

0.81, averaging 0.62. Earlier work on the iron meteorites with silicate inclusions has indicated that pyroxene is usually more abundant than olivine. For example, in the cases of the Campo del Cielo and Woodbine meteorites, the calculated modal ratio of olivine to (olivine + pyroxene) is 0.41 in each case, and for the Weekeroo Station meteorite the ratio is zero.

In summary, the chondritic silicate masses in the Netschaev meteorite appear to represent a chemical and mineralogical transition from the characteristics of the equilibrated H-group chondrites toward those of the enstatite chondrites. The Netschaev chondritic silicate masses are characterized by the following composition: (i) the amount of pyroxene is greater than the amount of olivine; (ii) the ratio of MgO to (MgO + FeO) for both pyroxene and olivine is at or above the upper extremum value for the H-group chondrites; (iii) the total content of metal plus sulfide (31 percent by weight) is higher than that of ordinary chondrites (15 to 25 percent) and tends toward the content in enstatite (5) chondrites (average, 50 percent); and (iv) the carbon content is three times higher than that of ordinary chondrites and approaches values observed in the enstatite chondrites. The Netschaev meteorite must represent a lower oxidation state than that of an H-group chondrite and may represent a somewhat higher equilibration temperature. Bunch *et al.* (1) calculated an equilibrium temperature of 870° to 890°C. An approximate equilibrium temperature of 900°C or more is indicated by the method of Olsen and Bunch (8). These temperatures are slightly higher than those estimated by Van Schmus and Koffman (9) for the ordinary chondrites but are close to the value obtained more recently by Williams (10).

The mechanism and meaning of chondrule formation and preservation are still matters of lively discussion, as is the exact relation of iron to chondritic meteorites, or the relation of iron meteorites with silicate inclusions to all other types of meteorites. Within the group of iron meteorites with silicate inclusions the silicate masses have varied bulk compositions and textures (1, 4, 11). Olsen and Jarosewich (4) have suggested an olivine fractionation relationship from a chondritic parent composition that would approximately

account for the unusual chemistry of the silicate inclusions in an iron meteorite like Weekeroo Station. In fact, the addition of about 50 modal percent olivine (85 percent forsterite) to the analysis values for the Weekeroo Station meteorite would yield a bulk analysis closely similar to that of the Netschaev meteorite (Table 2). The presence of chondrules in the silicate inclusions of the Netschaev meteorite may serve to connect the several diverse major groups of meteorites.

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12. We thank Dr. J. Wasson, University of California, Los Angeles, for suggesting that we examine this problem, and G. Moreland, U.S. National Museum, for preparing the polished thin sections. One of us (E.O.) was supported by NASA grant NGR-14-052-001.

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Inorganic Particles in Cigars and Cigar Smoke

Abstract. *A number of crystalline and optically isotropic inorganic materials are used in the manufacture of reconstituted tobacco sheets. These sheets, used primarily in inexpensive cigars, often contain diatomaceous earth, which exists in part in the silica mineral form cristobalite, a known fibrogen. Diatom fragments with this crystalline form have been observed in the main smoke stream of cigars made with these tobacco sheets.*

Many cigars today, generally those which retail at less than 30 cents each, are made up in part of reconstituted tobacco, commonly called tobacco sheets. The use of this material has increased since its introduction in the United States in 1954. It may be manufactured by one of several processes and may contain additives, up to 40 percent, including much inorganic particulate matter (1). Patents for tobacco

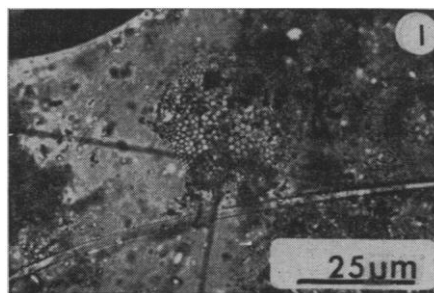


Fig. 1. Diatom body and ceramic fiber from ashed, reconstituted tobacco sheet seen between crossed Nicols with polarized light optics. The birefringent background material is made up in part of natural contaminants, including clays, oxalate crystals, and quartz grains.

sheets used exclusively to make cigars indicate that bentonite, heat-treated montmorillonite, acid-treated clays, glass fibers, and diatomaceous earth may be used in its manufacture (2, 3).

