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Jason M. Blackburn et al.
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these metals. By choice of metal and fluorophore, it is also possible to “hide” the barcode pattern in fluorescence images.

As interest grows in carrying out comprehensive analyses on classes of biologically relevant molecules (e.g., genomics, proteomics, metabolomics), there is a demand for multiplying high-level multiplexing in small sample volumes, and thus a corresponding need for new readout mechanisms. Solution arrays of highly encodeable and chemically diverse nanoparticles, such as those described herein, offer an intriguing solution to both requirements.

References and Notes
11. The membranes used in this work are Al2O3 and have a nominal pore diameter of 200 nm. However, the pores are 200 nm only at the surface of the membrane. SEM measurements indicate that the pores widen to ~400 nm in the central region of the membrane, with an average diameter of 318 ± 50 nm. All of the particles discussed in this report have diameters in this range [as determined by transmission electron microscopy (TEM) and SEM].
16. Particles were characterized electrochemically during the deposition process. After preparation, they were characterized by the following techniques: TEM, SEM, FE-SEM, energy-dispersive x-ray scattering, macroscopic extinction, microscopic reflectivity, atomic absorption, and chemical treatment (e.g., selective dissolution of less noble segments).
19. The equation for calculation of unique sequences for n segments will be shorter than 500 nm + 2(10%) = 600 nm, and >95% of all 2 X segments will be longer than 1000 nm – 2(10%) = 800 nm (25). For 350-nm segments, >95% of all 1 X segments will be <420 nm, whereas 95% of all 2 X segments will be >560 nm. Although the differences in these two lengths cannot be directly measured by optical microscopy, they should be distinguishable by differences in intensity. Note that we have prepared 230-nm stripes with 16% standard deviation, and we routinely prepare particles in the 4- to 8-μm range with <10% standard deviations in total length.
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24. More than 95% of all 1 X segments will be shorter than 500 nm + 2(10%) = 600 nm, and >95% of all 2 X segments will be longer than 1000 nm – 2(10%) = 800 nm (25). For 350-nm segments, >95% of all 1 X segments will be <420 nm, whereas 95% of all 2 X segments will be >560 nm. Although the differences in these two lengths cannot be directly measured by optical microscopy, they should be distinguishable by differences in intensity. Note that we have prepared 230-nm stripes with 16% standard deviation, and we routinely prepare particles in the 4- to 8-μm range with <10% standard deviations in total length.
28. DNA sequences: (a) “capture” oligonucleotide: 5’-biotin-AAAAACGGCTTACGAT-3’, (b) analyte: 5’-TAGGGTCGATACCAGCTGCGG-3’, (c) detection oligonucleotide: 5’-TCTCAGCTGCTCG-3’, where fluor = tetramethylrhodamine (TAMRA).
29. Particles were first derivatized with NeutrAvidin (0.1 mg/ml) and then incubated for an additional 30 min with a mixture of the detection antibodies, κ (antibody to rabbit IgG [heavy and light chains]) labeled with Texas Red; antibody to human IgG [γ specific] labeled with fluorescein isothiocyanate (FITC). After incubation with κ the sample was rinsed several times in buffer.
30. We thank T. Carado, P. Smith, W. Stonas, K. Shale, S. Norton, and L. Dietz for their help with particle synthesis and optical characterization. Supported by NIH grant HG02228 (C.D.K.).
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Deposition of Conformal Copper and Nickel Films from Supercritical Carbon Dioxide
Jason M. Blackburn, David P. Long, Albertina Cabañas, James J. Watkins*

Device-quality copper and nickel films were deposited onto planar and etched silicon substrates by the reduction of soluble organometallic compounds with hydrogen in a supercritical carbon dioxide solution. Exceptional step coverage on complex surfaces and complete filling of high-aspect-ratio features of less than 100 nanometers width were achieved. Nickel was deposited at 60°C by the reduction of bis(cyclopentadienyl)nickel and copper was deposited from either copper(I) or copper(II) compounds onto the native oxide of silicon or metal nitrides with seed layers at temperatures up to 200°C and directly on each surface at temperatures above 250°C. The latter approach provides a single-step means for achieving high-aspect-ratio feature fill necessary for copper interconnect structures in future generations of integrated circuits.

