not oxidize. This selective oxidation is also seen on Nichrome films which have been treated in air at 400°C for several minutes. Evaporation of a thin Al overlay on this oxidized Nichrome sample again results in reduction of the Cr_2O_3 component to Cr and oxidation of Al to Al_2O_3 as in reaction 2.

It is clear that under these experimental conditions Cr completely prevents oxidation of Ni. This observation is certainly counter to the prediction that the high surface electric fields prevent such selective oxidation schemes (*7*). The fact that oxygen has a higher affinity for Cr than for Ni apparently is the major factor in determining the reaction products and is responsible for the increased total surface concentration of Cr.

We know of no other analytical method that has the combination of depth resolution, sensitivity to elements and oxidation states, and low probing energy required to make these measurements. These results will be useful in a number of disciplines. In microelectronics, we postulate (*15*) an explanation for the failure mechanism of Nichrome resistors. These resistors, made by thin film deposition of Nichrome followed by an oxidizing treatment to adjust to the desired resistance, have Al contacts and conductors. Reaction 2 results in a high-resistance contact due to the presence of an Al_2O_3 interfacial film. We also expect bonding of one material to another, especially metals to oxides or oxidized surfaces, to involve this type of reaction. In addition, in catalysis this scheme may be relevant for understanding experimental observations involving the poisoning of catalytic surfaces, the dispersion of supported metals, and the behavior of metallic clusters.

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Cristobalitic Stage in the Diagenesis of Diatomaceous Shale

Abstract. *With increasing depth of burial, diagenetic cristobalite in the Monterey Shale of California shows a decrease in the* d(*101*) *spacing from 4.115 to 4.040 angstroms, indicative of a progressive change in its internal structure. The spacing is 0.004 to 0.015 angstrom smaller in porcellanite than in associated chert, probably because the cristobalite of porcellanite formed later than that of chert.*

Interest in diagenetic alteration of biogenic opal into chert has revived in recent years, largely because of the discovery of much chert in deep-sea sediments and the trouble caused by the chert in the drilling of these sediments. The experience of the Deep Sea Drilling Project has been described in many reports, of which only a few can be cited here (*1, 2*).

We have sampled thick sections of the Miocene Monterey Shale of California in the course of a geochemical study of Tertiary sedimentary rocks (*3*). Bramlette (*4*, pp. 16–17) recognized that metamorphism due to burial converted diatomaceous Monterey Shale first into "opaline" cristobalitic chert and porcellanite and finally into quartzitic chert and porcellanite. The use of x-ray techniques has allowed us to study these conversions in greater detail.

The main stages of diagenesis and the rock terms used by us are explained by reference to a typical exposure of Monterey Shale (Fig. 1). Rocks in the exposure are alternating layers of dark compact chert and light porous porcellanite, which are distinguished in the field on the basis of texture (*2, 4*) and whose mineralogy is determined in the laboratory through x-ray diffraction. Both chert and porcellanite of this exposure yield diffraction patterns of low cristobalite.

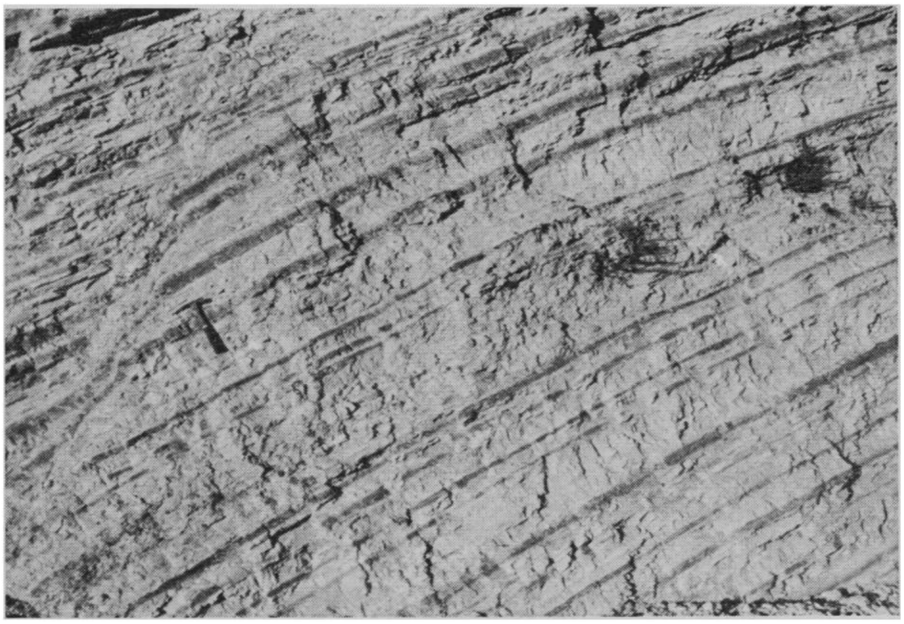

Fig. 1. Exposure of Monterey Shale along Sweeney Road east of Lompoc, California, consisting of thin dark beds of cristobalitic chert alternating with thicker light-colored beds of cristobalitic porcellanite. The hammer is 33 cm long.

