sample of distilled water and cooling the solution. Between 0° and 4°C the signal was inverted and at 4°C the signal vanished, in agreement with the temperature dependence of the thermal expansion coefficient of water. We have also observed in vitro acoustic transients produced by microwave pulses in such tissues as blood, muscle, and brain; similar transients have been observed in vitro in tissue after irradiation by a *Q*-switched laser (*8*).

The first reflection from the rear surface of the tank is shown in Fig. 1. Superficially, the initial transient and the following series of reflections (the "flutter echo") resemble a burst of white noise, which is exponentially damped with a time constant of about 3 msec as the sound energy is transferred to the walls of the container. The frequency spectrum of the burst depends upon the microwave pulse length and upon the geometry of the container; shortening the microwave pulse similarly shortens the initial transient but does not alter the decay time of the reflected pulses.

Using a variable band-pass filter (Kron-Hite), we have measured the band pressure levels of the acoustic transients that follow microwave pulses of different widths (Fig. 2). The solution at 25°C was contained in a large expanded polystyrene tank. The pressure levels were increased by 2.9 db to simulate measurements at 37°C. The incident total energy density per pulse, $I_0\tau$, was kept constant at 80 μj/cm^2. This is the approximate average threshold for microwave "hearing" in human subjects with normal hearing exposed to 2450-Mhz radiation, for pulses shorter than about 25 μsec repeated at a rate of three per second (*3*). For relatively long pulses, Fig. 2 shows that the $P_{\max}$ of the burst is directly proportional to I_0, consistent with Eq. 2. For shorter pulses, $P_{\max}$ depends upon $I_0\tau$ and upon the filter bandwidth. This is due to the exponential factor in Eq. 2 and to the broadened spectral distribution of the transients. Within the frequency band audible by bone conduction (200 hertz to 20 khz), the transition occurs at pulse widths of 20 to 25 μsec. In a psychophysical study Frey and Messenger showed, for pulsed 1245-Mhz radiation, that the loudness of the microwave "hearing" sensation depends only upon I_0 for pulse widths greater than about 30 μsec; for shorter pulses, their data show that the loudness is a function of the product, $I_0\tau$ (*1*). These results are consistent with our observations.

We observe that in water a microwave pulse, at the threshold for microwave "hearing" in humans, produces pressure transients of approximately 90 db relative to 0.0002-dyne/cm^2 peak amplitude within the frequency band 200 hertz to 20 khz. If occurring within the head, this stimulus could elicit a "click" when some of the sound energy is coupled into the skull. Neither the duration of the flutter echo produced inside the head by a microwave pulse nor the threshold for perception of this unusual stimulus is known. However, 90 db is above the expected threshold (~ 80 db) for perception, by bone conduction, of millisecond bursts of white noise incident upon a subject's skull in water (*9*). It is therefore reasonable to believe that these thermally induced transients elicit the microwave "hearing" sensations in humans.

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Surface Electronic Properties of Tungsten, Tungsten Carbide, and Platinum

Abstract. *The local electronic structures of the surface regions of tungsten, tungsten carbide, and platinum have been compared. Contrary to the hypothesis that the platinum-like catalytic activity of tungsten carbide results from the contribution of carbon valence electrons to the* 5d *band of tungsten, the width of the unfilled portion of the* d *band increases on going from tungsten to tungsten carbide.*

It has been shown (*1, 2*) that transition metal carbides have many of the desirable catalytic properties of "noble" metals (such as Pt and Pd) with respect to hydrogen oxidation and hydrogenolysis reactions, but there is no detailed understanding of this phenomenon. Levy and Boudart (*2*) have proposed that the increased catalytic activity of WC over W is due to the donation of electrons by carbon to the W *5d* band, resulting in an electronic structure similar to that of Pt. In this report we test their hypothesis by directly comparing the density of unfilled electronic states in the conduction bands of W, WC, and Pt by soft x-ray appearance potential spectroscopy (SXAPS) (*3, 4*). The measurements are sensitive to the catalytically active outermost few atomic layers. Contrary to the hypothesis of Levy and Boudart, we find that the width of the unoccupied portion of the *5d* band of W actually increases on going from W to WC. As expected, we find that the unoccupied portion of the *5d* band of Pt is quite narrow, indicating that the band is almost completely filled.

In SXAPS one monitors the total x-ray emission from a sample bombarded with electrons as a function of the energy of the incident electron beam. The resulting curve exhibits distinct structure corresponding to the excitation probabilities for core level electrons superimposed on a smoothly increasing bremsstrahlung background. The background is suppressed relative to the excitation structure by differentiating the curve with respect to energy. Neglecting the finite lifetime of

