

Reports

Radiohalos in Coalified Wood: New Evidence Relating to the Time of Uranium Introduction and Coalification

Abstract. *The discovery of embryonic halos around uranium-rich sites that exhibit very high $^{238}\text{U}/^{206}\text{Pb}$ ratios suggests that uranium introduction may have occurred far more recently than previously supposed. The discovery of ^{210}Po halos derived from uranium daughters, some elliptical in shape, further suggests that uranium-daughter infiltration occurred prior to coalification when the radionuclide transport rate was relatively high and the matrix still plastically deformable.*

Even though the biological fossil record has been extensively documented, the rather abundant fossil record of radiohalos that exists in the coalified wood from the Colorado Plateau has remained virtually undeciphered. Jedwab (1) and Breger (2) have determined some important characteristics of such halos: in fact, earlier (1, 2) as well as present investigations on these samples (3) agree that: (i) the microscopic-size radiocenters responsible for halos (Fig. 1a) in coalified wood are actually secondary sites that preferentially accumulated α -radioactivity during an earlier period of earth history when uranium-bearing solutions infiltrated the logs after they had been uprooted; (ii) although autoradiography shows some α -activity dispersed throughout the matrix (1, 2), most of it is still concentrated in the discrete halo radiocenters; (iii) variations in coloration among radiohalos cannot necessarily be attributed solely to differences in the α -dose because there is evidence that the coalified wood was earlier far more sensitive to α -radiation than at present (1); (iv) halos that appear most intensely colored in unpolarized transmitted light also show evidence of induration; that is, when polished thin sections of coalified wood are viewed with reflected light (Fig. 1b), such high α -dose halos exhibit high reflectivity and pronounced relief; and (v) some areas of coloration are of chemical rather than radioactive origin (1).

In addition to the above verifications, the studies reported here mark the first time that (i) radii measurements have been made to determine the type and stage of development of halos in coalified

substances and (ii) the radiocenters of such halos have been analyzed by modern analytical techniques. The discoveries reported herein raise questions relative to when U was introduced into the wood, the duration required for coalification, and the age of the geological formations.

Specifically, it was discovered that the halos (Fig. 1a) surrounding the α -active sites are typically embryonic, that is, they do not generally exhibit the outer ^{214}Po ring characteristic of fully developed U halos in minerals (4). Such underdeveloped halos generally imply a low U concentration in the radiocenter. However, electron microprobe x-ray fluores-

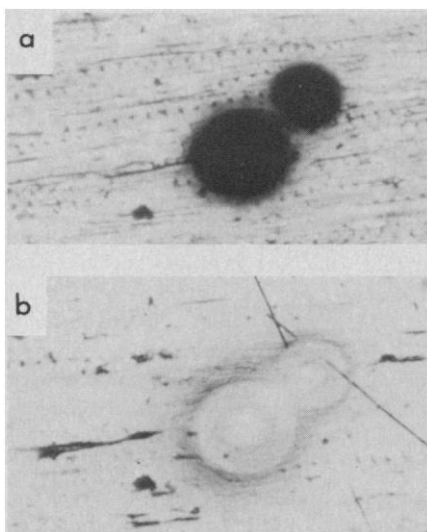


Fig. 1. (a) Coalified wood halos with U radiocenters in transmitted light ($\times 90$) [see (7)]. (b) The same halos in reflected light. The bright central spot in each halo is the radiocenter ($\times 90$).

cence (EMXRF) analyses (Fig. 2a) show many such radiocenters contain a large amount of U with the amount of daughter product Pb being generally too small to detect by EMXRF techniques (Fig. 2a). Although we discuss below the application of ion microprobe mass spectrometer (IMMA) techniques (5) to the problem of quantitatively determining the $^{238}\text{U}/^{206}\text{Pb}$ ratios, two important points deserve mention here: (i) if there was only a one-time introduction of U into the wood (2), these radiocenters date from that event unless subsequent mobilization of U occurred, and (ii) if U was introduced prior to coalification (1), then the $^{238}\text{U}/^{206}\text{Pb}$ ratios in these radiocenters also relate to the time of coalification.