Diatomaceous earth, although predominantly opal (amorphous hydrated silica), is occasionally partially crystalline, commonly in the form of the known fibrogens (4) tridymite and cristobalite (5). Lenses of well-crystallized cristobalite occur commonly in commercially worked deposits of diatomaceous earth (5). Industrially calcined diatomaceous earth, containing much cristobalite, may produce significant disease (diatomaceous earth pneumoconiosis) when inhaled (6). Less is known about the disease potential of fibrous glass materials, which vary chemically, structurally, and morphologically.

Tobacco sheet was introduced into the cigar industry primarily for economic purposes, to decrease tobacco loss by utilization of fines generated during manufacture and to decrease unit cost by introduction of more automation. However, cigar tobacco sheet patents claim that the additives also form strong

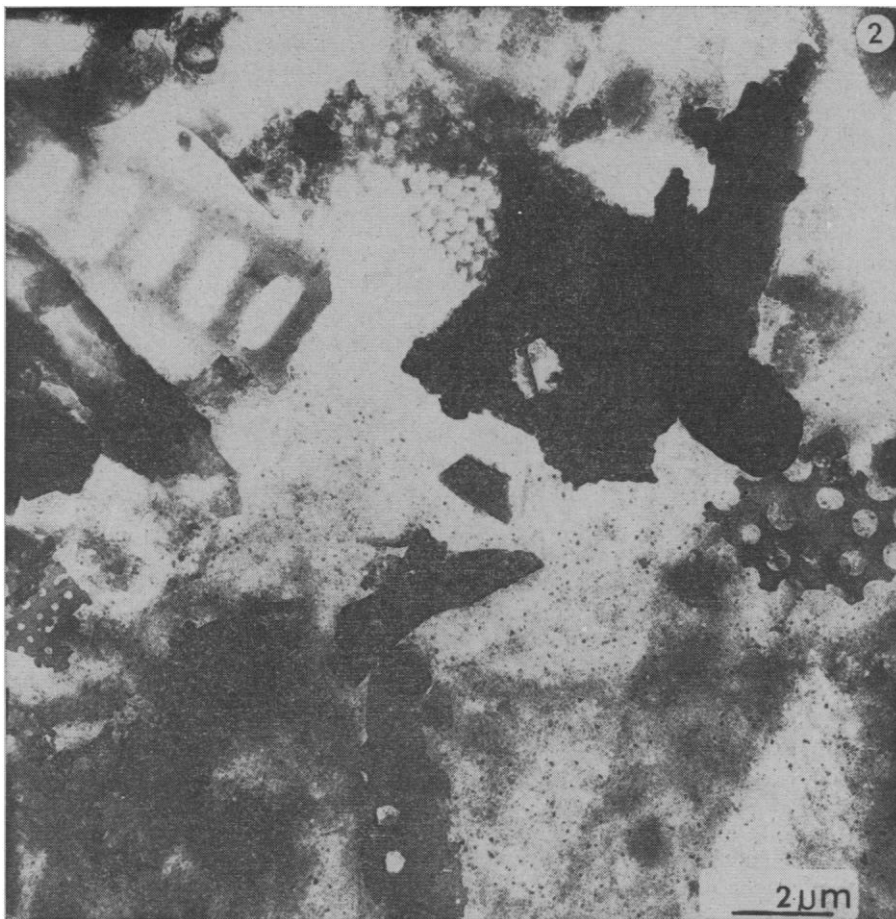


Fig. 2. Electron micrograph of a low-temperature ashed reconstituted tobacco sheet made with diatomaceous earth additives. Diatom fragments predominate. Short fibers are also present, but are rare (center of photograph).

coherent ashes, act as cracking catalysts for polycyclic hydrocarbons, improve combustion characteristics, and increase the porosity of the cigar to increase the aroma components of smoke.

We have investigated 19 "popular" cigars to determine the nature of the inorganic constituents in the unsmoked cigars, in the ash, and, in some samples, in the smoke. We have found fibers of ceramic aluminum silicate and diatom spicules, as well as other diatom fragments, in the reconstituted tobacco sheets of twelve of these cigars. Traces of other silicate minerals were also present, including clay minerals and quartz. We have determined by means of optical and electron microscopy, electron diffraction, electron microprobe analysis, and x-ray diffraction that most whole diatoms and large fragments do not survive the cigar flame temperature intact, but disintegrate into smaller particles and further devitrify into the silica polymorph cristobalite. Fragments of crystalline, respirable-size diatoms have been found in cigar smoke as well.