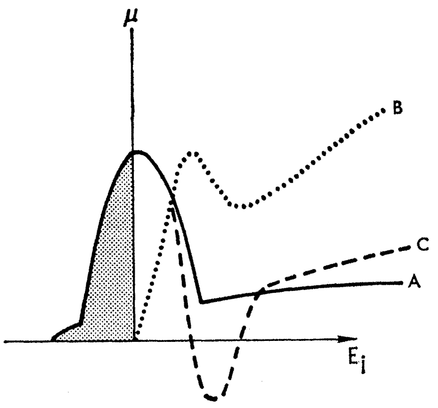

Fig. 1. Schematic illustration of the approximate determination of the density of unoccupied conduction band states by SXAPS. The shaded area corresponds to filled states. The solid curve (A) is a schematic illustration of the density of states for a "typical" transition metal. The Fermi enregy, μ, lies within a partially filled *d* band which rides upon a low *s*-*p* band. The dotted curve (B) illustrates the self-convolution of the density of unoccupied conduction band states. The dashed curve (C) is the derivative of curve (B) and corresponds to the experimental measurement.

the core vacancy, the excitation probabilty in a one-electron picture is given by (*4*)

$$P(E_i) = \int d\epsilon_1 |W_c(E_i;\epsilon_1,E_i - E_c - \epsilon_1)|^2 \times \rho_e(\epsilon_1)\rho_e(E_i - E_c - \epsilon_1) \quad (1)$$

In Eq. 1, E_i denotes the energy of level *i*, ρ_e the density of empty states in the conduction band, E_c the core electron binding energy, and W_c the matrix element for the transition, which depends on the particular core (c) level under consideration; ϵ_1 is a dummy integration variable. A schematic energy level picture for this process is given in (*4*). The main point to note is that since two electrons are involved, the incident electron and the ejected core electron, one sees the self-convolution of the density of empty states. Assuming that W_c is slowly varying near threshold, the portion of ρ_e relating to the *d* band density of states can be obtained fairly straightforwardly from the experimentally measured derivative spectrum, as indicated in Fig. 1. The width of the *d* band at its half-maximum position is essentially the same as the width at half-maximum of the positive first peak in the derivative spectrum, and the relative magnitudes of the peak and dip provide a measure of the relative contribution of the *s*-*p* band (*4, 5*). The finite lifetime of the core vacancy (*6*) and also the instrument response function will introduce some additional broadening, but these effects can be taken into account. This technique has been used previously to measure the widths of the unfilled portions of the *d* bands of the 3*d* transition metals (*5*), yielding results which display the systematic behavior predicted by electronic energy band calculations.

The samples used in our study consist of disks approximately 1¼ cm in diameter and ⅓ cm thick which were obtained from Materials Research Corporation. The W and Pt had a specified purity of 99.999 percent, and the WC had a purity of 99.9 percent. Before the actual measurements the samples were cleaned by bombardment with argon ions and annealing at high temperatures. This procedure was repeated until the spectra were free of impurity structure. The residual background pressure was about 10^{-9} torr. The actual measurements were made with an incident beam current of 10 ma and an oscillation amplitude of 2 volts peak to peak in the potential modulation differentiation scheme (*3*).

The resulting spectra in the neighborhood of the M_V levels of W and Pt are shown in Fig. 2. We can see in the upper level that, contrary to the hypothesis of Levy and Boudart (*2*), the width of the empty portion of the conduction *d* band actually increases in going from W to WC. As expected, the width of the peak in the Pt spectrum is narrower. To obtain actual values for the widths of the density of unoccupied *d*-like states, we must correct the measured values for the additional broadening due to the instrument response function and the core level lifetime. For simplicity we will use a Gaussian approximation (*5*) in which the measured width at its half-maximum position, Δ_m, is given by the quadratic sum of the width of the empty band at half-maximum, Δ_e, and the various additional broadening contributions, Δ_i; that is

$$\Delta_m^2 = \Delta_e^2 + \sum_i \Delta_i^2 \quad (2)$$

Using experimental core level lifetimes (*6*), a 1-ev spread in incident beam energy, and a 2-volt peak-to-peak oscillation amplitude, we obtain Δ_e values of 4.0 ev for W, 6.7 ev for WC, and 1.5 ev for Pt. The measured width for W falls between the values of 3.4 and 4.8 ev obtained by Mattheiss (*7*) using two different model potentials, while our width for Pt is somewhat larger than the calculated value of 0.7 ev obtained by Mueller *et al.* (*8*). We are not aware of any electron energy band calculations for WC. Because of the reduced coordination of an atom at the surface, we expect the density of *d*-like states to be somewhat narrower than in the bulk. This is offset, however, by the small difference in core electron binding energies between an atom at the surface and those lying deeper in the solid (*9*), which would introduce a slight additional broadening into the experimental values of Δ_e.

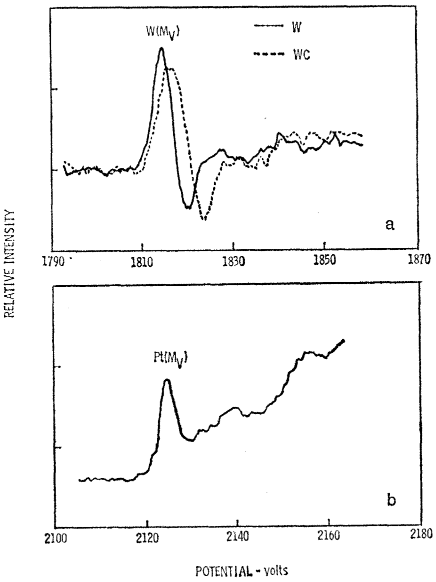

Fig. 2. SXAPS spectra in the neighborhood of the M_V levels of W and Pt. (a) The spectra for W and WC are superimposed; the W spectrum is shown as the solid line and the WC spectrum as the dashed line. (b) Spectrum for Pt.