Another class of more sharply defined halos was discovered possessing smaller inclusions (≈ 1 to $4\ \mu\text{m}$ in diameter) than the α -active sites. These inclusions exhibit a distinct metallic-like reflectance when viewed with reflected light. Three different varieties of this halo exist: one with a circular cross section, another with an elliptical cross section with variable major and minor axes, and a third most unusual one that is actually a dual halo, being a composite of a circular and an elliptical halo around exactly the same radiocenter (see Fig. 3, a to c).

Although the elliptical halos differ radically from the circular halos in minerals (6), the circular type resembles the ^{210}Po halo in minerals and variations in the radii of circular halos approximate the calculated penetration distances (≈ 26 to $31\ \mu\text{m}$) of the ^{210}Po α -particle (energy $E_\alpha = 5.3\ \text{MeV}$) in this coalified wood (7). Henderson (8) theorized that Po halos might form in minerals when U-daughter Po isotopes or their β -precursors were preferentially accumulated into small inclusions from some nearby U source. Although this hypothesis was not confirmed for U-poor minerals (9), it did seem a possibility in this U-rich matrix.

The EMXRF analyses (Fig. 2b) showed that the halo inclusions were mainly Pb and Se. This composition fits well into the secondary accumulation hypothesis for both of the U-daughters, ^{210}Po (half-life, $t_{1/2} = 138$ days) and its β -precursor ^{210}Pb ($t_{1/2} = 22$ years), possess the two characteristics that are vitally essential for the hypothesis: (i) chemical similarity with the elements in the inclusion and (ii) half-lives sufficiently long to permit accumulation prior to decay. This latter requirement is dependent on the radionuclide transport rate. In minerals the diffusion coefficients are so low that there is a negligible probability that ^{210}Po or ^{210}Pb atoms would migrate even $1\ \mu\text{m}$ before decaying, and thus the ori-

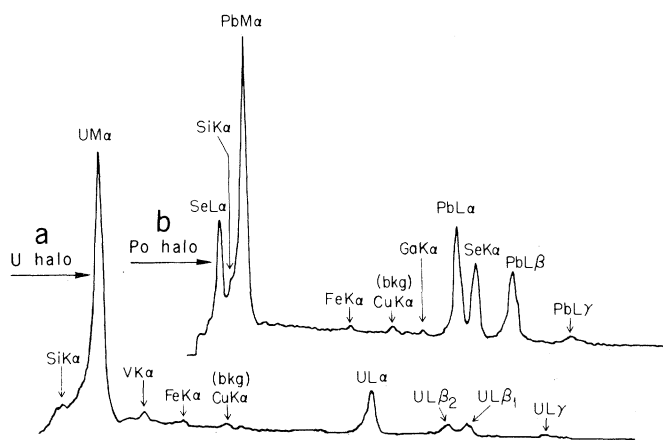


Fig. 2. Curve a, EMXRF spectrum of a U-rich radiocenter. Curve b, EMXRF spectrum of the radiocenter of a ^{210}Po halo.

gin of Po halos in minerals is still being argued (6, 10).

However, in this matrix the situation is quite different. A solution-permeated wood in a gel-like condition would exhibit a much higher transport rate as well as unusual geochemical conditions which might favor the accumulation of ^{210}Po and ^{210}Pb nuclides. Evidence that this accumulation was essentially finished prior to complete coalification comes from the fact that most Po halos are plastically deformed; furthermore, after coalification it is much more difficult to account for such rapid and widespread migration of the radionuclides (that is, within the ^{210}Po half-life). For example, a hundred or more ^{210}Po halos are sometimes evident in a single thin section (2 cm by 2 cm) of coalified wood, and they occurred quite generally in the thin sections examined (11). Of the thousands of Po halos seen in this matrix, only three show any trace of a ring that could possibly be attributed to ^{214}Po α -decay [that is, from the accumulation of the U-daughters ^{214}Pb ($t_{1/2} = 27$ minutes), ^{214}Bi ($t_{1/2} = 20$ minutes), or ^{214}Po ($t_{1/2} = 164 \mu\text{sec}$)], and none has been seen with a ring from ^{218}Po α -decay [that is, from the accumulation of short-lived ^{218}Po ($t_{1/2} = 3$ minutes)]. (Possibly these faint outer rings are of chemical rather than radioactive origin.)