The 19 cigars chosen for our study

were in three categories: cigars made entirely of natural tobacco leaf, cigars with natural leaf wrappers and reconstituted tobacco binders, and cigars with reconstituted wrappers and binders. The wrapper is the outer covering of the cigar; the binder is the layer directly

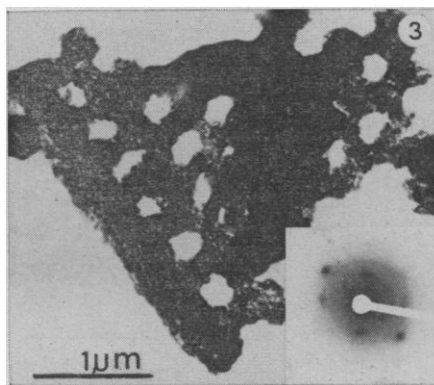


Fig. 3. Electron micrograph of a mottled diatom fragment in the main smoke stream of a cigar made with reconstituted tobacco sheet. The insert shows the polycrystalline pattern obtained by electron diffraction on this fragment. The major structure is high cristobalite, and some reflections suggest the presence of tridymite as well.

within the wrapper that holds together the loose tobacco filler. The filler may also contain tobacco sheet. Gravimetric analysis indicates that wrappers generally constitute 4 to 9 percent of the weight of the cigar and binders 7 to 18 percent. The ashed weight of the wrappers and binders was 1 to 3 percent of the weight of the cigar. This is approximately the weight of the inorganic residue and ranges from 40 to 143 mg in cigars made with tobacco sheet. We have observed proportionally high residues in all-tobacco cigars, the result of the natural silica content of the plant. (Other inorganic components in all-tobacco cigars include calcium oxalate crystals and admixed soil components.)

The wrappers, binders, and fillers were separated by hand and prepared for light microscopy. They were examined as found, ashed at a low temperature in nascent oxygen, and ashed at 800°C in a muffle furnace. Specimens were mounted in immersion oil (refractive index 1.515) on glass slides and examined by phase contrast and polarized light microscopy. Even through the light-dense tobacco sheet, fibrous particles and diatoms could be seen. Low temperature ashing of the tobacco sheet binder produced fields of free particles (Fig. 1) that included whole and fragmented diatoms, diatom spicules, ceramic silicate fibers, and traces of unidentified birefringent inorganic particles. The largest diatoms and fibers showed little or no birefringence when viewed between crossed Nicols, appearing to be isotropic. High-temperature preparations of the same tobacco sheet materials showed no whole diatoms and few extruded silicate fibers on the light microscope scale. A granular mass of particles, with average particle size 5 to 10 μm , and some short ceramic silicate fibers remained. The heating fostered particle disintegration. This has also been observed in tobacco sheets made with fibrous glass (3).

Materials ashed at low temperature were examined by electron microscopy. Diatom fragments predominated. A high-magnification view (Fig. 2) of some of these fragments shows mottling effects suggesting incipient, short-range, crystalline character.

Materials extracted at low temperature from a representative cigar, containing diatomaceous earth and ceramic silicate fiber, were suitably prepared and analyzed with an electron microprobe. Comparison with probe-analyzed standards of ceramic aluminum silicate fibers indicated that the largest fibers

are identical to Fiberfrax (long-staple fines) (Carborundum Co.). Also found were fibers of almost pure silica, likely diatom spicules, irregular silica (diatom) fragments, and irregular fragments high in calcium (calcium oxalate phases from the natural tobacco leaf).

The temperatures at which cigars burn during smoking were measured to determine the degree of opal devitrification and particle size reduction in the cigar flame. A Chromel-Alumel thermocouple was inserted 1.5 cm from the end of the cigar, and the signal obtained during burning was fed into the X-input (temperature) axis of the XY recorder of a differential thermal analyzer system. Volunteers puffed cigars, reproducing "normal" smoking conditions. The cigars burned at high temperatures, $690^{\circ} \pm 30^{\circ}\text{C}$, and two cigars were observed to burn at 800°C . Compared with the published data (1), these values are low, but the nature of the thermocouple design and the recording instrument suggests that they are reasonably accurate. Examination by light and electron microscopy of ash obtained at the same temperatures by muffle furnace heating shows that the ceramic fibers tend to fracture into shorter fibers and that most diatoms fragmentize into fine, mottled particles. Electron diffraction study of the latter fragments indicates that high (beta) cristobalite is the predominant crystalline phase, associated with minor tridymite. Whole diatoms have not been observed to survive the burn intact. We have examined ash residues of tobacco sheets by x-ray diffractometry and have observed a discernible high cristobalite peak at 4.2 Å. It is likely that the cristobalite phase is naturally present but is enhanced by cigar burning.

