reactivity of CuZnSOD in solution is the removal of the metal ions by treatment with the metal-ion chelating reagent EDTA (*9, 10*). The metal ions were removed from the encapsulated protein in xerogels under similar conditions, resulting in a colorless glass. The encapsulated apoprotein (metal-free protein) was remetallated by addition of metal ions, restoring to the glass both the color and the visible absorption spectrum, in a manner also identical to the solution process (*14*). This process, that is, removal and addition of metal ions, was repeated without any apparent change in the spectroscopic properties of the encapsulated CuZnSOD.

We also encapsulated ferricytochrome c and found no detectable change in its spectroscopic properties as a result of encapsulation (see Fig. 3). When the red-brown ferricytochrome c aged gels or xerogels were soaked in a solution of sodium dithionite, the glasses became salmon colored and the resulting spectra were virtually identical to that of reduced ferrocytochrome c in solution (see Figs. 1 and 3). The encapsulated ferrocytochrome c spontaneously reoxidized when exposed to air. This oxidation-reduction process was repeated without deterioration of spectroscopic properties.

The third protein system chosen for study was Mb. Met Mb, that is, containing iron in the Fe^{3+} state, was encapsulated, and the resulting brown gels (see Fig. 1) were soaked in a solution of sodium dithionite to give deoxy Mb, which contains iron in the Fe^{2+} state. The deoxy Mb in the gels was then reacted with O_2 by exposure to air to give oxy Mb, MbO_2, and with CO to give carbonyl Mb, MbCO. The spectroscopic changes associated with all of these reactions in the aged and the xerogels (*15*) were similar to those which occur under the same conditions in solution (see Fig. 4).

These experiments demonstrate that it is possible to create inorganic materials that contain biochemically active macromolecules. Specifically, we find that: (i) a wide variety of proteins may be encapsulated in sol-gel matrices giving optically transparent glasses; (ii) the proteins are remarkably stable in such matrices; (iii) these proteins undergo characteristic reversible reactions in the gel glasses; and (iv) spectroscopic changes occurring in the gel-glasses can be readily quantified with optical spectroscopy. The prospects are excellent for the use of these novel materials in biosensors.