The increasing complexity and decreasing dimensions of devices for microelectronic, system-on-a-chip, data storage, and other applications is placing stringent demands on deposition technologies that, to date, have not been fully satisfied. These include reductions in the thermal budget during fabrication, mitigation of the negative environmental impact of current processes, conformal coverage of complex surfaces, and complete filling of narrow, high-aspect-ratio structures. The difficulties associated with achieving the latter two requirements are particularly severe. For example, to keep pace with the historical increase in process speed popularly referred to as Moore’s Law, Cu interconnect structures for integrated circuits must drop below 10 nm in width with aspect ratios that exceed 3 after 2005. According to the Semiconductor Industry Association’s International Technology Roadmap for Semiconductors...
(ITRS), however, there are no viable means for Cu deposition at these dimensions (1).

We have developed a technique, called chemical fluid deposition (CFD), that can meet each of the criteria outlined above, for interconnect technology in particular, and device fabrication in general. CFD involves the chemical reduction of soluble organometallic compounds in supercritical carbon dioxide (sc CO2) to yield high-purity deposits. Hydrogen, which is miscible with sc CO2, is typically used as a reducing agent. Recently, we demonstrated the utility of this approach for the deposition of Pt, Pd, Au, and Rh films on planar surfaces (2–4). These reports indicate that pure, continuous films can be deposited at low temperatures (40°C to 80°C) using precursors that produce comparatively benign effluents. Whereas this advance addressed the issues of thermal budget and environmental acceptability, planar films similar to those deposited in these examples can be obtained by conventional methods, including chemical vapor deposition (CVD) and line-of-sight techniques such as sputtering. Here, we report the deposition of device-quality Cu and Ni films for use in interconnect and data storage applications, respectively. For Cu, we developed a cold-wall reactor in which metal deposition occurs exclusively on the heated substrate. Moreover, we demonstrate that the conditions used yield unprecedented step coverage that can not be achieved via CVD or physical vapor deposition techniques under practical conditions and can provide filling of sub–100-nm, high-aspect-ratio features in a single step.

The benefits of CFD are a consequence of the physicochemical properties of supercritical fluids (SCFs), which lie intermediate between those of liquids and gases. Consequently, CFD can be viewed as a hybrid of solution plating and vapor phase techniques. Table 1 compares the deposition conditions for each. Like electroless plating, CFD is solution-based, but the transport properties of SCFs, which are more akin to those of a gas, afford distinct advantages that are typically associated with CVD including low viscosity, rapid diffusion, and the absence of surface tension. These properties, when combined with the miscibility of H2 with sc CO2, alleviate the sluggish mass transfer typical of liquid-phase reductions and promote conformal coverage. The enabling distinction between CFD and CVD is the mode of precursor transport. In CVD, the limited volatility of suitable precursors, including organometallics, leads to low-vapor-phase concentrations and mass transfer–limited reactions that preclude uniform depositions. In CFD, precursor concentrations in sc CO2 solution are up to three orders of magnitude greater.

First, a continuous Cu seed layer is deposited within the feature using physical vapor deposition (PVD). This seed layer is then used as a cathode for electrolytic Cu deposition, which fills the trench. Because PVD (sputtering) is essentially a line-of-sight technique, difficulties are encountered when attempting to deposit uniform seed layers in confined geometries. In principle, CVD could be used for this purpose, but to date it has not been successfully integrated. A primary obstacle is precursor volatility constraints, which lead to low-vapor-phase concentrations, mass transport–limited depositions, and ultimately, poor step coverage.

Copper was deposited during CFD by the reduction of CO2 solutions of either Cu(I) or Cu(II) organometallic compounds in a high-pressure cold-wall reactor (5). The substrate was placed on a resistively heated stage and maintained at an elevated temperature relative to the bulk solution. At substrate temperatures of 200°C or less, deposition by H2 reduction of the Cu(II) (betadiketonates), Cu(II) bishexafluoroacetylacetonate [Cu(hfac)2], and Cu(II) tetrabenzylidenemalonate [Cu(mhd)2] occurred only on the heated stage and was selective for metal surfaces or metal oxide surfaces seeded with catalytic clusters over the bare oxide. For example, H2 reduction of 0.7 weight percent (wt%) Cu(hfac)2 solutions in CO2 at substrate temperatures between 175°C and 200°C and a pressure of 200 atm (20.27 MPa) proceeded readily on Ni films or on silicon wafers seeded with small Pd clusters deposited by CFD, but not on the native oxide.

