus—is a fascinating natural example of a supramolecular cage compris-

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