

1°K km near the surface) requires quite high central temperatures. The dashed curve in Fig. 1 presents the results of this calculation. A physically realistic model of J IV, in which known phase transitions in the NH<sub>3</sub>-H<sub>2</sub>O system are allowed for, is given as the solid curve in Fig. 1. Here the temperature gradient is calculated on the assumption that the crust has a pure-ice composition and that there is an adiabatic temperature gradient in a liquid H<sub>2</sub>O mantle and a core of hydrous silicates. I do not pretend that the temperature gradient in the mantle and core can be calculated to better than a factor of 2, but the only parameter changed substantially by allowing for these uncertainties is the central temperature, which can range from ~400° to ~800°K. All other important features of the model, including the thickness of the crust and the depth of the mantle, are unchanged.

The boundary condition for both models is an average surface temperature of  $160/\sqrt{2}$ °K. The factor  $1/\sqrt{2}$  arises from the fact that the radiating surface of the satellite,  $4\pi R^2$ , is four times larger than the cross section,  $\pi R^2$ , irradiated by the sun: energy balance requires that

$$c\pi R^2 T_0^4 = 4c\pi R^2 \bar{T}^4$$

or

$$\bar{T} = T_0 (1/\sqrt{2})$$

Here  $c$  is a constant  $\simeq 1$ ,  $T_0$  is the surface temperature in the subsolar region, and  $\bar{T}$  is the mean or effective surface temperature averaged over the entire satellite. The central conclusion from such thermal models must be that these massive satellites have thin icy crusts, constituting only a few percent of the overall mass, overlying an extensive convective mantle of ammoniacal liquid water and a core of hydrous silicates and iron oxides. It is tempting to compare the conditions in the interior of such an icy satellite with the conditions necessary for the production of the mineral assemblages observed in the carbonaceous chondrites. Whereas present-day bodies in the solar system with radii of less than 600 km cannot have central temperatures above the NH<sub>3</sub>-H<sub>2</sub>O eutectic point, it is possible that, in the early days of the solar system, much larger heat sources were available and much smaller bodies could have been extensively melted. In addition to the long-lived radionuclides, which by themselves contributed sev-

eral times the present-day heat flux  $4.5 \times 10^9$  years ago, there are the possible contributions from short-lived radionuclides, accretion energy, and dissipation of energy by tidal interactions. We therefore might look for evidence of differentiation on objects much smaller than the Galilean satellites, including satellites as well as asteroids near the outer edge of the belt. The temperature gradient in the crust of a large icy satellite is roughly 1°K km<sup>-1</sup> at present, but may have been larger, by a factor of 10,  $4.5 \times 10^9$  years ago, even in the absence of short-lived radionuclides and intense dissipation of energy by tidal interactions.

Certainly liquid objects with thin icy crusts would be extraordinarily sensitive to the effects of hypervelocity impacts or intense tidal forces, either of which could easily break the crust. Reiffenstein (8) has suggested, on dynamical grounds, that destruction of liquid satellites just within Roche's limit could give rise to Saturn's ring system. This suggestion has been severely criticized on the grounds that the present-day gray-body equilibrium temperatures of Saturn are far below the melting point of ice (9). However, the melting point of ice has no significance in a multicomponent system. In addition, the effects of internal heat sources are plainly of immense importance in determining the temperature profile and melting behavior within such an object.

The crust of any such satellite that is massive enough to have undergone differentiation ( $R > 500$  km) will be largely made up of ices. Thus its reflectivity at radar wavelengths may be

exceptionally low, and detection of the Galilean satellites by active radar astronomy should be very difficult. A possible exception is Io (J I).

A general discussion of the physics and chemistry of the satellites of the outer planets, with a consideration of atmospheric composition, will appear elsewhere (10).