REFERENCES AND NOTES

1. K. Mosbach, Ed., *Immobilized Enzymes and Cells*, vol. 135B of *Methods in Enzymology* (Academic Press, New York, 1987).
2. S. Braun *et al.*, *Mater. Lett.* **10**, 1 (1990).
3. C. J. Brinker and G. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic Press, Boston, 1990).
4. L. C. Klein, *Annu. Rev. Mater. Sci.* **15**, 227 (1985).
5. These results complement those of another study, which showed that a number of enzyme systems (glucose oxidase, peroxidase, chymotrypsin, and trypsin) encapsulated in transparent silica glass matrices by this method remained enzymatically active. [S. A. Yamanaka *et al.*, unpublished results; L. M. Ellerby *et al.*, unpublished results].
6. J. McKiernan, J. C. Pouxviel, B. Dunn, J. I. Zink, *J. Phys. Chem.* **93**, 2129 (1989); J. C. Pouxviel, B. Dunn, J. I. Zink, *ibid.*, p. 2134; J. M. McKiernan, S. A. Yamanaka, B. Dunn, J. I. Zink, *ibid.* **94**, 5652 (1990).
7. L. L. Hench and J. K. West, *Chem. Rev.* **90**, 33 (1990).
8. L. Esquivias and J. Zarzycki, in *Proceedings of the Third International Conference on Ultrastructure Processing*, J. D. Mackenzie and D. R. Ulrich, Eds. (Wiley, New York, 1988), pp. 255–270.
9. J. S. Valentine and M. W. Pantoliano, in *Copper Proteins*, T. G. Spiro, Ed. (Wiley, New York, 1981), pp. 291–358, and references therein.
10. J. S. Valentine and D. Mota de Freitas, *J. Chem. Ed.* **62**, 990 (1985).
11. P. M. Harrison, Ed., *Metalloproteins*, parts I and II (VCH Publishers, Deerfield Beach, FL, 1985).
12. The silica sol was prepared by mixing tetramethylorthosilicate (TMOS, 15.22 g) and deionized water (3.38 g) followed by the addition of HCl (0.04 M, 0.22 g), which was used to catalyze the reaction. After sonication of the reaction mixture had proceeded for 20 minutes, sonicated sol (2 ml) was mixed with buffer (2 ml, 0.01 M sodium phosphate, pH 6.0). The protein solution (0.01 to 5 mM. 1 ml, 0.01 M sodium phosphate, pH 6.0) was then added directly to the buffered sol.
13. J. A. Fee and B. P. Gaber, *J. Biol. Chem.* **247**, 60, 1972.
14. CuZnSOD in aged gels showed different behavior. Removal of the metal ions to prepare the apoSOD in aged gels proceeded smoothly. However, addition of Cu^{2+} and Zn^{2+} to these apoSOD aged gels resulted in the appearance of a visible absorption band at 650 rather than at 680 nm. We do not understand the source of this difference since demetallation and remetallation of the CuZnSOD xerogel (that is, prepared by drying of an aged gel) gave spectral changes virtually identical to those occurring in solution for the same processes. One possible explanation is that the apoprotein was trapped in a nonnative configuration, because polymerization of the silanol groups is still proceeding actively at that stage in the aged gel, and remetallation thus cannot restore the native conformation. In contrast, polymerization in the xerogel should be much closer to completion.
15. In the case of Mb, the aged gel was washed with 0.05 M tris, 0.1 M sodium sulfate, pH 7.5, prior to drying.
16. In some instances, the aged gels show a sloping base line, which we tentatively attribute to scratching of the surface during handling. For xerogels, which are rigid glasses, this phenomenon is usually not observed.
17. Supported by grants from the NSF (DMR90-03080 to B.D. and J.I.Z. and the CHE88-08170 to J.S.V.) and the NIH (GM28222 to J.S.V.). C.R.N. is a predoctoral trainee supported in part by USHHS National Institutional Research Award (T32 GM-08375).

18 September 1991; accepted 2 January 1992

Rectification of STM Current to Graphite Covered with Phthalocyanine Molecules

M. POMERANTZ, A. AVIRAM, R. A. MCCORKLE, L. LI, A. G. SCHROTT

The scanning tunneling microscope (STM) can be used to measure current-voltage characteristics on an atomic scale. The attachment of copper phthalocyanine molecules, in contrast to a variety of other molecules, to graphite changes the electrical characteristics of the STM from relatively symmetric to highly asymmetric or rectifying. Evidence is presented to show that the asymmetry arises because of the electronic energy levels of the copper phthalocyanine. The organic molecules were bonded to the graphite by an acid-base reaction that may have wide applicability.

THE STM INCORPORATES A SHARP metallic tip that is used to observe and affect the properties of surfaces on an atomic scale. The tip has been used as an electrode with which asymmetric, or rectifying, electrical characteristics have been observed on some surfaces. [Examples include pure semiconductors (*1, 2*), a metal (*3*), and semiconductors with atomic or small molecular adsorbates (*4*).] Reviews of STM experiments on organic and biological molecules (*5, 6*) do not mention unusual electrical characteristics, such as rectification. We have been studying the effects of organic molecules because it is expected that, when the electronic energy levels of the adsorbates are close to the Fermi level E_F of the electrodes, the molecules might strongly affect the tunneling characteristics (*7*). This offers the possibility of measuring the molecular energy levels. Also, because the energy levels of organic molecules depend on their structure and composition, there is the possibility of choosing the energy levels to obtain desired electrical properties. It is advantageous to choose molecules that are large enough so that it is possible to make chemical substitutions, in order to chemically bond them to particular electrodes, with minimal changes in the electronic structures of the molecules. We report here that the asymmetry of the STM current-voltage (*I-V*) characteristics of graphite surfaces (Fig. 1A) is changed by an order of magnitude when copper phthalocyanine molecules are chemically attached (Fig. 1, B and C). Other molecules that we attached to graphite did

---

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, NY 10598.

not affect the asymmetry within the same voltage range. We correlate the differing effects on the conductivity with the occupied electronic energy levels of these molecules.