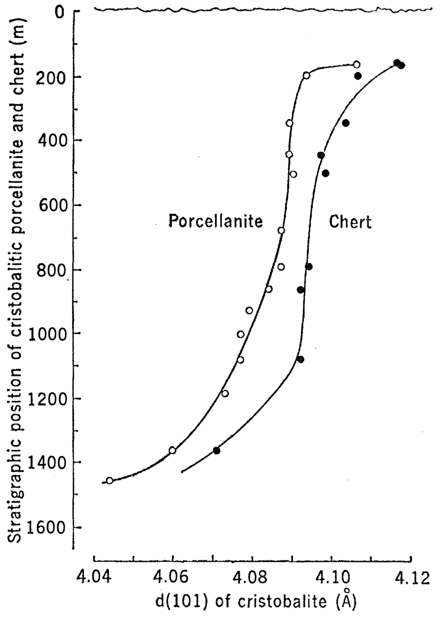

Fig. 2. Variation with depth of the $d(101)$ spacing of cristobalite in porcellanite (open circles) and chert (closed circles) at Chico Martinez Creek. Depths are relative to the top of the Monterey Shale and represent minimal depths of burial.

Another and earlier diagenetic stage is represented higher in the section, where there are alternating layers of chert and diatomaceous mudstone; only the chert is cristobalitic, and free silica of the associated mudstone consists of unaltered biogenic opal (diatom frustules) that is amorphous to x-rays. The final diagenetic stage is found at other localities, where chert and porcellanite in the lower part of the Monterey are both quartzitic.

Our observations suggest that the alteration of biogenic opal occurred first in layers of purest diatomite through dissolution of diatom frustules and precipitation of cryptocrystalline cristobalite. These layers, which originally had a density of about 0.5 g/cm^3, also served as loci of deposition for some silica dissolved out of adjacent diatomaceous mudstone and were gradually converted into compact cristobalitic chert with a density of about 2.0 g/cm^3. The change of diatomaceous mudstone into cristobalitic porcellanite occurred some time afterwards (*4*, p. 54). The ratio of chert to porcellanite in the exposure of Fig. 1 is believed to reflect approximately the ratio of diatomite to diatomaceous mudstone in the original sediment.

Cristobalitic porcellanite is a dominant type of rock in the Monterey Shale at many places. At the classic Miocene locality of Chico Martinez Creek in western Kern County (*5*), there is about 1300 m of cristobalitic porcellanite accompanied by variable amounts of cristobalitic chert. Below the cristobalitic diagenetic zone, porcellanite and chert in an additional 730 m of Monterey Shale are uniformly quartzitic.

Diagenetic cristobalite of the Monterey Shale manifests an increasing sharpness of x-ray reflections and a decreasing $d(101)$ spacing in successively older samples that represent increasing depth of burial. Such changes in response to x-rays have been ascribed (*6*) to a progressive ordering of the disordered atomic structure of the first-formed cristobalite, which is favored by increasing temperature and pressure. Cristobalitic porcellanite and chert of Chico Martinez Creek (and of other California localities as well) unexpectedly have separate curves relating their $d(101)$ spacing to depth of burial (Fig. 2). At any particular horizon, the spacing of porcellanite is 0.004 to 0.015 Å smaller than that of associated chert, probably because porcellanite formed later (at a higher temperature) than the chert.

The total variation of $d(101)$ spacing of cristobalite in the Monterey Shale is 4.040 to 4.115 Å, with a standard deviation of determination of 0.0026 Å. The numerical value of the spacing in angstroms seems to be a useful index of structural state, and a notation such as Cr(4.110), Cr(4.085), and Cr(4.050) could be substituted for the qualitative terms disordered, partly ordered, and ordered in describing diagenetic cristobalite. The porcellanite in Fig. 1 is Cr(4.103), the chert, Cr(4.107). Precise characterization of cristobalite would add welcome detail to an important stage in the diagenesis of siliceous shales.

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Nitric Oxide Reduction Coupled with Carbon Monoxide Oxidation in the Presence of Soluble Metal Catalysts

Abstract. *Solutions of* $RhCl_3 \cdot xH_2O$ *in ethanol and* $Ru(NO)_2[P(C_6H_5)_3]_2$ *in benzene catalyze the reduction of nitric oxide to nitrous oxide concomitant with the oxidation of carbon monoxide to carbon dioxide at ambient temperature and atmospheric pressure. The reaction, which is followed by gas chromatography and by the decrease in pressure of the system, proceeds to 47 percent conversion of the reactants after 63 hours.*

Oxides of nitrogen, NO_x, comprise an important environmental problem, and this has led to increased study of the reactions of the parent member of this series, nitric oxide. The decomposition of nitric oxide to the elements has been known and studied for years by using noble metal and metal oxide catalysts at high temperatures (*1*). However, this decomposition also leads to the formation of NO_2 by the rapid reaction $NO + \frac{1}{2}O_2 \rightarrow NO_2$. A more promising approach has been to reduce NO by using CO, H_2, or NH_3 as reductants with the aid of noble metal, copper oxide, or rare earth manganite catalyst systems (*2*). Temperatures for these reactions are generally in excess of 200°C. We now report that the coupled reaction of NO reduction and CO oxidation proceeds readily at ambient temperature and atmospheric pressure in the presence of soluble metal complexes to yield N_2O and CO_2. Moreover, this coupled reaction is catalytic in metal complex.

Catalyst solutions employed in this study include $RhCl_3 \cdot xH_2O$ in ethanol