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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 $^{238}U/^{234}U$ value.
20. Less than 2.5 percent of the halos with U radiocenters have any trace of an outer ring. It is difficult to associate these with sequential α-decay from ^{238}U because such weak rings do not correlate with the U content. These weak rings may have resulted from diffusion of α-radioactivity out of the radiocenter prior to induration of the halo region by the α-radioactivity. Alternatively, these weak rings may have resulted from the accumulation of small amounts of ^{222}Rn, ^{214}Pb, or ^{226}Ra. In fact, the size of the dark halo region around the U-rich sites admits of the possibility that the inner halos may have formed from the accumulation of minute amounts of ^{226}Ra or ^{210}Pb, or both. Their more diffuse radiocenters, however, would prevent the formation of well-defined boundaries as in the case of the Pb-Se inclusions.
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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 ($La_{0.7}Pb_{0.3}MnO_3$) 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 ($La_{0.7}Pb_{0.3}MnO_3$) 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 $La_{0.7}Pb_{0.3}MnO_3$ 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_6 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_6 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_3H_6 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_3H_6 rate at 250°C (10^{-5} mole sec^{-1} m^{-2}, Pt surface)§
			Pt-Al_2O_3				
		50.0*				0.9	1.0
			Single crystals of manganite				
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		
			Polycrystals of manganite				
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."

crucibles, despite their similarity in bulk composition, crystal structure, and manner of preparation.

Our tests were carried out on two separate batches of crushed single crystals of $La_{0.7}Pb_{0.3}MnO_3$ grown from a molten lead borate flux in Pt crucibles (*2*). These crystals were tested in both the unetched (samples A and B, Table 1) and etched (samples A-E, B-E, and C-E) condition. Etched single crystals of manganite containing no Pt (sample D-E) were grown by the same molten flux method but in MgO crucibles. We also prepared polycrystalline Pt-free $La_{0.7}Pb_{0.3}MnO_3$ by calcining a coprecipitated mixture of hydroxides in an Al_2O_3 crucible at 600°C for 24 hours (*2*). The hydroxides were precipitated from a nitrate solution with KOH. Both unetched (sample F) and etched (sample F-E) materials were tested.

X-ray diffraction analysis indicated that all of these samples were characterized by a single phase with well-defined perovskite structures. We measured the specific surface areas of the catalysts using four-point nitrogen isotherms obtained with a modified Perkin-Elmer Sorptometer. Our activity measurements were made in a flow reactor under conditions of low conversion; this system has been described (*3*). We tested the catalysts in simulated automotive exhaust (0.5 percent CO, 0.025 percent C_3H_6, 3 percent O_2, 10 percent H_2O, with the balance N_2) at a flow rate of 16.5 liter/min.

The method of preparation and treatment given each catalyst prior to testing are listed in Table 1, columns 1 and 2. The total surface area at the completion of the test is given in column 3. To rank the various catalysts we have calculated their specific reaction rates for CO and C_3H_6 oxidation at 250°C (columns 5 and 6), using the expression $r_s = XF/S$. Here X is the fraction of CO or C_3H_6 converted, F is the feed rate in moles per second, and S is the sample surface area in square meters. From these rates it is apparent that the only catalysts having high activity are the etched Pt-containing single crystals of manganite (samples A-E, B-E, and C-E). All of the Pt-free materials, including single crystals of manganite grown in MgO (sample D-E), have CO and C_3H_6 rates that are lower by roughly one and two orders of magnitude, respectively, than those of the etched crystals grown in Pt crucibles (samples A-E and B-E).

Comparing the x-ray photoemission Pt 4*f* peak heights in the $La_{0.7}Pb_{0.3}MnO_3$ spectra with those from a clean Pt foil allows one to obtain a relative Pt concentration for the roughly 11-Å layer (five atom layers thick) analyzed by this method (*5*). This analysis yields Pt concentrations higher by over an order of magnitude than the measured bulk value. There is, however, no substantial reason for assuming such an enrichment of the five outer atomic layers. The Pt concentrations shown in Table 1, column 4, are calculated on the assumption that this Pt was concentrated in the first layer of atoms, as it would be in a completely dispersed Pt-Al_2O_3 catalyst.

Using the surface Pt concentrations as determined by x-ray photoelectron spectroscopy (XPS) and assuming complete dispersal of the Pt on the outermost layer, we have converted the activity of the etched single crystals of manganite grown in Pt crucibles at 250°C (Table 1, columns 5 and 6) from moles per second per square meter of manganite surface to moles per second per square meter of Pt surface. These rates, listed in Table 1, columns 7 and 8, are similar to those measured for Pt on a Pt-Al_2O_3 catalyst, an indication that both the CO and C_3H_6 activity of the etched Pt-containing crystals can be well accounted for by the concentration of Pt found segregated on the surface, provided the Pt has the same specific activity as Pt supported on Al_2O_3.