One difference between our methods and those of others who studied phthalocyanine molecules with the STM is that they deposited the molecules by sublimation (*8–10*), whereas we bonded the molecules to the graphite surface by means of an acid-base reaction. Our purpose was to inhibit motion of the molecules caused by thermal agitation or the force exerted by the tip when the STM is operating. The first step in the bonding was to attach acid groups (*11*) to the surface of highly oriented pyrolytic graphite (HOPG) by immersing the HOPG in a solution of CrO_3 in aqueous acetic acid. To these acid groups we then bonded a base-substituted copper phthalocyanine, Cu 4,4′,4″,4‴-tetraaza-29*H*,31*H*-phthalocyanine (CuTAP) (inset to Fig. 1B). The N atoms in the outer rings have the desired basic character by which one or more corners of the molecule may bind to the acidified surface.

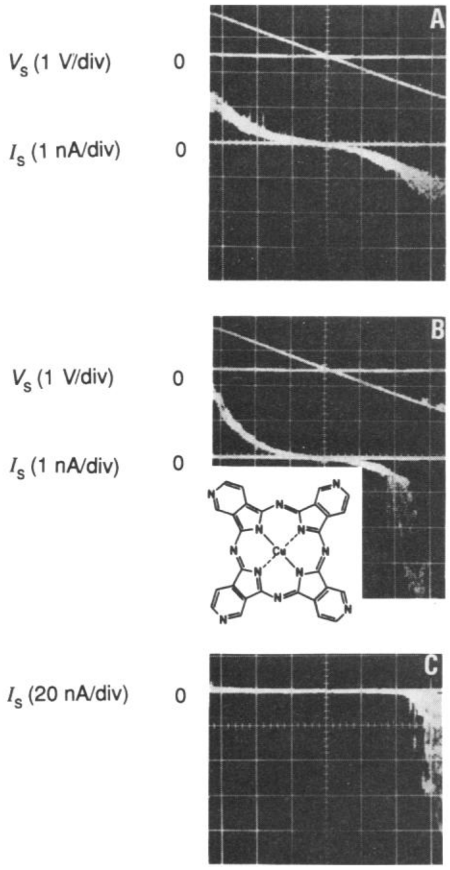

Fig. 1. Storage-scope traces of the voltages and currents of the STM versus time. (**A**) The sample is pure graphite. V_s is the voltage between the sample and tip, scanned between +1.2 and −1.2 V in 38 ms. I_s is the resulting tunnel current. (**B**) The sample is acidified graphite after reaction with CuTAP. The scales are the same as in (A). The current has gone offscale at V_s = −1.2 V. The inset shows the planar structure of CuTAP. (**C**) Same as (B) but the scale of I_s is 20-fold larger in order to show the entire asymmetric current. The feedback current = 0.4 nA at +0.7 V.

The resulting surfaces were characterized by several spectroscopies. Details will be presented elsewhere (*12*), but the results were as follows: By angle-dependent x-ray photoelectron spectroscopy (XPS) we observed that the molecular planes were tilted to the surface, as is commonly found for phthalocyanines at high coverage (*13, 14*). From the comparison of the XPS intensities of C and N of a thick layer of CuTAP, we found the coverage of a typical sample to be about 50%, if the molecules were on edge. A similar result for the coverage by tilted molecules was deduced from the Auger intensities of C and N. Omitting the acidification step reduced the amount of CuTAP by a factor of ~7. The infrared absorption by the chemisorbed molecules matched that of the starting material, showing that the molecular structure was not degraded. This was confirmed by ultraviolet photoemission spectroscopy (UPS), which showed line shapes for thick (50 Å) film samples similar to that of these thin films.

