# Mineralogical Evolution of Meteorites

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he approximately 250 mineral species found in meteorites record the earliest stages of the birth of our solar system. Refractory minerals that formed during the violent deaths of other stars and during condensation of our own solar nebula mixed with a wide range of silicates, sulfides, and metals to form the most primitive chondritic meteorites. Subsequent aqueous alteration, thermal metamorphism, and shock metamorphism further diversified the minerals found in meteorites. Asteroidal melting at first increased and then dramatically decreased mineralogical diversity, before a new phase of igneous differentiation that presaged the processes that would occur in terrestrial planets.

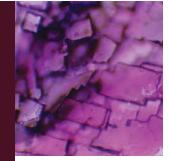
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# FRAGMENTS FROM THE BEGINNING

As Earth evolved over the last 4.5 billion years, its mineralogy changed. As we peer back through Earth's history, it seems logical to think that our lens would grow increasingly fogged and our light ever more dim. How do we see beyond the oldest preserved rocks and minerals, after billions of years of volcanism, plate tectonics, and weathering? How do we see past the Moon-forming collision, which would have melted the early Earth? Where is the starting point for the mineralogical evolution of Earth and the other terrestrial planets?

Scientists are fortunate that gravitational perturbations from Jupiter prevented the formation of a planet in what is now the asteroid belt. Asteroids, cosmic relicts of our solar system's formation, not only preserve this earliest history, they also generously shed pieces that carry their treasure trove of information to Earth. This continuing flux of meteorites provides a clear picture of early mineralogical evolution.

This earliest record is more diverse and more complicated than we might have ever imagined from the mineralogy of Earth alone. Earth's mineralogical evolution began long before there were planets. The nebula from which our solar system originated was seeded with minerals formed in the cauldrons of dozens of dying earlier-generation stars. As the solar nebula cooled, minerals formed, reacted with the gas, and disappeared, but pieces were sequestered and preserved along the way. Even these earliest-formed minerals were reworked by chemical reactions, heating, and alteration in the solar nebula. Once asteroids accreted, water ice melted and alteration minerals appeared. Impacts transformed minerals under intense heat and pressure. Radiogenic heating produced mild metamorphism at first,



Halite crystals from the Monahans chondrite contain fluid inclusions, which indicate significant water-rock interactions in the meteorite's parent body. Image width ~5 mm. COURTESY OF M. ZOLENSKY AND R. BODNAR

but eventually transformed some asteroids into molten worlds that formed crusts, mantles, and cores reminiscent of our own planet. It is this history—from the earliest beginnings to the melting of planets—that we explore in this article.

### THE STELLAR CAULDRON

Earth's mineralogical evolution began not in the heat of an early molten planet but in the blast furnace of stars that predated our

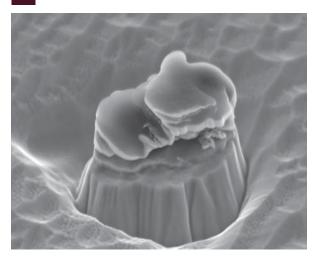
solar system. More than 4.6 billion years ago, presolar grains formed when temperatures in the expanding envelopes of red giants or in supernova ejecta fell sufficiently to allow condensation. These grains entered the interstellar medium, where many were destroyed by supernova shocks and sputtering by stellar wind. Eventually, grains from a diversity of stars were incorporated into the dense molecular cloud from which our solar system formed, and they accreted to form asteroids.

Although the existence of presolar grains was inferred from hydrogen, noble gas, and oxygen isotope anomalies in meteorites (Black and Pepin 1969), these grains were positively identified only in the late 1980s. Using chemical dissolution and physical separation steps (akin to burning down the haystack to find the needle), the earliest workers identified diamond, silicon carbide, and graphite in meteorites (Zinner 2004; Bernatowicz et al. 2006). These grains typically are up to only a few micrometers in size, and their abundance ranges from parts per billion to hundreds of parts per million. Subsequent to these discoveries, a range of presolar grains were identified. The ion microprobe and transmission electron microscope were used to study both individual grains within acid residues after chemical dissolution of the meteorite and in situ grains, particularly in interplanetary dust particles (IDPs). These presolar minerals include the nitrides osbornite (TiN) and nierite ( $\alpha$ -Si<sub>3</sub>N<sub>4</sub>); the carbide cohenite [(Fe,Ni,Co)<sub>3</sub>C]; the alloy "kamacite" (Fe,Ni); the oxides rutile (TiO<sub>2</sub>), corundum (Al<sub>2</sub>O<sub>3</sub>), spinel (MgAl<sub>2</sub>O<sub>4</sub>), and hibonite (CaAl<sub>12</sub>O<sub>19</sub>) (Fig. 1); and the silicates forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and perovskite-structured MgSiO<sub>3</sub> (Zinner 2004).

