RESEARCH: OCEAN CHEMISTRY

Black Carbon and the Carbon Cycle

Thomas A. J. Kuhlbusch

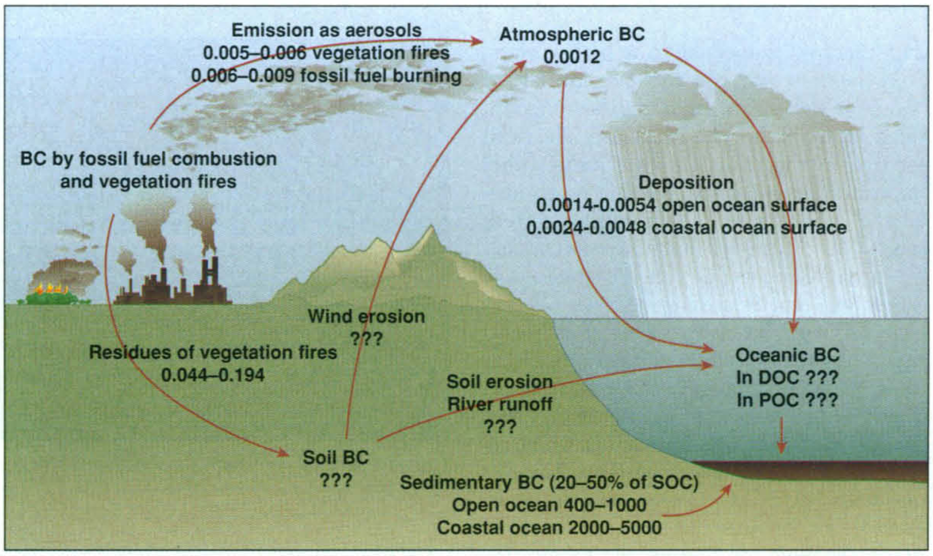
Black carbon is a product of incomplete combustion of vegetation and fossil fuels. It is ubiquitous and can be found in soils, ice, sediments, and the atmosphere. The interest in black carbon is manifold and includes its aerosol form as the main light-absorbing constituent, in sediments and ice cores that reveal fire history, as a sink of atmospheric CO_2 in the short-term atmospheric-biospheric carbon cycle, and as a possibly substantial source of oxygen over geological time scales. Now on page 1911 of this issue, Masiello and Druffel (*1*) report the age of sedimentary organic and black carbon; they found black carbon to be 2400 to 13,900 years older than the concurrently deposited sedimentary organic carbon. They (*1*) conclude from this age difference that sedimentary black carbon must have been stored in an intermediate pool, most likely oceanic dissolved organic carbon.

The figure summarizes current knowledge concerning the life cycle of black carbon. The first measurements of black carbon in ocean sediments were published by Smith *et al.* in 1973 (*2*). They proposed sedimentary black carbon as a unique tool for studying the history of vegetation fires. In 1980, Seiler and Crutzen (*3*) reported a substantial sink of atmospheric CO_2 by the formation of black carbon in vegetation fires. They argued that a relatively unknown (at that time) fraction of the vegetation exposed to fire is converted to a refractory form of carbon. Because this black carbon will not be degraded, it is believed to represent a sink for the fast atmospheric-biospheric carbon cycle and a source for the long-term geological carbon cycle. In 1990, Crutzen and Andreae (*4*) estimated annual global black carbon formation to be 200 to 600 Tg (10^{12} g) and noticed that this carbon sink may have been an important source of oxygen over geological time scales. Kuhlbusch and Crutzen (*5*) updated the annual global black carbon formation estimate on the basis of measurements in residues of vegetation fires. They calculated annual formation rates for black carbon of 50 to 200 Tg, with the major fraction (>80%) produced in the residues of fires. This rate of black carbon formation reduces net CO_2 release by permanent deforestation by 2 to 18% and may constitute a substantial fraction of the "missing carbon" in the anthropogenically disturbed global carbon balance (*5*). An estimate of oxygen release assuming 10% of today's formation rate of black carbon over the last 340 million years [from the oldest documented record of charcoal (*6*)] gives 8 times more O_2 than the current atmospheric O_2 content (*5*). An estimate of oxygen released by the amount of sedimentary organic carbon gives a value of 25 times the present atmospheric oxygen content (*7*). Some measurements of black carbon in open-ocean sedimentary organic carbon showed that black carbon can constitute a substantial fraction of sedimentary organic carbon [on average 20 to 50% (*1*, *8*, *9*)]. These results indicate that estimates of past terrestrial carbon storage should include the fraction of black carbon stored in soils and sediments and that black carbon formation by vegetation fires may be important for our past and current atmospheric oxygen concentrations as well.