The STM measurements were made with a Nanoscope I (Digital Instruments, Santa Barbara, California) modified to allow the feedback circuit to be periodically interrupted while the *z*-piezo voltage was held constant. During such an interval of fixed tip height, the voltage applied between the sample and the tip was scanned in a sawtooth wave form in less than 100 ms. The tip current was displayed on a Kikusui storage scope, with which single traces are readily seen. A computer system (*15*) was combined with the Nanoscope I so that topographs could be recorded and processed digitally. The STM was operated in air at room temperature.

Our experimental protocol was to cut a Pt/Ir tip for each new sample and check it on freshly cleaved HOPG. If the tip gave atomic resolution on HOPG, we further tested it by going to the *I-V* scanning mode. The tip was then manually moved the full range of the *x* or *y* piezos, while we scanned the voltage between +1.5 and −1.5 V. An acceptable tip gives the kind of *I-V* characteristics shown in Fig. 1A. In the upper trace, the voltage to the graphite was scanned between +1.2 and −1.2 V in 38 ms. Below this are shown several traces of the tunneling current, which is equivalent to an *I-V* characteristic because the voltage scan is uniform in time between its peaks. The characteristics are symmetrical within a factor of 2, that is, the asymmetry ratio $R = |I(-V)|/|I(+V)| \leq 2$ for the pure HOPG surface. The reproducibility of these characteristics during traversal was a criterion that the STM was performing properly and we could proceed to the test sample.

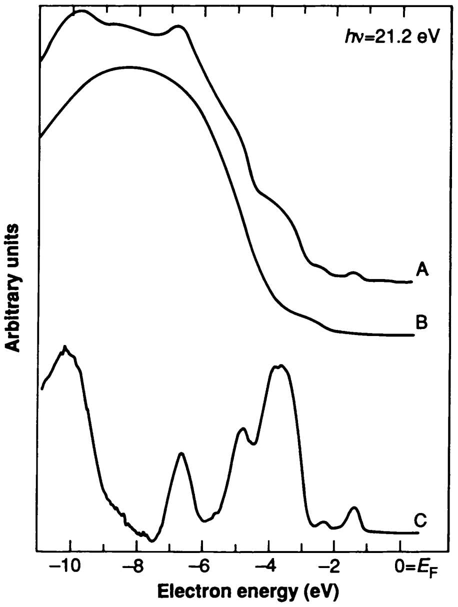

Fig. 2. Ultraviolet photoemission spectra of samples with and without CuTAP. Curve A, acidified graphite reacted with CuTAP. Curve B, acidified graphite. Curve C, the difference between curves A and B, which gives the occupied CuTAP energy levels measured from E_F. The spectra were taken with He I light and at perpendicular takeoff angle of the electrons.

On HOPG to which CuTAP had been bonded, we observed the *I-V* characteristics shown in Fig. 1B, which is several stored traces. At a positive voltage of 1.2 V the current is 50% larger than for the pure HOPG, but at negative bias of −1.2 V the current has gone offscale. By enlarging the scale 20 times (Fig. 1C), we found that the peak of the current sometimes exceeded 80 nA. Thus, on the CuTAP-covered surface, the asymmetry ratio can reach values of about 50.

This asymmetry persists even when the tip is stationary, thereby excluding tip contact as a possible cause. Because there are various artifacts on surfaces of HOPG and because of concerns about doing STM experiments in air, we repeated the experiments on at least ten different samples. In every case we saw asymmetry factors of at least 10 over about 60% of the area of treated samples and asymmetry ratios of 40 or more over about 10% of the area.