To date, these dozen or so minerals are the only record of the minerals that accreted to form our solar system, but this is far from a complete inventory. Presolar-grain research is perhaps the most active area in the field of meteoritics, and new minerals are being discovered continually. Among the materials known but not yet character-



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**FIGURE 1** Secondary electron image of a presolar hibonite grain that grew as multiple connected plates. The grain rests on a gold foil that has been ablated around the grain, leaving it perched on a gold pedestal. The grain is about 5 micrometers across. IMAGE COURTESY OF LARRY NITTLER AND RHONDA STROUD

ized as minerals are Ti-, Fe-, Zr-, and Mo-carbides (Zinner 2004), a new Al<sub>2</sub>O<sub>3</sub> structure (Stroud et al. 2007), FeO (Floss et al. 2008), and TiO<sub>2</sub> (Nittler et al. 2008). Further, much of the presolar material observed in IDPs and primitive chondrites is amorphous, nonstoichiometric, or partially crystalline. While not qualifying as minerals, these materials certainly suggest that a much more robust selection of solid matter accreted to form the early solar system. The methods for detecting presolar grains-either harsh chemical dissolution or in situ study of extremely small areaslimit our ability to characterize fully these solid materials. Finally, the processes in the early solar system almost certainly destroyed many presolar materials. Thus, while our current inventory of presolar minerals is small, our mineralogical view of this epoch may change dramatically over the next decade.

### **FROM THE NEBULA**

The earliest materials formed within our own solar system are the so-called calcium-aluminum inclusions (CAIs). These millimeter- to centimeter-sized, rounded to irregular, typically light-colored particles first drew significant attention after the fall of the Allende carbonaceous chondrite meteorite in February, 1969, although they had been described a year earlier by Christophe Michel-Lévy (1968). The Allende meteorite provided researchers with hundreds of kilograms of material containing centimeter-sized CAIs. Early attention focused on the similarity between CAI mineralogy and the first phases predicted to condense out of a gas of solar composition (Grossman 1972). We now recognize that nearly all CAIs experienced prolonged histories of reaction with nebular gas, multiple heating and/or melting episodes, and alteration in the nebula and/or the asteroid parent bodies. Nonetheless, their fascinating hightemperature mineralogy reflects their formation from hightemperature condensates in the solar nebula.

While some two dozen mineral phases are known from CAIs, a few dominate, including spinel (MgAl<sub>2</sub>O<sub>4</sub>–FeAl<sub>2</sub>O<sub>4</sub>), melilite [gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) to åkermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>)], perovskite (CaTiO<sub>3</sub>), hibonite, calcic pyroxene, anorthite, and forsterite. Less common minerals include grossite (CaAl<sub>4</sub>O<sub>7</sub>), corundum, and rhönite [Ca<sub>4</sub>(Mg,Al,Ti)<sub>12</sub>(Si,Al)<sub>12</sub> O<sub>40</sub>] (MacPherson 2004; Beckett et al. 2006). Even at this earliest stage of mineralogical evolution, all the major

crystal systems were represented. Although the different types of CAIs vary among different classes of chondritic meteorites, spinel–pyroxene-rich and melilite-rich CAIs are found in virtually all chondrites (MacPherson 2004). Further, these minerals are highly depleted in volatile trace elements, such as alkali metals, and iron. As is the case for presolar grains, the mineralogy of CAIs is incompletely understood. The field of nanomineralogy (e.g. Ma et al. 2009) is revealing a broad array of minerals found only at the scale of a few to ten micrometers. Each of these minerals testifies to unique combinations of chemical composition and intensive variables (e.g. temperature, pressure, and oxygen fugacity).