Masiello and Druffel (*1*) have concluded from mass and $\Delta^{14}C$ measurements that black carbon may represent a substantial fraction (4 to 22%) of the oceanic carbon pool. They also argue that the main source of black carbon in the open ocean is the deposition of carbonaceous aerosols. Thus, aerosol black carbon, which is also the main aerosol constituent absorbing solar radiation, may also be an important route by which terrestrial organic carbon is transported to the oceanic carbon pool.

Suman *et al.* (*10*) estimated atmospheric deposition of aerosol black carbon to coastal and open ocean to be 7 ± 3 Tg of C per year, with about 50% of the carbon deposited onto the coastal ocean. Comparing these deposition rates with sedimentation rates for coastal and open-ocean areas, they found, in agreement with Masiello and Druffel (*1*), that eolian transport is the most important source of open-ocean black carbon. On the other hand, riverine and surface runoff may be the most important source of oceanic black carbon closer to the coast, because atmospheric deposition could only explain about 30 to 40% of the sedimentary deposition rate.

Another important conclusion by Masiello and Druffel (*1*) is the long residence time of black carbon (2400 to 13,900 years) in an intermediate pool, either in soils or in the ocean. This has important implications for the marine carbon cycle and the interpretation of sediment records of black carbon to reconstruct fire history. Assuming the ocean to be the most important intermediate pool, oceanic transport will dominate the location of sedimentation. In this case, no link of the studied sediment site and source region can be easily made. On the other hand, Verardo and Ruddiman (*9*) found a correlation of sedimentary black carbon and eolian siliciclastic fluxes in an Atlantic deep-sea core. On the basis of their



In the black. Masiello and Druffel (*1*) determined age differences of 2400 to 13,900 years between sedimentary organic carbon (SOC) and black carbon (BC). Thus, they conclude that sedimentary black carbon must have spent considerable time in an intermediate pool. Candidates are terrestrial soils and the oceanic dissolved organic carbon (DOC) pool [data from (*5*, *7*, *10*)]. All values are in petagrams (1 Pg = 10^{15} g) per year.

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results, they hypothesize that black carbon fluxes to deep-sea sediments are linked to wind speed and direction. In this case, soils would be the main intermediate pool for sedimentary black carbon. Certainly, further measurements of black carbon in sediments as well as in river and ocean water are necessary to address the above question. Additionally, the source strength of aged black carbon from soils becoming airborne by wind erosion should be investigated as well.

But, most importantly, we need to develop an experimentally acceptable definition of black carbon and intercalibrate the various analytical techniques if we wish to build a meaningful data set. Certainly, to understand the role of black carbon and thus of any combustion process in the environment, a complete understanding of the life cycle of black carbon is necessary.