Positive identification for the ^{210}Po halos comes from the IMMA analyses. Compared to a ^{238}U halo radiocenter, a ^{210}Po halo inclusion should contain much less ^{238}U (perhaps none at all) and much more of the ^{210}Po decay product ^{206}Pb . The IMMA analyses of Po halo inclusions showed that the ^{238}U content was low, the $^{238}\text{U}/^{206}\text{Pb}$ ratios varying from 0.001 to 2.0. [These values were corrected for the different ionization efficiencies ($\sim 2:1$) of Pb^+ and U^+ in this matrix.] This small ^{238}U content implies that only an extremely small amount of Pb could have been generated by in situ U decay. There are certainly three other

possible sources for the Pb in these inclusions: (i) common Pb, (ii) Po-derived radiogenic Pb generated by in situ decay of secondarily accumulated ^{210}Pb and ^{210}Po , or (iii) U-derived "old" radiogenic Pb that had accumulated in the hypothesized (12) Precambrian U ore deposit (which is one possible source of the U now in the Colorado Plateau) prior to the time it was carried with the U in solution into the wood. Since the ^{204}Pb count rates, which are unique indicators of common Pb, ranged from undetectable to a few counts per second above background when ^{206}Pb count rates were several thousand counts per second, it was evident that relatively little common Pb was present. Thus only $^{206}\text{Pb}/^{207}\text{Pb}$ ratios had to be measured to obtain evidence of ^{206}Pb originating from the decay of ^{210}Po ; the results were indeed confirmatory.

The ratios obtained were as follows: $^{206}\text{Pb}/^{207}\text{Pb} = 8 \pm 0.5, 11.6 \pm 0.3, 11.7 \pm 0.4, 13.3 \pm 0.7, 13.4 \pm 1.0, 13.7 \pm 0.6, 13.9 \pm 0.6, 14.8 \pm 0.9, 15.8 \pm 1.1, \text{ and } 16.4 \pm 0.5$. The variation in this ratio can easily be understood to have resulted from the addition of an increment of ^{206}Pb (generated by in situ ^{210}Po decay) to the isotopic composition of the "old" radiogenic Pb. The lowest Pb ratio, obtained from a very lightly colored ^{210}Po halo, differs slightly from the lowest Pb isotope ratio previously determined on bulk samples of Colorado Plateau U ore specimens (12).

What is the meaning of these Po halos? Clearly, the variations in shape can be attributed to plastic deformation which occurred prior to coalification. Since the model for ^{210}Po formation thus envisions that both ^{210}Po and ^{210}Pb were accumulating simultaneously in the Pb-Se inclusion, a spherical ^{210}Po halo could develop in 0.5 to 1 year from the ^{210}Po atoms initially present and a second similar ^{210}Po halo could develop in 25 to 50 years as the ^{210}Pb atoms more slowly β -decayed to produce another crop of ^{210}Po

atoms. If there was no deformation of the matrix between these periods, the two ^{210}Po halos would simply coincide. If, however, the matrix was deformed between the two periods of halo formation, then the first halo would have been compressed into an ellipsoid and the second halo would be a normal sphere. The result would be a dual "halo" (Fig. 3c). The widespread occurrence of these dual halos in both Triassic and Jurassic specimens (13) can actually be considered corroborative evidence for a one-time introduction of U into these formations (1, 2), because it is then possible to account for their structure on the basis of a single specifically timed tectonic event. The fact that dual halos occur in only about 1 out of 100 single Po halos is of special significance (14).