Although the CAIs were highly processed within the solar nebula, the range of CAI bulk compositions and, by extension, the minerals that formed from them may largely reflect the temperature of condensation of the CAI precursor. Thus, the precursors to refractory Type A CAIs rich in melilite, spinel, and hibonite formed at higher temperatures than the precursors of Type B CAIs rich in melilite, calcic pyroxene, anorthite, and spinel (MacPherson 2004). The minerals in CAIs record the first appearance in the solar system of distinct environments with different intensive variables (e.g. temperature). This creation of differing environments over the next 4.5 billion years produced the mineralogical diversity observed today.

While calcium-aluminum inclusions exhibit some of the most important mineralogical diversity observed among primitive nebular materials, they represent a volumetrically minor component of these materials. The full range is shown by chondritic meteorites, which are essentially cosmic sedimentary rocks (Scott and Krot 2004). Millimetersized spheres called chondrules (Fig. 2) were formed during flash melting in the solar nebula and volumetrically dominate chondritic meteorites (Lauretta et al. 2006). The finegrained matrix between the chondrules and CAIs is largely silicate material but contains a diversity of metals, sulfides, oxides, and phosphates. The chondrites themselves are diverse, particularly with respect to oxygen fugacity, and range from the highly reduced enstatite chondrites to the oxidized carbonaceous chondrites and R chondrites. Metamorphism, aqueous alteration, and shock all modified

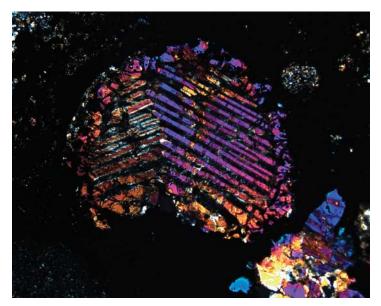


FIGURE 2 Millimeter-sized chondrules, like this one from the Allende meteorite, formed as molten droplets in the solar nebula. The bands are olivine lamellae. Field of view is ~1 mm in width.

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chondritic meteorites. To see through these later stages of alteration, meteorite scientists focus on the least altered, least metamorphosed chondrites, which are termed *petrologic type 3.0*. Within these least altered meteorites, the diversity of components formed under a wide range of oxygen fugacity and temperature conditions produced nearly 60 minerals (Brearley and Jones 1998).

Among these minerals, Mg-rich olivine, Mg-rich pyroxene, and plagioclase dominate the silicate mineralogy. Most of the mineralogical diversity is observed among the minor minerals. In the highly oxidized meteorites, minerals such as pentlandite and magnetite are prevalent. In contrast, the highly reduced enstatite chondrites include very unusual carbides (cohenite), silicides [perryite, (Ni,Fe)<sub>8</sub>(Si,P)<sub>3</sub>], phosphides [schreibersite, (Fe,Ni)<sub>3</sub>P], and, especially, sulfides [oldhamite, CaS; caswellsilverite, NaCrS<sub>2</sub>; niningerite, (Mg,Fe,Mn)S] (Keil 1989). Many of these minerals were first described from, and some are only known from, enstatite meteorites. Their presence testifies to the ability of the early solar nebula to create a broad range of chemical and physical environments, some of which were never duplicated during the later history of the Earth.