To further examine the specificity of CuTAP as the cause of the asymmetry, we have done several tests. To determine whether the asymmetry is due to the CuTAP or to the acidification, we substituted a surface of HOPG that had been acidified but not exposed to CuTAP. The *I-V* character-

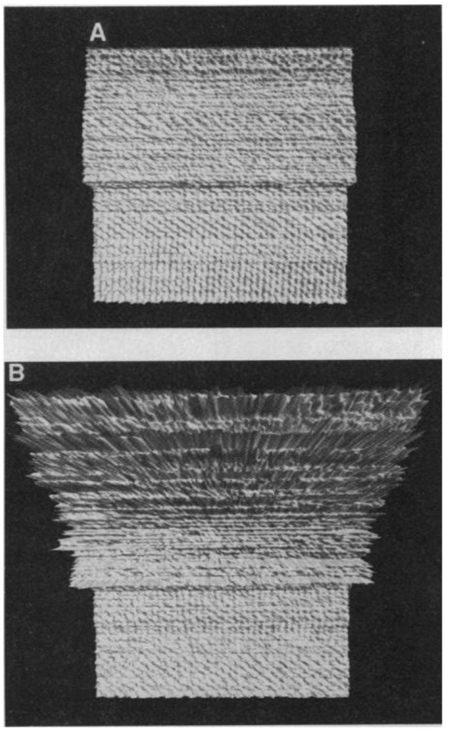

Fig. 3. STM topographs of CuTAP-covered graphite at various biases to the sample. (**A**) Positive bias voltage = +1.0 V (from the top edge to the middle) and +0.4 V (from the middle to the bottom edge). The tip steps downward here to maintain the feedback current. (**B**) Topograph of the same area as in (A), with negative bias voltages = −1.0 and −0.4 V. At −1 V, the z excursions above the graphite average ≈1 nm. In all cases the bias current was set to 1 nA. The x and y dimensions are about 10 nm. The view is perpendicular to a plane parallel to the lower half. The data were not processed, except to show the heights in perspective.

istics were like those of pristine graphite. We also exposed HOPG to CuTAP but omitted the acidification of the surface. Corresponding to the lower concentration of CuTAP observed on this sample, the asymmetry occurred over about 10% of this surface and was typically about 10. Moreover, the *I-V* characteristics were less stable. We also bound other molecules to the acidified surface, namely, an amine thiol, H–S–$(CH_2)_2$–NH_2, and a bisquinone that was attached to the thiol end of the amine thiol. Their coverages, as measured by Auger spectroscopy, were similar to those of CuTAP. With either of these molecules on the HOPG, the *I-V* characteristics were like those of pristine graphite. Thus, not every molecule and not acidification alone produces large asymmetry. We now consider what specific property of CuTAP may lead to rectification.

Previous examples of asymmetry of the STM currents have been explained (*1, 2, 16*) as due to a difference in the joint density of states (DOS) of the sample and tip above E_F compared to below E_F. We thus hypothesized that the asymmetry we observed is due to changes in the DOS of the sample arising from the molecular energy levels. To test this, we used UPS to measure the changes in the occupied energy levels of the sample upon addition of the molecules. The spectrum of an acidified surface to which CuTAP is bonded is shown in Fig. 2, curve A. The spectrum with only acidification of the surface is shown in Fig. 2, curve B. The difference, Fig. 2, curve C, emphasizes the peaks below the E_F of HOPG, which arise from the occupied levels of CuTAP. A negative bias of 1.2 V applied to the sample could bring the highest level (at about 1.3 V below E_F) to coincidence with empty states of the tip, which would account for the enhanced tunneling we observed. By comparison, with the amine thiol there are no additional observable peaks in the UPS spectrum within several electron volts of the E_F of HOPG. The absence of accessible occupied energy levels associated with the amine thiol accords with the fact that this molecule does not produce enhanced asymmetry at a bias of −1.2 V. A requirement for electrical asymmetry is material or geometrical asymmetry. Our STM experiment indicated that the system has geometrical asymmetry because the molecules are closer to the graphite than to the tip. This is different from an earlier proposal (*7*) in which electrical asymmetry was based on the (material) asymmetry of the molecular structure.