In halos with U radiocenters, the low Pb abundance made it generally quite difficult to measure U/Pb ratios with EMXRF (Fig. 2a) techniques. More sensitive IMMA measurements on these U radiocenters revealed $^{238}\text{U}/^{206}\text{Pb}$ ratios (15) of approximately 2230; 2520; 8150; 8300; 8750; 18,700; 19,500; 21,000; 21,900; and 27,300 (again corrected for different ionization efficiencies). Typically, the U^+ ion signals from which these ratios were derived were greater than 3×10^4 counts per seconds (cps); for example, the 19,500 value was obtained from a halo with a U^+ signal of 10^6 cps (± 5 percent) with background ≈ 3 cps. We checked the $^{238}\text{U}/^{235}\text{U}$ ratio independently (and found it normal) by excising several radiocenters and analyzing them directly on the filament of a high-sensitivity thermal ionization mass spectrometer (16).

Even without attempting to subtract out the ^{206}Pb component of the common and "old" radiogenic Pb (15), these $^{238}\text{U}/^{206}\text{Pb}$ ratios raise some questions. For example, if the $^{238}\text{U}/^{206}\text{Pb} = 27,300$ value is indicative of the formation time of the radiocenter, this is more recent by at least a factor of 270 than the minimum (Cretaceous) and more recent by a factor of 760 than the maximum (Triassic) geological age estimated for the introduction of U into the logs (12, 17, 18). To obtain $^{238}\text{U}/^{206}\text{Pb}$ ratios that more accurately reflect the amount of Pb from in situ U decay, a search was made for sites with even higher ratios, for such areas possibly contained negligible amounts of extraneous Pb. Two halo radiocenters were found that exhibited $^{238}\text{U}^+$ signals of 4×10^4 and 6.4×10^4 cps, respectively, while the $^{206}\text{Pb}^+$ signals were indistinguishable from background (≈ 3 cps) in both cases (^{207}Pb also absent).

Such extraordinary values admit the

possibility that both the initial U infiltration and coalification could possibly have occurred within the past several thousand years. At the same time it may be argued that this view is quite improbable for there exists another explanation that could invalidate the association of the U/Pb ratios with the initial introduction of U. This explanation would admit that, although Po halos constitute evidence that U infiltration and hence U radiocenter formation occurred prior to coalification, some U may have been added or Pb may have been selectively removed, or both, by groundwater circulation after coalification. Hence variable U/Pb ratios would be expected, and the highest ratio would simply reflect the last time when U remobilization or Pb remobilization, or both, occurred. Although this hypothesis has been used to account for U disequilibrium (18, 19) in bulk specimens of U-impregnated Colorado Plateau material, there are some questions about its applicability here.

For example, if Pb was removed from the U sites, it must have been a very selective removal for both the EMXRF and IMMA results show that considerable quantities of Pb still remain in the nearby (within $\approx 50 \mu\text{m}$ of the U sites) Po halo Pb-Se inclusions. If Pb loss was minimal, then to explain the high $^{238}\text{U}/^{206}\text{Pb}$ ratios by remobilization requires that significant quantities of U were introduced into the U radiocenters quite recently. In any event, whether the hypothesis is U addition or Pb removal, the crucial point that seems quite difficult to explain under either assumption is the fact that, in general, the halos around U sites are embryonic (20). That is, since it seems clear that the U radiocenters formed during the initial introduction of U and if this were as long ago as the Triassic or Jurassic are generally thought to be, then there should be evident not only fully developed, but overexposed U halos as well (21).