### **ASTEROIDS: BAKED AND STIRRED**

Although the mineralogical evolution of minerals in meteorites began in the fiery cauldrons of other stars, it progressed to a frozen snowball stage. Perhaps the most important mineral that accreted during the formation of chondritic asteroids is one that has never been documented in any meteorite—ice (H<sub>2</sub>O)! Much as the Earth has a snow line that separates ecosystems, the early solar system had a snow line that separated the ice-free rocky planets and asteroids from the ice-rich gas giant planets, ice-rich asteroids, and comets. As asteroids grew and began to experience modest heating by the decay of short-lived radionuclides (e.g. <sup>26</sup>Al, whose half-life is 720,000 years), the melting of ice and the subsequent alteration of the asteroids at low temperatures (<100°C) produced many new minerals (Brearley and Jones 1998; Brearley 2006). The evidence for this alteration is most prominent in the finegrained matrix of carbonaceous chondrites (particularly the CI and CM groups), but can be found in unexpected forms in other meteorite groups. As ice melted and water reacted with the olivine-rich matrix, many minerals emerged for the first time. These included the phyllosilicates montmorillonite [(Na,Ca<sub>0.5</sub>)<sub>0.33</sub>(Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·  $nH_2O$ ], chrysotile [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>], and cronstedtite [(Fe<sub>2</sub><sup>2+</sup>,  $Fe^{3+})_3(Si, Fe^{3+})_2O_5(OH)_4]$ ; the oxides magnetite and ferrihydrite  $(5Fe_2O_3 \cdot 9H_2O)$ ; the sulfides pyrrhotite and pentlandite; the carbonates dolomite and calcite; and the sulfates gypsum and epsomite (MgSO<sub>4</sub>·7H<sub>2</sub>O). As in earlier eras, some of the products of this alteration were not well crystallized and thus do not qualify as minerals. An alteration product termed PCP (poorly crystallized phase) is common in some carbonaceous chondrites.

While carbonaceous chondrites most dramatically illustrate aqueous alteration, other types of meteorites contain spectacular evidence for the melting of ice. Aqueous alteration of ordinary chondrites formed smectite, maghemite, Ni-rich pyrrhotite, and calcite in the matrix of the type 3.0 chondrite Semarkona. While evidence of such alteration was thought to be confined to the least metamorphosed ordinary chondrites, Zolensky et al. (1999) demonstrated that the Monahans ordinary chondrite contained fluid inclusion–bearing halite crystals in the matrix (Fig. 3).

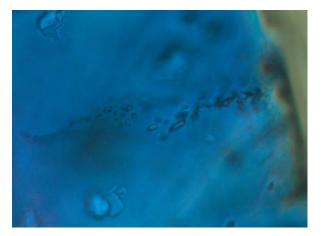
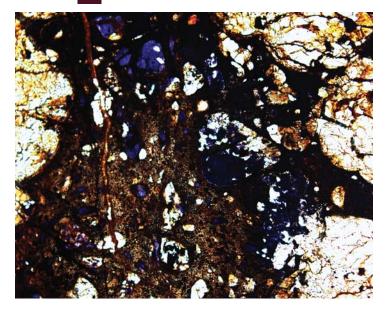


FIGURE 3 Halite crystals in the Monahans ordinary chondrite contain trains of fluid inclusions filled with trapped ancient water. Field of view is ~0.15 mm. PHOTO COURTESY OF MIKE ZOLENSKY

Emerging from their frozen state, many asteroids continued to warm. While heating of ice-bearing carbonaceous chondrites produced extensive aqueous alteration, heating of largely anhydrous ordinary and enstatite chondrites produced new minerals as a result of thermal metamorphism at temperatures up to the FeNi–FeS cotectic temperature of ~950°C (Brearley and Jones 1998; Huss et al. 2006). As sodium-rich chondrule glass recrystallized, albitic plagioclase appeared in metamorphosed ordinary chondrites. Oxidation of phosphorus may have been largely responsible for the formation of the phosphates apatite and merrillite. Nepheline, rutile, and cristobalite have all been observed in metamorphosed ordinary chondrites. In the highly reduced enstatite chondrites, cristobalite was joined by tridymite and quartz. Other minerals apparently formed during metamorphism of enstatite chondrites include the nitride sinoite (Si<sub>2</sub>N<sub>2</sub>O), the amphibole richterite [Na(CaNa) Mg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>], and roedderite [KNaMg<sub>2</sub>(Mg<sub>3</sub>Si<sub>12</sub>)O<sub>30</sub>]. While relatively few new minerals formed during metamorphism of the water-poor chondrites, collectively they suggest that recrystallization of glass and other poorly crystalline phases in type 3.0 chondrites, coupled with oxidation and reactions during metamorphism, provided new environments for the formation of minerals.