The segregation of Pt on the surface of the unetched crushed manganite crystals (Table 1, sample A) in concentrations 100 times larger than in the bulk suggests that at least part of the Pt is in the form of Pt-rich inclusions which serve as cleavage points, thus concentrating the Pt on the surface when the crystal is crushed. These Pt-enriched cleavage sites could well be the PbO inclusions that Gallagher *et al.* (*6*) recently reported finding in these materials.

We find, however, that, despite the presence of appreciable Pt on the surface, the unetched crystals have significantly lower CO and C_3H_6 activity than crystals that have been etched in HNO_3, as shown by the specific CO and C_3H_6 rates of sample A (unetched) and sample A-E (etched) in Table 1, columns 5 and 6. Etching increases the activity of this sample by over an order of magnitude. Although no x-ray photoemission measurements were made on sample B in the unetched condition, these crystals also showed a large increase in activity after etching. Chemical shift data from our XPS studies indicate that the "activation" of the surface during this acid etching is due to an alteration in surface composition leading to the exposure of a more reduced form of Pt on the surface. We found that the strongly etched single crystals grown in Pt crucibles have a $4f_{7/2}$ electronic binding energy only slightly higher than the 71.4 ev that we measure for clean Pt foil. Unetched (inactive) crystals show a 1-ev increase in this binding energy, characteristic of a heavily oxidized Pt surface layer.

Furthermore, we have found that the HNO_3 etch alters the surface morphology and composition considerably. Whereas the freshly cleaved and presumably stoichiometric surface appears microscopically smooth (Fig. 1a), etching converts this relatively inactive surface into a loosely adhering layer with a relatively high surface area (Fig. 1b). Chemical and energy-dispersive x-ray analysis indicated that the bulk composition of this layer was highly enriched in Mn and O and depleted in both La and Pb. We have found this same surface layer on the etched Pt-free single crystals of manganite (sample D-E). The fact that these crystals are among the less active manganite samples indicates that this Mn-rich layer is itself a relatively poor CO and C_3H_6 oxidation catalyst. Our results show that it is the Pt segregated on this surface in reduced form which accounts for the higher activity of the Pt-containing crystals.

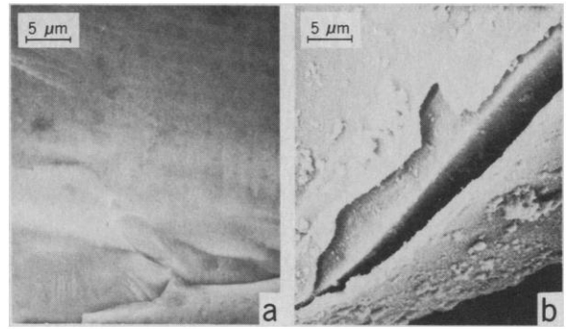

Fig. 1. (a) Scanning electron micrograph of a cleaved unetched $La_{0.7}Pb_{0.3}MnO_3$ single crystal. (b) Micrograph of the Pt-enriched manganese oxide scale which forms on the manganite crystals during the etching treatment. This scale has a specific CO and C_3H_6 activity that is higher by over an order of magnitude than the stoichiometric manganite surface shown in (a).

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Phosphatases in Lake Water: Characterization of Enzymes from Phytoplankton and Zooplankton by Gel Filtration

Abstract. *Sephadex gel filtration was used to characterize phosphomonoesterases in two small lakes in northern Sweden. Two fractions, here termed phosphatase A and phosphatase B, were found both as free enzymes and associated with seston. The activity of phosphatase A was correlated with the presence of algal biomass. Phosphatase B, on the other hand, was derived from zooplankton. Phosphate served as an effective inhibitor of phosphatase A but had no such effect on phosphatase B. Both fractions had* pH *optima between 6.5 and 7.0.*

After Steiner (*1*) found an increase of inorganic phosphorus in lake water incubated with dead plankton organisms, several investigations were made of enzymatic hydrolysis of different phosphorous compounds in lakes and oceans. The phosphomonoesterases are the most studied enzymes of the many different phosphatases.

Phosphomonoesterases in the aquatic environment are produced by bacteria (*2*), algae (*3, 4*), and zooplankton (*1, 5, 6*). Besides being associated with living cells or particulate cell debris, the phosphomonoesterases are also found as free dissolved enzymes (*7–9*).