Clearly, it was important to determine whether these phenomena were characteristic only of the U-rich Colorado Plateau coalified wood (2, 3). We therefore initiated studies on coalified wood fragments which are occasionally found in the Chattanooga shale (3, 11, 22). Thus far only embryonic halos have been seen, and the $^{238}\text{U}/^{206}\text{Pb}$ ratios are much too high ($> 10^3$) to correlate with the geological age of the formation (Devonian). The low U content of the Chattanooga shale (1 to 50 parts per million) makes it quite difficult to see how U remobilization could account for these very high isotope ratios. Thus the evidence does not appear to support the remobilization

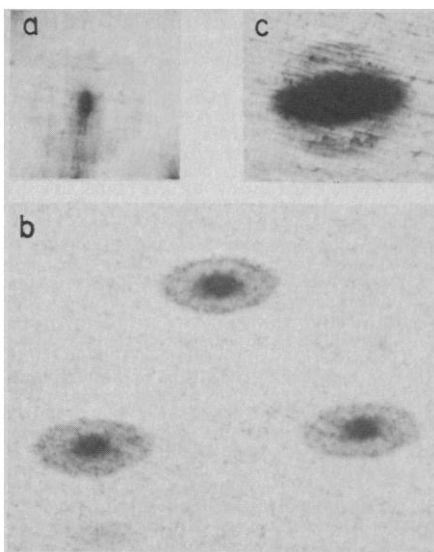


Fig. 3. (a) Circular ^{210}Po halo ($\times 180$). (b) Compressed ^{210}Po halos ($\times 180$). (c) Circular and compressed ^{210}Po halo ($\times 180$).

hypothesis as a general explanation of these unusual $^{238}\text{U}/^{206}\text{Pb}$ ratios in either the Colorado Plateau or Chattanooga shale specimens.

If remobilization is not the explanation, then these ratios raise some crucial questions about the validity of present concepts regarding the antiquity of these geological formations and about the time required for coalification. Finally, in addition to again focusing attention on the question of the origin of Po halos in minerals (6, 10), the existence of U-derived single and dual Po halos in different formations suggests that the original source of U may have been a Precambrian ore deposit that was geographically not far removed from the present Colorado Plateau. Thus, in view of America's energy requirements, it might be profitable to search for such an ore deposit by deep drilling into selected areas around and within the Colorado Plateau.