Cigar smoke was also examined for disintegrated crystalline particles. Several representative cigars were "smoked" through a Casella air sampler and the smoke trapped on Millipore AA membrane filters. We also drew cigar smoke into an electrostatic precipitator and collected particles on an electron microscope grid. The membrane filters were prepared for electron microscopy by dissolving with acetone vapor. Examination of the membrane filters by light microscopy demonstrated the presence of fibrous particles that were optically isotropic and were either diatom spicules or broken ceramic fibers. Electron microscopic examination showed particles of disintegrated diatoms to be present (Fig. 3). They

appeared to be identical with the mottled diatom fragments observed after high-temperature ashing. Electron diffraction patterns obtained from these fragments indicate that they are, in part, high cristobalite (Fig. 3, insert). Although quantitation was not attempted, the number of these particles observed in the smoke appears to be small. The biological effects that might be associated with the inhalation of these particles has not been studied.

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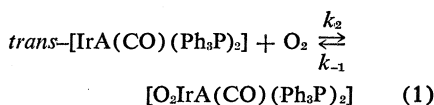
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Oxygen-Carrying Iridium Complexes: Kinetics, Mechanism, and Thermodynamics

Abstract. *The rates of oxygenation and deoxygenation of a series of iridium complexes increase and decrease, respectively, with increasing electron-releasing tendency of the anionic ligands (A) attached to the metal atom in the oxygen-carrying compounds, $[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$. Calculated heats of oxygenation ($-\Delta H_2^0$), related to $\text{Ir}-\text{O}_2$ bond energies, are proportional to the previously reported O-O bond lengths in the oxygen adducts, $[\text{O}_2\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$.*

We report some dynamic data for the reversible uptake of molecular oxygen by a group of isoelectronic and isostructural metal complexes in solution (Eqs. 1–3 and Table 1), and a correlation of these results with the electronic and structural properties of the oxygen-carrying compounds (Figs. 1 and 2). While the rates of oxygenation of a number of transition metal complexes have been widely studied in recent years (1–4), direct measurements of deoxygenation (k_{-1} in Eqs. 1 and 2 and Table 1) of monomeric $\text{M}-\text{O}_2$ species, and the resulting thermodynamic parameters, do not seem to have been reported previously.



A is a univalent anionic ligand (Table 1); Ph_3P is $(\text{C}_6\text{H}_5)_3\text{P}$ (triphenylphosphine)

$$\frac{d[\text{O}_2\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]/dt = k_2[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2][\text{O}_2] - k_{-1}[\text{O}_2\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2] \quad (2)$$

$$K_2 = \frac{k_2}{k_{-1}} = \frac{[\text{O}_2\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]}{[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2][\text{O}_2]} \quad (3)$$

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Our work is based on a simple oxygen-carrying synthetic system [(5), ligand A is Cl in Eq. 1] which has reawakened interest in this class of compounds and led to widespread current research in the field. Significant

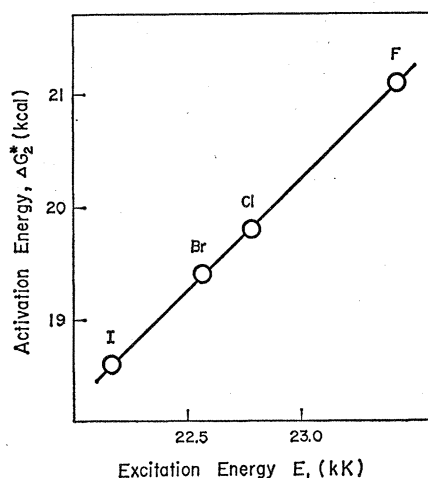


Fig. 1. Free energy of activation ($\Delta G_2^* = \Delta H_2^* - T \Delta S_2^*$) for the oxygenation of $[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$ (Eq. 1; Table 1) as a function of the electronic excitation energy (E_1) corresponding to an absorption band in the visible spectrum of $[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$ (1) in benzene solution; ligands are F, Cl, Br, and I.