Even while this aqueous alteration and thermal metamorphism were occurring in asteroids, an era of intense bombardment began, and impacts would continue for the entire 4.5 billion years of solar system history. Impact fragmentation would reshape asteroids to what we observe today, form the Earth's moon, and scar the inner rocky planets. Not surprisingly, these impacts formed new minerals as chondritic asteroids were subjected to intense heat and pressure (Brearley and Jones 1998; Sharp and DeCarli 2006). The dominant mafic silicate olivine [(Mg,Fe)<sub>2</sub>SiO<sub>4</sub>] was transformed into the high-pressure spinel polymorph ringwoodite (FIG. 4) and the high-pressure orthorhombic polymorph wadsleyite. Ringwoodite is a particularly important mineral and is thought to be a major component of Earth's mantle. Pyroxene in these heavily shocked rocks was transformed into the high-pressure garnet structure majorite, the ilmenite structure akimotoite, and the perovskite structure. SiO<sub>2</sub> was transformed into the coesite and stishovite forms. Rubin and Scott (1996) suggested that submicron-sized diamonds discovered in the impact melt breccias of the Abee enstatite chondrite were formed by shock.

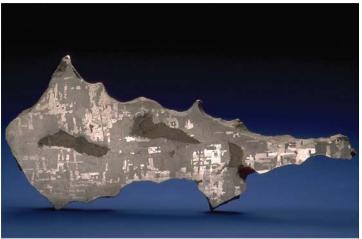


**FIGURE 4** Impacts on asteroidal bodies produced high-pressure minerals, such as purple (in plane polarized light) ringwoodite in the Coorara chondrite. Field of view is ~2 mm.

## **MELTING BEGINS**

As heating continued in some asteroids, the solidus temperature of ~950°C was exceeded and melting began. The earliest partial melts formed from FeNi metal and the iron sulfide troilite, but they also incorporated minerals like chromite and phosphates. Under the low-pressure conditions of asteroidal bodies, these melts could move efficiently by forming veins. Thus, these early partial melts migrated through the essentially undifferentiated silicates, eventually forming meteorites like the acapulcoites, winonaites, and IAB irons (Fig. 5). As the temperature continued to increase, silicate melting ensued, forming pyroxene-plagioclase-rich melts. The residual rocks remaining after silicate melting are represented by meteorite groups like the ureilites and lodranites, while the pyroxene-plagioclase-rich melts could have formed basalts, but we have not found meteorites with such compositions (McCoy et al. 2006). At first glance, it would seem that such melting would decrease mineralogical diversity, as many minerals are incorporated into these melts. In fact, the melts sequestered a range of incompatible elements, including phosphorus, sulfur, and carbon. Through reactions with unmelted silicates and crystallization of the metallic melts, many new minerals emerged (Buchwald 1975, 1984; Mittlefehldt et al. 1998; Mittlefehldt 2004; Haack and McCoy 2004). Most prominent among these are a host of phosphates, including the Na-Ca-Mg phosphates chladniite, panethite, brianite, and johnsomervilleite, and the carbides cohenite and haxonite  $[(Fe, Ni)_{23}C_6]$ .

If melting and differentiation had continued to the extreme, mineralogical diversity may have decreased to essentially nil. At greater than 60% melting, perhaps only the mafic silicate olivine and a solid metallic phase would have persisted. But such extensive melting ultimately led to a rebirth of mineralogical diversity. For the first time, volumetrically significant melt pools formed, and the differentiation that occurred sequestered the siderophile (metal-loving) elements from the lithophile (silicate-loving) elements (McCoy et al. 2006; Chabot and Haack 2006). As the siderophile and lithophile components crystallized separately to form the core and crust, respectively, of the parent body, incompatible elements were concentrated for the first time. Within the crust, minerals like potassium



**FICURE 5** The Youndegin IAB meteorite formed from a metallic melt rich in phosphorus, carbon, and sulfur, which cooled and crystallized to form a host of new minerals. The orthogonal texture was formed during slow cooling of the metal, when low-Ni kamacite exsolved from high-Ni taenite. The elongated kamacite lamellae contain cohenite. The dark-colored inclusions are rich in troilite (FeS) and graphite. The specimen is ~40 cm long.