The presence of a peak in the DOS should have a profound effect on the STM topographs (*16*), taken at constant current. When the bias to the sample is set at a negative value sufficient to raise the molecular energy level to coincidence with empty states of the tip, the molecules contribute more to the tunneling, especially because they protrude into the gap between the HOPG and the tip. The tip will then retract from the surface to maintain the current at the set point. Under large enough negative bias the tip should track above the molecules, but at other biases it will neglect the molecules and follow the HOPG. This is demonstrated in Fig. 3, a set of topographs (at constant current) of a CuTAP-covered surface. Figure 3A is a top view of a topograph taken with positive bias of +1 V for the upper half. Atoms of HOPG are resolved. Halfway down the image, the bias voltage was reduced to +0.4 V. The tip steps downward toward the surface (in order to keep the current constant) and the atomic resolution improves (*17*). Figure 3B shows a rerun of the topograph of the same area, but with negative biases. In the upper half, the bias = −1.0 V; the surface looks very rough. In the lower half the bias was set at −0.4 V and we again observe graphite atoms. This shows that the topography in the upper half was not caused by a bad tip or other extraneous effect but is an effect of the adsorbate. Repeated runs at −1.0 V bias show the large fluctuations but they differ among runs.

The range of height variations in the upper part of Fig. 3B is many times larger than the corrugations of the graphite atoms. Although the magnitudes of these variations cannot be specified with precision because the topograph was made in air where contaminants may influence the apparent size of the corrugations, they average about 1 nm. This scale of sizes is closer to the length of the molecule (about 1.3 nm) than to its thickness (about 0.3 nm). These large excursions are expected because we have observed (by angle-dependent XPS) that the molecules are tilted to the surface. Even though they are hinged at the surface, their upper ends can move as a result of thermal and mechanical forces. Considering the exponential dependence of current on distance in the tunneling process, it is expected that a little motion will cause considerable fluctuation in the observed current and topography when the molecules are conducting. (Lowering the temperature should reduce the fluctuations.) Thus, the unusual topographs and the large but variable asymmetry have a simple explanation based on the asymmetric DOS of a surface covered with tilted CuTAP molecules.

Alternative explanations of the asymmetric *I-V* characteristics have been considered. (i) Differences in the work function between tip and sample would lead to a greater current flow when a positive bias is applied to the side with the smaller work function than to the side with the larger work function (*18*). The work function (*19*) of the Pt/Ir tip (≥5.2 eV) is larger than that of pure graphite (≤4.6 eV). We have measured a decrease in the work function upon bonding of the CuTAP to HOPG, from the cutoff energy of ultraviolet photoemitted electrons (decrease of 1 eV). Thus the sample has a lower work function than the tip. Contrary to the predictions of this model, we observe that the current is higher when the negative bias is applied to the side with the lower work function. (ii) The CuTAP forms a rectifying Schottky-Mott barrier at the graphite interface (*20*). The theory of such barriers is not complete (*21*), but a surface dipole does not readily explain the large z excursions seen when the surface is highly conducting. (iii) Electrical breakdown may occur, but it is not clear why this should be asymmetric. (iv) The dipole associated with the acid-base bond, pointing from the acid group toward the N on the molecule, is acted on by the gradient of the electric field between the tip and sample. It is readily seen that the polarity that might swing the molecule upward, and thus increase the current, is in the opposite sense to the observed rectification. (v) The geometrical asymmetry of the curved tip and the flat sample, which can give rise to asymmetry (*2*), predicts the wrong polarity for the rectification. Compared to all the mechanisms we have examined, the DOS model is the most compatible with all the experimental observations. To more fully verify the DOS model requires a theory along the lines of the effect of single atoms on the bias dependence of the STM current (*22*) to sort out the structural from the DOS contributions.