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2. I. A. Breger, in *Formation of Uranium Ore Deposits, Proceedings of a Symposium, Athens, 6-10 May 1974* (International Atomic Energy Agency, Vienna, 1974), pp. 99-124.
3. I. A. Breger donated Colorado Plateau coalified wood specimens from the following mines: (i) Jurassic—Peanut and Virgin No. 3, Colorado; Corvusite, Utah; and Poison Canyon, New Mexico; (ii) Triassic—Lucky Strike No. 2, Dirty Devil No. 2, Adams, and North Mesa No. 9, all in Utah; and (iii) Eocene—Docamour, Colorado. J. S. Levinthal provided 16 other specimens. However, only those from the Rajah 49 mine [Salt Wash member of the Morrison Formation (Jurassic)] were sufficiently well preserved to exhibit halos. The Chattanooga shale coalified wood (Devonian), which came from near Nashville, Tennessee, was donated by I. A. Breger and V. E. Swanson. Breger's analysis of this coalified wood yielded 0.001 to 16 percent U, 54 to 84 percent C, 3 to 7.5 percent H, 0.3 to 1.8 percent N, 6 to 38 percent O, and 0.6 to 14.5 percent S. Except where stated, all experimental results refer to work on Colorado Plateau coalified wood (Triassic and Jurassic formations). A thin section of a coalified wood specimen (earlier obtained from I. A. Breger) was provided by J. Jedwab and was used along with Breger's other specimens. Although personal communications with Breger and Jedwab proved of great value, this in no way implies that either Jedwab or Breger necessarily concurs with the results presented here.
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7. If the appropriate formulas [G. Friedlander, J. W. Kennedy, J. M. Miller, *Nuclear and Radiochemistry* (Wiley, New York, ed. 2, 1964), pp. 95-98] are used for computing α -ranges in various solids, the ranges of a 5.3-MeV α -particle in coalified wood [see (3)] of density 1.3 and 1.6 g/cm^3 would be 31 and $25 \mu\text{m}$, respectively. Uniform shrinkage of the matrix could also reduce the radius.
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11. This occurrence of Po halos refers to the Colorado Plateau coalified wood.
12. L. R. Stieff, T. W. Stern, R. G. Milkey, *U.S. Geol. Surv. Circ.*, **271** (1953).
13. Dual halos have thus far been found in specimens from the North Mesa No. 9 mine in Utah and the Virgin No. 3 and Rajah 49 mines [see (3)].
14. The coloration pattern of the dual halo provides the key to understanding its rarity. If U with its daughters were concurrently flushed out of some Precambrian ore deposit, even with a relatively short transit time from the ore deposit to the wood, equilibrium conditions still require that more than 50 times as much ^{210}Pb as ^{210}Po be available for accumulation. If the wood exhibited constant sensitivity to α -induced coloration, then the outer circular halo resulting from ^{210}Pb accumulation would be expected to be much darker than the elliptical halo resulting from ^{210}Po accumulation. The fact that just the opposite is true is in good agreement with the evidence found by Jedwab [(1)] and private communication indicating that during the U infiltration the gel-like wood exhibited much higher sensitivity to α -induced coloration as compared to the later stages of coalification. Possibly then, a relatively dark halo could have formed rather quickly from as few as 10^4 to 10^5 ^{210}Po atoms, whereas some 20 to 50 years later the change in the coloration sensitivity of the matrix might require an α -dose 50 to several hundred times higher from the ^{210}Pb decay sequence to produce even a light halo. Thus possibly only in rare cases would the Pb-Se inclusions accumulate large enough quantities of ^{210}Pb to subsequently generate the outer circular halo.
15. The variation in the $^{238}\text{U}/^{206}\text{Pb}$ ratios may be attributed primarily to the "old" radiogenic Pb component and secondarily to ^{226}Ra and ^{210}Pb , which, in varying amounts, were also incorporated into the U-rich radiocenters. Evidence for this "old" radiogenic Pb was also found in larger, millimeter-size U-rich regions which also contained varying amounts of Na, Al, K, Ca, Ti, V, Fe, Y, Zr, Ba, and the rare earths. Such regions exhibit variable (but not very high) U/Pb ratios and very little common Pb.

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19. Nondestructive γ -ray spectrometry was utilized to check on U disequilibrium in gram-size specimens of the Colorado Plateau coalified wood. We found significant differences in the γ -spectra that could reasonably be attributed to U disequilibrium. By removing microportions of U-rich areas and physically smearing the material onto steel planchets for α -counting, we observed one α -spectra that unambiguously indicated U disequilibrium between ^{234}U and ^{230}Th , or ^{230}Th and ^{226}Ra , or both. Excess α -activity in the ~ 4.7 -MeV region was not attributed to excess ^{234}U because mass spectrometry measurements on a separate specimen showed an equilibrium $^{238}\text{U}/^{234}\text{U}$ value.
20. Less than 2.5 percent of the halos with U radio-
21. This would be true even if coalified wood is only 1/10 as sensitive to α -coloration as biotite.
22. I. A. Breger and J. M. Schopf, *Geochim. Cosmochim. Acta* **7**, 387 (1955); V. E. Swanson, *U.S. Geol. Surv. Prof. Pap.* **300** (1956), p. 451. J. Jedwab informed me of halos in this material.
23. I thank I. A. Breger, J. S. Levinthal, V. E. Swanson, and J. Jedwab for supplying coalified wood specimens. Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation, and by Columbia Union College under NSF research grant DES 74-23451.

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Rare-Earth Manganites: Surface-Segregated Platinum Increases Catalytic Activity

Abstract. Crushed and etched lanthanum lead manganite ($\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$) crystals containing as little as 0.005 atomic percent platinum have significantly higher catalytic activity than free platinum crystals. This higher activity is due to an almost 100-fold segregation of platinum on the surface. The surface platinum concentration found, 0.5 atomic percent, is sufficient to account for the enhanced activity provided that the platinum has the same activity as platinum supported on alumina.