References

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CONDENSED MATTER PHYSICS

Hot Electrons in Magnetic Oxides

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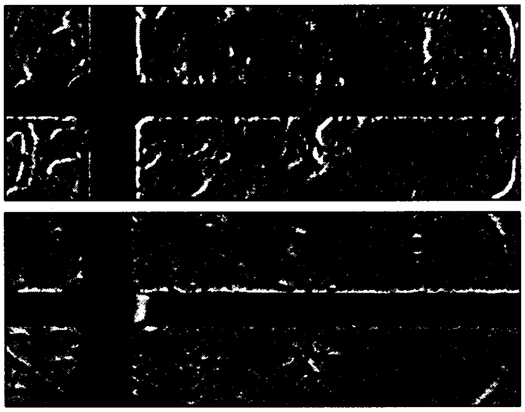
An electron subjected to a high electric field inside a material can become fast or "hot" enough to ionize impurities encountered in its path. The secondary electrons set free in the collision then ionize other impurities and so forth, leading to an avalanche of electrons. The resulting current surge is exploited in common semiconductor devices such as photodiodes, microwave oscillators, and electronic switches (*1*). On page 1925 of this issue, Fiebig *et al.* report the observation of an avalanche instability in an oxide material very different from ordinary semiconductors (*2*). It belongs to a class of magnetic oxide compounds whose resistivity is exceedingly sensitive to modest magnetic fields ("colossal magnetoresistance"). By driving this material far from thermodynamic equilibrium and monitoring its response, Fiebig *et al.* have developed an approach that promises to reveal new physics and, over time, may also lead to novel device applications.



Current events. Images of current flow inside a material exhibiting a metal-insulator transition that produces a change in reflectivity. The phase transition is induced by pulses of laser light while voltage is applied; this allows current to flow, maintaining the conducting state. (**Top**) Sample in reflected light showing its normal insulating state. (**Bottom**) After phase transition is initiated, highly reflecting regions show current path.

The states near the Fermi level of the compound they investigated, $\mathrm{Pr_{0.7}Ca_{0.3}MnO_3}$, derive predominantly from the Mn 3d orbitals, and the average number of electrons per Mn atom is 3.7. The five degenerate atomic d orbitals are split into a triplet and a doublet by interactions with the crystalline environment. The lower-lying triplet on each Mn atom is filled by three electrons that form a local spin-3/2. The remaining 0.7 electrons partially occupying the doublet are forced by intra-atomic Coulomb interactions to align with the local spin. (This is analogous to the familiar Hund's rule of atomic physics.)

Two different thermodynamic phases can occur in this and related manganite compounds: an insulating phase in which the electrons in the doublet are also localized and crystallize in a regular pattern with an antiferromagnetic spin alignment, and a metallic phase in which they are delocalized (see figure). The former phase is favored by electrostatic interactions and forms when $\mathrm{Pr_{0.7}Ca_{0.3}MnO_3}$ is cooled to low temperatures ($\leq$200 K) in zero magnetic field (*3*). In this insulating phase, the additional static charge localized on the Mn site lifts the degeneracy of the doublet by distorting the surrounding lattice (the so-called Jahn-Teller effect), thus lowering the energy of the occupied state. Furthermore, the electrons spend most of their time far away from each other when they are localized, so that their mutual Coulomb repulsion is also minimized. However, according to the Heisenberg uncertainty principle, the kinetic energy of a quantum particle increases as it is localized. When an external magnetic field aligns the local spins ferromagnetically and facilitates hopping of the conduction electrons from site to site, the energy balance is tipped in favor of this kinetic term, and the material undergoes a first-order transition to the metallic phase. This is the basic mechanism of the colossal magnetoresistance effect.

Contrary to conventional semiconductors, where the conduction electrons are dilute and weakly interacting, this phenomenology indicates that both electron-lattice and electron-electron interactions are strong in these oxides. This has been corroborated by numerous experimental studies under equilibrium and near-equilibrium conditions. What happens when such a strongly interacting quantum system is driven far from equilibrium?

On the face of it, the observations reported by Fiebig *et al.* (*2*) in $\mathrm{Pr_{0.7}Ca_{0.3}MnO_3}$ actually bear much resemblance to the behavior of some conventional semiconductors under similar conditions (*4*). In both systems, application of a high electric field, sometimes enhanced by laser irradiation, results in the formation of highly conducting

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