This demonstration that molecules consisting of tens of atoms can produce asymmetry, and that a substitution can be made to allow bonding to a desired substrate, opens up a range of chemical structures that may be studied. We believe that, if the energy levels of the molecules are suitably matched to that of the electrodes, it will change the *I-V* characteristics of the STM in dramatic ways. The bonding technique may be extended so that different kinds of molecules are attached to different electrodes on the same sample (*23*). The STM may thus prove useful in measuring the electronic energy levels of adsorbed molecules, and the molecules may provide control of the STM characteristics.

REFERENCES AND NOTES

1. R. M. Tromp, R. J. Hamers, J. E. Demuth, *Science* **234**, 304 (1986).
2. R. M. Feenstra, J. A. Stroscio, A. P. Fein, *Surf. Sci.* **181**, 295 (1987).
3. W. J. Kaiser and R. C. Jaklevic, *IBM J. Res. Dev.* **30**, 411 (1986).
4. Ph. Avouris, *J. Phys. Chem.* **94**, 2246 (1990).
5. L. L. Soethout, H. Van Kempen, G. F. A. Van De Walle, *Adv. Electron. Electron Phys.* **79**, 153 (1990).
6. X. L. Wu and C. M. Lieber, *Prog. Inorg. Chem.* **39**, 431 (1991).
7. A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29**, 277 (1974).
8. J. K. Gimzewski, E. Stoll, R. R. Schlittler, *Surf. Sci.* **181**, 267 (1987).
9. P. H. Lippel, R. J. Wilson, M. D. Miller, Ch. Wöll, S. Chiang, *Phys. Rev. Lett.* **62**, 171 (1989).
10. W. Mizutani *et al.*, *Jpn. J. Appl. Phys.* **28**, L1460 (1989).
11. W. M. Heckl *et al.*, *Langmuir* **5**, 1433 (1989).
12. A. Aviram, L. Li, M. Pomerantz, P. Roland, A. G. Schrott, in preparation.
13. W. R. Barger, A. W. Snow, H. Wohltjen, N. L. Jarvis, *Thin Solid Films* **133**, 197 (1985).
14. B. Simic-Glavaski, S. Zecevic, E. Yeager, *J. Am. Chem. Soc.* **107**, 5625 (1985).
15. P. H. Schroer and J. Becker, *IBM J. Res. Dev.* **30**, 543 (1986).
16. R. M. Tromp, *J. Phys. Condens. Matter* **1**, 10211 (1989).
17. G. Binnig *et al.*, *Europhys. Lett.* **1**, 31 (1986).
18. J. G. Simmons, *J. Appl. Phys.* **34**, 2581 (1963).
19. G. A. Haas and R. E. Thomas, in *Techniques of Metals Research*, E. Passaglia, Ed. (Interscience, New York, 1972), vol. 6, p. 91.
20. R. O. Loutfy, J. H. Sharp, C. K. Hsiao, R. Ho, *J. Appl. Phys.* **52**, 5218 (1981).
21. D. Wöhrle and D. Meissner, *Adv. Mater.* **3**, 129 (1991).
22. N. D. Lang, *Phys. Rev. B* **34**, 5947 (1986).
23. P. E. Laibinis *et al.*, *Science* **245**, 845 (1989).

24. We thank R. Kaufman and C. Joachim for the Nanoscope modifications; P. A. Roland and R. G. Schad for Auger measurements; D. W. Abraham for the loan of a Nanoscope base; A. C. Callegari, J. E. Demuth, and D. P. E. Smith for helpful discussions; and C. Pickover for the graphics of Fig. 3.