feldspar (KAlSi<sub>3</sub>O<sub>8</sub>), titanite (CaTiSiO<sub>5</sub>), zircon (ZrSiO<sub>4</sub>), and baddeleyite (ZrO<sub>2</sub>) formed. For the first time, crystallization produced a host of new minerals rich in incompatible elements. This process repeated itself throughout the history of our planet, providing a powerful driving force for mineralogical diversification. In the core, mineralogical diversity was controlled both by fractional crystallization and solid-state transformations during cooling. In this environment, minerals that are rare in chondrites became common, such as the phosphide schreibersite and the metallic phase tetrataenite (FeNi). Other minerals, such as the nitride carlsbergite (CrN), the sulfide brezinaite ( $Cr_3S_4$ ), and the phosphates sarcopside and graftonite  $[(Fe, Mn)_3(PO_4)_2]$  appeared for the first time (Buchwald 1975, 1984; Mittlefehldt et al. 1998; Mittlefehldt 2004; Haack and McCoy 2004).

### **CONCLUSIONS (OR BEGINNINGS?)**

In meteorites, we see the earliest stages of the mineralogical evolution of our planet. Many meteoritic minerals are unknown on Earth. The solar system records ranges of temperature, chemistry, and oxygen fugacity never duplicated on Earth. In some cases, the very processes that formed these minerals can never be repeated, processes such as the condensation of the nebular gas that produced many of the minerals in calcium-aluminum inclusions. In other cases, like impacts, the record exists on Earth but is obscured by billions of years of weathering, volcanism, and plate tectonics. While these exceptional minerals attract much of the attention, the more remarkable feature of meteorites is that they record a range of processesaqueous alteration, metamorphism, igneous differentiation-that formed and continue to form many of the diverse minerals found on Earth. Long after asteroids stopped falling-save for the occasional impact-Earth continued to evolve, creating new combinations of the same chemicals delivered by meteorites but combined into the myriad of minerals we know today.

## ACKNOWLEDGMENTS

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# Assistant/Associate Professor of Critical Zone Science

Appointment: This is a 9 month, tenure track position with responsibilities divided between research (80%) and teaching (20%).

Position Description: The Department of Plant and Soil Sciences (http://ag.udel.edu/plsc/) in coordination with the newly formed Delaware Environmental Institute (http://denin.udel.edu/) invites applications for a tenure track faculty position at the Assistant or Associate Professor level in the area of Critical Zone Science. Longstanding strengths in environmental sciences at the University of Delaware are expanding through interdisciplinary investigations of human and earth system processes that govern terrestrial ecosystems of the critical zone - the top of the plant canopy to the base of the weathering zone. Successful candidates will complement environmental research at the University through expertise in the role and importance of soils to large scale issues such as climate change and the biogeochemical cycling of nutrient elements. The successful applicant will develop or bring a nationally recognized research program supported by extramural funding and will teach one course per year at the undergraduate or graduate levels.

Qualifications: The candidate must have a Ph.D. and research interests focused on soil processes relevant to land use issues and emergent impacts on ecosystems. Desirable areas of expertise include geomorphology, geochemistry, biogeochemistry, pedology, eco-hydrology, and land-atmosphere exchange. Candidates with experience bridging laboratory and field-scale investigations as well as interdisciplinary studies are especially encouraged to apply. Interest and ability to contribute effectively to collaborative research efforts is essential.

Salary: Commensurate with experience and training. The University of Delaware provides an excellent employee benefits package including health and dental insurance, retirement contributions, pre-tax flexible spending accounts, and complete tuition remission for family members.

Facilities: Teaching and research facilities are located at the University of Delaware, Newark, DE. The University is a Land Grant, Sea Grant & Space Grant institution located midway between Philadelphia and Baltimore. Further information on the Environmental Sciences at the University of Delaware (http://www.environmentalportal.udel.edu), the Delaware Environmental Institute and the Christina River Basin Critical Zone Observatory (www.udel.edu/czo/) can be found on the web.

Date Position is Available: As early as Sept 1, 2010.

Application Process: By March 19th, interested persons should submit: (i) letter of application; (ii) resume; (iii) two page statement of research and teaching interests; (iv) names, e-mail and postal addresses, and telephone numbers of three references. Complete applications should be assembled into a single pdf document and sent by e-mail to: Dr. K. Eric Wommack, Search Committee Chair: PLSC-faculty-search@an.udel.edu.

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