The change in the properties of the density of states in going from W to WC bears no obvious relation to the increased catalytic activity observed by Levy and Boudart (*2*). The failure of a simple band-filling picture is not surprising in view of the different structural properties of the materials in question (*10*); that is, as far as the bulk properties are concerned, W is body-centered cubic, Pt is face-centered cubic, and WC is hexagonal. We conclude that, although the electric properties of a material are no doubt important in determining its catalytic activity, the relation appears to be considerably more complex than Levy and Boudart suggest.

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Silurian Trilete Spores and Spore Tetrads from Gotland: Their Implications for Land Plant Evolution

Abstract. *Land-plant type spores occur in argillaceous limestones and platform graptolitic mudstones of Wenlock-Ludlow age in Sweden. Analysis of the stratal sequence demonstrates that occurrence of abundant spores is a function of depositional ecology, particularly water depth and shoreline proximity. This ecological analysis and the seeming absence of any correlation between the first appearances of abundant spores and megafossils of land-plant type raise the possibility that land plants evolved far earlier than the megafossil record suggests.*

The island of Gotland, situated in the Baltic Sea about 100 km east of the Swedish mainland, is the classic region for Silurian invertebrate megafossil remains. Especially noteworthy are the excellent exposures of unmetamorphosed bedrock in the coastal cliffs and elsewhere, with their abundance of unusually well preserved invertebrate remains that have claimed the attention of naturalists since the beginning of the 18th century. These rocks have also yielded rock-forming calcareous algae (*1*) and have proved to be rich in planktonic marine organic microfossils, such as chitinozoans (*2*).

Because the Gotland Silurian sequence appears to be wholly marine and has always been interpreted as having been deposited some distance from the nearest shoreline, the seeming absence of land plant remains is not unexpected (*3*). Nevertheless, the time interval during which these rocks were deposited appears to have been critical in the evolution of land (vascular) plants, all of whose earliest pre-Devonian remains are recovered from marine strata.

The purpose of this report is to call attention to a variety of microscopic plant remains recovered from a sampling of the Silurian sequence of Gotland and adjacent Scania (Table 1) (*4*) and whose source would appear to be land plants, even if it cannot be demonstrated from their morphology and environment of occurrence that they stem from land vascular plants (*5*). Insofar as it is possible from observations made to date, it is also our purpose to provide new information on the rate of evolution of plants producing land-plant type spores and to add to the growing body of paleoecological data regarding the early environments of possible land plants.

Standard series	Gotland	Scania
Pridoli		Öved Sandstone
Ludlow	Sundre Beds	
	Hamra Beds	Öved-Ramsåsa Siltstone
	Burgsvik Beds and Eke Beds	
	Hemse Beds	
	Klinteberg Beds	
Wenlock	Mulde Beds	
	Halla Beds	
	Slite Beds	
	Högklint Beds	
	Upper Visby Beds	
Llandovery Upper	Lower Visby Beds	

Fig. 1. Correlation of the Silurian stratigraphic units from Gotland and Scania, together with their position relative to the standard Silurian sequence.

Although the Gotland trilete spores and spore tetrads are not the oldest known (*6–8*), they are important additions to the growing number of widespread, durable pre-Devonian spores of the land-plant type that predate megafossil remains attributed to land and to land vascular plants. Their excellent preservation matches that of the other Gotland Silurian fossils; they are also among the more abundant and diversified pre-Pridoli spore assemblages of which there is published record (*9*), particularly in the Burgsvik Sandstone, where trilete spores and spore tetrads are most common.

The Gotland Silurian sequence includes well-dated strata of late Llandovery through Ludlow age, units that represent essentially the upper half of the Silurian (Fig. 1). These rocks were deposited in a marine, reef-controlled, warm-water regime near the western edge of the Russian Platform (*10*); platform graptolitic mudstones crop out to the southwest in Scania and on the island of Bornholm, and occur to the south in boreholes drilled in northern Poland and in Germany. The uppermost Silurian (late Ludlow to Pridoli) beds in Scania consist of shallow water marine carbonate rocks and mudstones grading up into high intertidal or nonmarine red beds essentially lacking megafossils (*11*).

The Gotland Silurian is normally thought of as a marine carbonate sequence having little connection with fossils of possible nearshore or nonmarine origin. However, the varying plant spore distribution, correlated with the varying acritarch abundance and diversity (Table 1), is consistent with the conclusion that some of the rock units were deposited under deeper water than others (or that some were deposited at different distances from the shoreline, or under different conditions of marine current activity). The evidence that supports this conclusion has been given elsewhere (*7*). The water depth–shoreline correlation provided by the organic microfossils from the Gotland