26 October 1991; accepted 2 January 1992

Rhenium-Osmium Isotope Constraints on the Age of Iron Meteorites

M. F. HORAN, J. W. MORGAN, R. J. WALKER, J. N. GROSSMAN

Rhenium and osmium concentrations and the osmium isotopic compositions of iron meteorites were determined by negative thermal ionization mass spectrometry. Data for the IIA iron meteorites define an isochron with an uncertainty of approximately ±31 million years for meteorites ~4500 million years old. Although an absolute rhenium-osmium closure age for this iron group cannot be as precisely constrained because of uncertainty in the decay constant of ^{187}Re, an age of 4460 million years ago is the minimum permitted by combined uncertainties. These age constraints imply that the parent body of the IIAB magmatic irons melted and subsequently cooled within 100 million years after the formation of the oldest portions of chondrites. Other iron meteorites plot above the IIA isochron, indicating that the planetary bodies represented by these iron groups may have cooled significantly later than the parent body of the IIA irons.

IRON METEORITES ARE DIVIDED INTO groups on the basis of their internal structures and chemical compositions. In most instances, irons of the same group were likely derived from the same parent body. Most iron meteorites, such as those in groups IIAB and IIIAB, are fragments of the cores of small planets. They are called magmatic irons because their compositions are consistent with fractional crystallization of the core of an initially chondritic body that melted to form a separate metal sulfide core and silicate mantle (*1*). Some iron meteorites, such as group IAB irons, are termed nonmagmatic irons because their chemical compositions suggest that they originated as silicate-metal segregations resulting from impact on or near the surface of their parent body. Determining the crystallization ages of iron meteorite groups to within several tens of millions of years is critical to understanding the timing of parent body accretion, melting, segregation of metal, and subsequent cooling. However, the ages of iron meteorite groups are still poorly constrained. Conventional long-lived radiogenic isotopes such as U, Th, K, Sm, Rb, and Lu are not useful for directly dating irons because of their low abundances in metallic phases. These isotopic systems have generally been applied only to dating silicate inclusions within some iron groups (*2–6*). Studies of the Pd-Ag system, based on the decay of ^{107}Pd to ^{107}Ag (half-life of 6.5 × 10^6 years) (*7–10*), apparently limits the age of IIB and IIIAB meteorites to no more than about 65 million years (10 half-lives) younger than the maximum age [~4560 million years ago (Ma)] of calcium-aluminum inclusions in chondrites (*11*). Absolute Pd-Ag ages cannot be determined, however, because the initial ^{107}Pd/^{108}Pd ratio is not known.

The highly siderophile elements Re and Os occur in relatively high abundances in many iron meteorites. The Re-Os isotope system ($^{187}\text{Re} \rightarrow {}^{187}\text{Os}$ by β decay) is thus ideal for dating iron meteorite groups. Early attempts to apply the system to dating irons, however, suffered from the poor precision of the analytical techniques (*12*). The subsequent application of ion microprobe and resonance ionization mass spectrometry techniques significantly improved precision. Luck and co-workers (*13, 14*) analyzed iron meteorites from different groups (IA, IIA, IIIA, and IVAB) and obtained a Re-Os isotope isochron with a slope of 0.0706 ± 0.0014; Walker and Morgan (*15*) obtained results for two irons (IA and IIA) that were consistent with this isochron. Luck and Allègre (*14*) also combined their iron data with results for metal separated from ordinary chondrites and obtained an isochron with a slope of 0.0716 ± 0.0019. They assumed that the age of iron meteorites and ordinary chondrites is 4550 Ma and used the isochron to determine a decay constant of $1.52 \pm 0.04 \times 10^{-11}$ year^{-1}. A significantly different decay con-

---

M. F. Horan and J. W. Morgan, U.S. Geological Survey, Mailstop 981, Reston, VA 22092.
R. J. Walker, Isotope Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20742.
J. N. Grossman, U.S. Geological Survey, Mailstop 990, Reston, VA 22092.