![Fig. 1](image)

**Fig. 1.** XPS analysis of metal films deposited by chemical fluid deposition conducted after Ar+ sputtering to remove atmospheric contaminants. (A) Analysis of a Cu film deposited onto Ni-seeded Si at 200°C by the reduction of Cu(hfac)2, with H2 in CO2 solution in a cold-wall reactor reveals Cu peaks at the appropriate binding energies. There is no significant C contamination (C 1s binding energy = 284 ev). (B) Characterization of a Ni film deposited onto glass (60°C) by the co-reduction of NiCp2 (0.2 wt%) with H2 and CpPd(C8H7) (0.02 wt%) in CO2 solution reveals Ni peaks at the appropriate binding energies. There is no significant C contamination. Characteristic peaks for Pd at 335 and 340 eV were not observed until additional Ar+ sputtering exposed a Pd-rich region adjacent to the substrate surface.
of a Si wafer. This approach affords opportunities for selective film growth through control of the spatial distribution of the seed layer.

In all cases, the deposited films are continuous, highly reflective, and essentially free of impurities. X-ray photoelectron spectroscopy (XPS) indicates insignificant C or F contamination of a Cu film deposited on Ni from Cu(hfac)$_2$ (Fig. 1A). High purity is facilitated by the high solubility of the ligand by-products in sc CO$_2$. In fact, F nuclear magnetic resonance (NMR) analysis of the reaction products isolated from the reactor effluent reveals a single peak at ~77 ppm that corresponds to hexafluoropentanedione, which suggests the reduction proceeds cleanly at 200°C with no detectable ligand fragmentation. In addition to promoting film purity, intact desorption of precursor decomposition products provides opportunities for ligand recovery and recycle.

Although deposition from Cu(hfac)$_2$ yields high-purity films, the presence of F is undesirable because of environmental and device performance concerns. Because transport in CFD occurs in solution, non-fluorinated precursors that exhibit insufficient vapor pressure for use in CVD are suitable for CFD. For example, deposition from Cu(tmhd)$_2$ in H$_2$/CO$_2$ solutions proceeded readily to yield pure Cu films. Secondary ion mass spectrometry (SIMS) analysis of such a film deposited onto Pd-seeded, etched Si at a substrate temperature of 200°C reveals C and O concentrations of less than 0.2 atomic percent (at%) in the bulk of the film. Further analysis reveals that the high reagent concentrations and favorable fluid-phase transport properties inherent to CFD facilitate conformal deposition. Figure 2A shows a scanning electron microscope (SEM) image of the film cross-section that demonstrates excellent step coverage in narrow (~100 nm by 800 nm) trenches. The sample cross-section was prepared using a focused ion beam (FIB).

Fig. 2. (Left) FIB SEM micrographs of Cu films deposited by CFD onto (A) a Pd-seeded test wafer by hydrogen reduction of Cu(tmhd)$_2$ in CO$_2$ solution at a substrate temperature of 200°C and a pressure of 207 atm and (B) onto a bare Si test wafer by hydrogen-assisted reduction of Cu(hfac)(2-butyne) in CO$_2$ solution at a substrate temperature of 225°C and a pressure of 200 atm. Both depositions were conducted in a cold-wall high-pressure reactor. Fig. 3. (Right) SEM micrographs of Ni films deposited onto etched Si wafers by the hydrogen reduction of NiCp$_2$ in CO$_2$ solution in a hot-wall continuous-flow reactor. (A) A FIB SEM image of a film deposited at 60°C and 140 atm provides evidence of a narrow seam within the trenches, indicating uniform film growth from opposing feature surfaces. (B) An SEM image of a fracture cross section of a Ni film deposited conformally at 60°C and 180 atm on a test wafer containing features as narrow as 45 nm that were not etched completely during wafer fabrication (far right).

It is highly desirable to eliminate the seed layers and deposit high-purity, conformal films in a single step. Presently, no such single-step process exists for Cu interconnect metallization. Using CFD, we deposited Cu films directly onto the native oxide of Si at 250°C and onto Cu diffusion barriers such as TiN at slightly lower temperatures by H$_2$ reduction of Cu(tmhd)$_2$. SIMS analysis of a 380-nm-thick film deposited from Cu(tmhd)$_2$ at 225°C onto TiN indicates that C and O concentrations in the bulk of the films are less than 0.5 at%. The resulting film had low resistivity (~2.0 microohm-cm) after annealing, which approaches that of bulk Cu (1.7 microohm-cm) and is well below the upper limit for interconnect structures specified by the ITRS (2.2 microohm-cm).