Phosphatases are often classified as either alkaline or acid, with *p*H optima well above or well below *p*H 7. Different phosphatases produced by aquatic organisms have been separated by fractionation monitored with assays of *p*H-dependent phosphatase activity (*4, 7*).

Production of phosphatases in different species of algae increases when phosphorus is a limiting factor (*4, 10*); phosphatases have been suggested to be ecologically essential because they release phosphate. Synthesis of phosphatases, on the other hand, often seems to be repressed by high concentrations of phosphate in water or in cells (*4, 8, 11, 12*).

The study reported here provides additional information on the different fractions of phosphomonoesterases occurring in the natural aquatic environment, their origin, and some of their characteristics. All specimens were taken from two adjacent lakes, Lake Magnusjaure and Lake Hymenjaure, situated at 68°27′N and 18°27′E in the subarctic region of northern Sweden. The lakes are small, each with an area of about 2 ha and with maximum depths between 4.5 and 5.5 m. Summer mean water temperatures are 9.5° to 10.5°C and conductivity is 1.6 to 1.8 millisiemens per meter. The lakes were originally oligotrophic, but a program of artificial enrichment with phosphorus and nitrogen (*13*) has brought them toward more eutrophic conditions. The work was done during the ice-free season (15 June to 10 October) in 1975.

Molecular weight was chosen as the criterion for characterization of different phosphomonoesterases. The enzymes were separated by Sephadex gel filtration, a technique that has been applied to phosphatases from bovine liver (*14*) and human placenta (*15*).

Sephadex of different grades (G-75 and G-200) and Sepharose 4B were packed in tubes of Plexiglas 2 cm in diameter and 50 cm long. The flow rate was 0.5 ml/min, with tris buffer used as eluent; the void volume was determined with blue dextran.

For separation of free dissolved phosphatases, 300 ml of lake water was filtered through membrane (Sartorius SM 11107, 0.2 μm) and the enzymes in the filtrate were concentrated 40-fold by ultrafiltration (Diaflo filter PM10; Amicon ultrafiltration cell model 50); 2 ml of the concentrated enzyme solution was refiltered before being applied to Sephadex columns.

For analysis of seston-associated enzymes, 1500 ml of lake water was passed through a glass fiber filter (Whatman GF/C); the filter was placed in tris buffer and homogenized. After homogenization the sample was centrifuged, and 2 ml of the supernatant was placed on the Sephadex column. In both analyses, phosphatase activity was determined in each 5-ml fraction collected from the column.

Phosphomonoesterase activity was assayed by the method of Perry (*11*), with 3-*O*-methylfluoresceinphosphate as substrate. The samples were incubated at 20°C in tris-HCl, *p*H 6.5. The buffer solution and all glassware were autoclaved before analysis to prevent microbial growth. Enzyme activity was measured at *p*H 6.5 because the phosphatases of the two lakes had their only *p*H optimum at 6.5 to 7.0, which is also the *p*H of the lakes.

Sephadex G-200 elution diagrams showing the composition of free and seston-associated enzymes (Fig. 1, a and b) indicated similar patterns for free and seston-associated phosphatases. One fraction, called phosphatase A, was not separated by the gel and eluted with the void volume. Another fraction, phosphatase B, was well separated and, after calibration with proteins of known molecular weight, was calculated to have a molecular weight of about 80,000. Elution from Sephadex G-75 gave only one peak at the void volume.

To determine whether the phosphatase A peak could be fractionated, the experiment was repeated with Sepharose 4B, which has an upper separation limit of molecular weight 3×10^6 for dextrans. However, phosphatase A still eluted with the void volume and can therefore be assumed to consist either of very large molecules, molecules associated with colloidal material, or fragments small enough to pass through a 0.2-μm filter. The question of whether phosphatase A consists of more than one fraction was not answered by this experiment.

A decrease in phosphatase activity often follows the addition of phosphate to a medium containing phosphatase-producing organisms. In many cases repression of the enzyme synthesis rather than inhibition of the enzyme itself causes such a decrease (*4, 12*). To test how the two phosphatase fractions found in Lake Hymenjaure and Lake Magnusjaure reacted to additions of phosphate, the following experiment was performed. Free phosphatases were concentrated and filtered on Sephadex G-200 as described above. A parallel sample was concentrated and NaH_2PO_4 was added immediately before gel filtration. Elution diagrams for the two samples (Fig. 1c) show an almost total inhibition of phosphatase A by added phosphate but no effect on phosphatase B. The fact that phosphate was added to a sterile filtered sample shows that the decrease in enzyme activity was a result of inhibition and not repression. The con-