As a result of claims that lanthanum lead manganite ($\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$) rivaled Pt in its ability to catalyze the oxidation of CO (1, 2), Katz *et al.* examined the potential of this compound for the treatment of automotive exhaust emissions

(3). These tests, which were carried out under simulated automotive conditions, showed that, on the basis of the surface area of the catalyst, Pt was not only more active than manganite for the oxidation of CO but also significantly more

active for the oxidation of hydrocarbons.

We also found that the only $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ samples having high activity were etched single crystals grown from a molten flux in Pt crucibles. These crystals, which were found to contain 50 to 75 parts per million (ppm) (atomic) Pt, had an activity for CO and C_3H_8 that was higher by more than an order of magnitude than that of Pt-free polycrystalline manganite prepared by ceramic methods. These results, together with data showing that single crystals of manganite exhibited oxidation kinetics similar to those of Pt (3) whereas ceramically prepared Pt-free manganite did not, led us to suggest that the higher activity of these manganites was due to traces of Pt impurities. A similar suggestion was made by Yao (4) on the basis of other evidence obtained from these materials.

We have conducted further tests to determine if the Pt is responsible for the higher activity of the manganite single crystals grown in Pt crucibles, and, if so, how such a small amount of Pt causes such a large increase in specific activity. These tests included x-ray photoemission measurements which indicated that the Pt in these crystals is segregated about 100-fold on both the unetched and etched cleaved surfaces. The approximately 0.5 atomic percent Pt found on the surface is sufficient to account for the higher activity of these crystals, provided that the Pt has roughly the same activity as Pt supported on alumina (Al_2O_3). Furthermore, we have grown Pt-free manganite single crystals which have a specific CO and C_3H_8 activity appreciably lower than those grown in Pt

Table 1. Manganite surface and catalytic properties; NM, not measured.

Sample	Preparation	Sample surface area (m ²)	Surface Pt concentration (atomic %)	CO rate at 250°C (10 ⁻⁷ mole sec ⁻¹ m ⁻² , manganite surface)	C ₃ H ₈ rate at 250°C (10 ⁻⁹ mole sec ⁻¹ m ⁻² , manganite surface)	CO rate at 250°C (10 ⁻⁴ mole sec ⁻¹ m ⁻² , Pt surface)§	C ₃ H ₈ rate at 250°C (10 ⁻⁵ mole sec ⁻¹ m ⁻² , Pt surface)§
<i>Pt-Al₂O₃</i>							
		50.0*				0.9	1.0
<i>Single crystals of manganite</i>							
A	Molten flux in Pt, crushed, no etch (100 to 250 μm)	3.6	0.55	< 0.4	< 0.3	< 0.07	< 0.005
A-E	A, etched 5 minutes†	21.0	0.25	4.8	21.0	1.7	0.74
B	Molten flux in Pt, crushed, no etch (37 to 250 μm)	28.9	NM	0.64	0.11		
B-E	B, etched 7 minutes†	19.0	0.23	20.0	45.0	7.7	1.7
C-E	Molten flux in Pt, crushed, etched 5 minutes† (37 to 250 μm)	51.0	1.1	14.0	34.0	1.1	0.27
D-E	Molten flux in MgO, uncrushed, etched 7 minutes†	47.5	< 0.1	0.54	0.13		
<i>Polycrystals of manganite</i>							
F	Precipitated hydroxide (600°C), no etch	130.0	< 0.1	0.25	0.18		
F-E	F, etched 5 minutes‡	664.0	< 0.1	0.74	0.25		

*The Pt surface area was determined by hydrogen chemisorption. †Etched in 20 percent HNO_3 at 80°C. ‡Etched in 15 percent HNO_3 at 60°C. §Assuming that a surface Pt atom is 13 percent larger than a surface manganite "atom."