High-purity Cu films were also deposited in a single step via CFD of Cu(I) compounds of the general type (β-diketonate)CuLn, where L is a Lewis base, and n is 1 or 2. These compounds are known to undergo ther-
We deposited high-purity Cu films onto the native oxide of Si wafers as well as Cu diffusion barriers including TiN by hydrogren-assisted reduction of Cu(hfac)(2-butyne) in CO2 solution at substrate temperatures of 225°C and a pressure of 200 atm. Here, the disproportionation reaction provides a pathway for the initial Cu deposits, which in turn yield active surfaces for H2 reduction of Cu(hfac)2 generated by the decomposition of the Cu(I) precursor. This scenario allows for higher deposition efficiency relative to that of the disproportionation reaction alone, because Cu(hfac)2 generated in situ is also reduced to yield Cu. XPS analysis of films deposited from Cu(hfac)(2-butyne) yields results similar to that for Cu(hfac)2. SIMS analysis indicates F contamination is of the order of 1 at%, whereas C and O concentrations are less than 0.5 at%. Figure 2B is a FIB SEM image of a Cu film deposited onto an etched Si wafer from a CO2 solution of Cu(hfac)(2-butyne) at 225°C. Step coverage is exceptional despite the presence of a number of trenches that are considerably more narrow at the entrance (<100 nm) than the midpoint. The trench asymmetry is a consequence of wafer preparation prior to metallization. The depositions are not yet optimized, but resistivity of films deposited from Cu(hfac)(2-butyne) in initial experiments is about 2.7 microhm-cm, which is typical of films deposited by CVD. At substrate temperatures of 200°C or less, we find the deposition is selective for metal surfaces including Pt, Pd, and Ni over the native oxide of Si wafers.

The deposition of Ni is of interest for the fabrication of contacts in microelectronic devices and for data storage applications. CFD deposition of Ni from sc CO2 solutions of bis(cyclopentadienyl)nickel (NiCp2) proceeds readily at 60°C and 200 atm in the presence of H2 over Ni, Pd, or Pt films. Low-temperature plating on noncatalytic surfaces such as polymers or metal oxides is accomplished by seeding the deposition.

We deposit Ni in batch or continuous hot-wall reactors at 60°C using two strategies (7, 8). The first involves the use of a Pd-seed layer in the same manner as used for the Cu depositions. In the second, solutions of NiCp2 and an easily reduced organopalladium compound such as 2-methylallylcyclopentadienyl)Pd(II) [CPd(C5H5)] are prepared in stoichiometric ratios ranging from 0.005:1 to 0.1:1 (Pd:Ni). The reduction of CPd(C5H5) proceeds immediately in CO2 upon the addition of H2 (9) to yield catalytic clusters that serve as nucleation sites for the reduction of NiCp2. Once the incipient metal surface is formed, growth of the Ni film proceeds readily. This scenario is confirmed by composition analysis by XPS depth profiling, which reveals a Pd-rich Ni deposit at the substrate-metal film interface that is overlain by a pure Ni film. At temperatures above 120°C, Ni can be deposited nonselectively by reduction of NiCp2/CO2 solutions without the need for a seed layer or co-reduction by an organopalladium reagent. In all cases, the reduction of NiCp2 proceeds to completion to yield only the relatively benign hydrocarbon decomposition products and Ni metal. The metal coatings prepared by CFD are reflective, continuous, and free of contamination (10).

Deposition of Ni onto patterned Si wafers is highly conformal. Figure 3 shows SEM micrographs of films deposited within trenches of etched Si wafers from solutions of NiCp2 using the continuous-feed hot-wall deposition process. Figure 3A is a FIB SEM image of a film deposited onto a Pd-seeded Si wafer at 60°C and 180 atm. The narrow seams in the 100-μm-wide by 800-μm-deep trenches reveal that film growth occurs uniformly from both sides of the trench. Figure 3B is a SEM image of a fracture cross section of a Ni film grown on a substrate containing 75-nm trenches. In this example, two of the trenches were not etched completely during fabrication of the test wafer and left features as narrow as 45 nm (far right), which are filled upon Ni deposition. The deposited films can be grown to virtually any thickness in the flow reactor. For example, we have grown 2-μm-thick Ni films that uniformly fill 450 nm wide trenches in etched Si wafers.

Table 1. Comparison of reduction media for the deposition of metal films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Liquid</th>
<th>SCF</th>
<th>Gas (CVD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1</td>
<td>0.1–1</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Viscosity (Pa·s)</td>
<td>10⁻⁸</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>Diffusivity (cm²/s)</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
<td>10⁻¹</td>
</tr>
<tr>
<td>Surface tension (dynes/cm)</td>
<td>20–50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Precuror conc. (M/cm³)</td>
<td>10⁻³</td>
<td>10⁻⁵</td>
<td>10⁻⁸</td>
</tr>
<tr>
<td>Deposition temp. (°C)</td>
<td>25–80</td>
<td>40–250</td>
<td>250+</td>
</tr>
</tbody>
</table>

Although we have focused on the utility of CFD for device fabrication, the use of nonfluorinated precursors eliminates emission problems typically associated with CVD and the use of CO2 as the deposition medium obviates the need for aqueous plating baths used for electrolytic and electroless plating that generate large amounts of contaminated wastewater. This is particularly acute for Ni plating: due to large volumes and environmental and human toxicity, nickel is one of 17 high-priority pollutants targeted by the U.S. Environmental Protection Agency for reduction under its 33/50 program (11).

References and Notes
5. All Cu depositions were conducted in a dual flange cold-wall reactor in batch mode. The stainless steel reactor has a total volume of 70 ml and contains a resistively heated stage. Precursor and a single substrate were loaded into the reactor. The vessels were sealed, purged, and charged with CO2 using a high-pressure syringe pump. The substrate was heated to the desired temperature (typically 200° to 250°C) and the reactor walls were maintained at a lower temperature (typically 60° to 80°C). Film deposition was initiated by the addition of excess of H2 using a small, pressurized manifold (70 ml). The quantity of H2 admitted into the vessel was calculated using the pressure-drop measured in the manifold.
7. All bath depositions were conducted in 17-ml high-pressure stainless steel reactor at 60°C using a single substrate (~1 cm by 7 cm) and a known amount of precursor were loaded at ambient conditions. The vessels were sealed, purged with CO2, weighed, placed in a thermal bath, and allowed to equilibrate to the desired temperature. Carbon dioxide was then added to the desired pressure via a high-pressure syringe pump. Film deposition was initiated by the addition of excess of H2 using a small, pressurized manifold (3.6 ml). The quantity of H2 admitted into the vessel was calculated using the pressure-drop measured in the manifold.
8. Continuous depositions were conducted in a 1.3 cm i.d. by 10.2 cm long hot-wall reactor operating at 60°C and 180 atm. Three computer-controlled high-pressure syringe pumps were used to meter resistive and carrier gas streams to the reactor. The precursor feed stream was either admitted directly to the reactor or was diluted with pure CO2 upstream of the reactor inlet. Deposition was initiated by metering a ~2 mol% solution of H2 in CO2 into the vessel at the desired flow rate. After dilution by all streams, the concentration of precursor at the reactor inlet was approximately 0.2 wt.%.. The reactor effluent was directed to an activated carbon bed before venting. Prior to Ni deposition, the substrates were seeded by Pd deposition via hydrogenolysis of CpPd(C5H5) in CO2 solution.
10. XPS analysis of a film co-deposited at 60°C and 140 atm from a CO2 solution of NiCp2 and CpPd(C5H5).

R E P O R T S

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Organic Carbon Composition of Marine Sediments: Effect of Oxygen Exposure on Oil Generation Potential

Yves Gélinas,1† Jeffrey A. Baldock,2 John I. Hedges3

Anaerobic sedimentary conditions have traditionally been linked to the generation of the source rocks for petroleum formation. However, the influence of sedimentary redox conditions on the composition of freshly deposited organic matter (OM) is not clear. We assessed the effect of in situ exposure time to oxic conditions on the composition of OM accumulating in different coastal and deep-sea sediments using solid-state 13C nuclear magnetic resonance (NMR). 13C NMR spectra were resolved into mixtures of model components to distinguish between alkyl carbon present in protein and nonprotein structures. There is an inverse relation between the length of exposure to oxic conditions and the relative abundance of nonprotein alkyl (alkylNP) carbon, whose concentration is two orders of magnitude higher in coastal sediments with short exposure times than in deep-sea sediments with long exposure times. All alkylNP-rich samples contain a physically separate polymethylene component similar in composition to algaenans and kerogens in type I oil shales. The duration of exposure to oxic conditions appears to directly influence the quality and oil generation potential of OM in marine shales.

Sedimentary burial of a small fraction (<0.5% (1–3)) of organic matter (OM) produced in the surface ocean is responsible for the generation of fossil fuels over geologic time scales (4–5). Although the major precursors of these fuels are well characterized within the diagenetic continuum ranging from phytoplankton (6–8) to kerogens (9–14), the variables that control selective preservation of these “protofuels” are still debated (15–17). Oxygen-limited margin environments have long been associated with petroleum source rock formation (4) and, more recently, enhanced OM concentrations (3) and burial efficiencies (16). Yet the link between oxygen levels and the transformation of recently deposited OM into hydrogen-rich petroleum-forming kerogens is not clear. The elucidation of this link requires studies on organic carbon (OC) compositions in sediments with contrasting oxygen exposure histories. Unfortunately, such studies are hampered, because most OM in marine sediments cannot be characterized at the molecular level (2).

The extent of OM preservation in marine sediments appears to reflect the average period during which accumulating particles are exposed to oxic sedimentary conditions (15, 16, 18). The oxygen exposure time (OET) corresponds to the depth of O2 penetration into pore waters divided by sediment accumulation rate (3). Such an “oxygen effect” is explained by the lower degradation rate exhibited by recalcitrant macromolecules (such as pollen (19), lignin (20), cutin (13), hydrocarbons (21), and algaenans (7, 8, 12)) under anoxic as compared with oxic conditions. These molecules can be selectively preserved during anoxic diagenesis and generate fuels after thermal catagenesis (4, 13). The oil generation potential of kerogens in marine shales may be determined at the first stage of diagenesis (22) and thus coupled to OET. If this hypothesis is valid, OM from recent diagenetically stabilized sediments with short OETs should be enriched in alkyl functional groups relative to OM from sediments with long OETs.

To test this hypothesis, we developed a demineralization method (23) designed to concentrate OM from marine sediments and used solid-state 13C nuclear magnetic resonance (NMR) (24) to compare the chemical compositions of bulk OM in 15 marine sediments representing a wide range of analogies and oxygen exposure histories (Table 1). These samples include an OC-rich sulfidic Black Sea sediment (sample 1) and OC-rich sediments from O2-deficient zones (ODZs) along the Indian (sample 2), Peruvian (sample 3), and Mexican coasts (samples 4 and 5), as well as below (sample 6) and above (sample 7) the Mexican ODZ. Also included are sediments from the Arabian Sea (samples 8 and 9), which exhibits a productivity-driven seasonal pattern of O2-deficient waters; typical margin deposits accumulating below oxygenated waters on the Washington shelf (sample 10) and upper slope (sample 11); and organic-poor sediments from the Washington coast Cascadia basin (sample 12), Southern Ocean (sample 13), and equatorial Pacific Ocean (samples 14 and 15). This sample set comprises nearshore clastic sediments and carbonate and siliceous oozes, as well as pelagic red clay sediments. 613C and elemental measurements suggest that OM accumulating at these sites is predominantly marine-derived (3).

Major resonances corresponding to alkyl carbon [0 to 45 parts per million (ppm)] dominate all cross-polarization/magic angle spinning (CP/MAS) 13C NMR spectra (Fig. 1), with varying contributions from N-alkyl/methoxyl (45 to 60 ppm), O-alkyl (60 to 95 ppm), di-O-alkyl (95 to 110 ppm), aromatic/olefinic (110 to 145 ppm), phenolic (145 to 165 ppm), and carboxyl/amide (165 to 190 ppm) carbon. The seven organic-rich samples (Fig. 1, A through C) exhibit similar intensities within these chemical shift regions. Although variations in the relative contribution of each type of carbon increase among the five samples with intermediate OC concentrations (Fig. 1, D through F), resonances shapes and chemical shift values at maximum resonance intensity are similar to those obtained for organic-rich samples. Such variations between, rather than within, the different types of carbon functionalities may reflect mixtures of similar components at varying proportions. In contrast, spectra obtained for samples with low OC concentrations show greater variation in resonance shapes and relative intensities (Fig. 1, G through I). The