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19 February 1971

## Runoff of Deicing Salt: Effect on Irondequoit Bay, Rochester, New York

**Abstract.** *Salt used for deicing the streets near Rochester, New York, has increased the chloride concentration in Irondequoit Bay at least fivefold during the past two decades. During the winter of 1969–70 the quantity and salinity of the dense runoff that accumulated on the bottom of the bay was sufficient to prevent complete vertical mixing of the bay during the spring. Comparison with 1939 conditions indicates that the period of summer stratification has been prolonged a month by the density gradient imposed by the salt runoff.*

The use of salt for deicing has increased sharply during the past few decades. Both calcium and sodium chloride are used, but the latter in far greater proportion (1, 2). Prior to 1941,

it was common practice to apply chloride-treated sand to hills, curves, and intersections (3). By the late 1940's the use of pure chloride became common in a few localities. In more recent years,

the use of salt has increased as a consequence of the conversion from abrasives to pure salt and because of the adoption of a "bare pavement policy" for the main roads in many communities.

Nationally the increase in salt used for deicing has been nearly exponential with a doubling time of about 5 years (Fig. 1). In the Irondequoit Bay drainage basin, and in Monroe County which includes this drainage basin, the increase is somewhat greater. It is notable that in the winter of 1969–70, the Irondequoit Bay drainage basin (435 km<sup>2</sup>) with a 1970 population of about 206,000 received 1 percent of the total salt used for deicing in the United States, and Monroe County (1750 km<sup>2</sup>) with a population of 712,000 received about 2.5 percent. The disproportionate use of salt, particularly in the bay drainage basin, may be typical of densely populated suburban areas that experience numerous snowfalls, but statistics are not readily available to show this.

Although historical records of chloride concentration are few, enough data exist (Fig. 2) to show that the chloride concentrations in both Irondequoit Bay and Irondequoit Creek, the bay's principal input (~ 3 m<sup>3</sup>/sec), have risen ten times since 1910. The increase has been particularly rapid since the early 1950's, and this increase correlates reasonably well with the increase in salt used for deicing. The rate of increase seems to have slackened slightly since 1965, perhaps because the bare pavement policy has been fully implemented and subsequent increases resulted largely from the number of additional roads salted.

The chloride curves for the bay and creek cross at about 1959 (Fig. 2). This suggests, among other things, that a significant amount of chloride enters the bay during the winter and is subsequently released in the summer, or that it is partly derived from the smaller creeks that enter the bay directly. Both statements are correct, as will become clear when the data for 1969–70 are examined.

During the winter of 1969–70, Irondequoit Bay (43°17'N, 77°32'W) provided a rather striking example of salt accumulation for the following reasons. (i) It is a relatively small body of water (1.5 by 6 km; area, 6.7 km<sup>2</sup>; volume, 0.046 km<sup>3</sup>; maximum depth, 23 m) that received the runoff from a small basin, a part of which is densely populated. (ii) A bare pavement policy

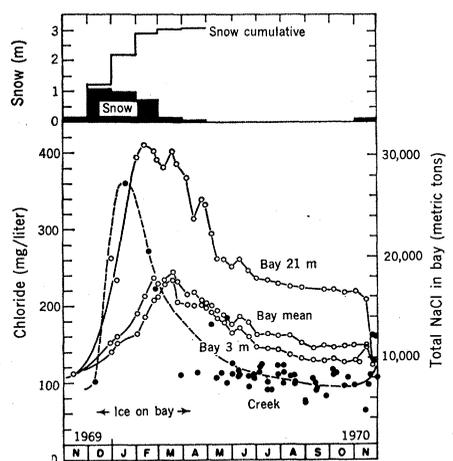
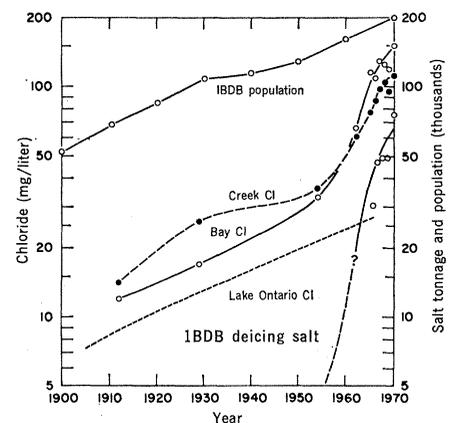
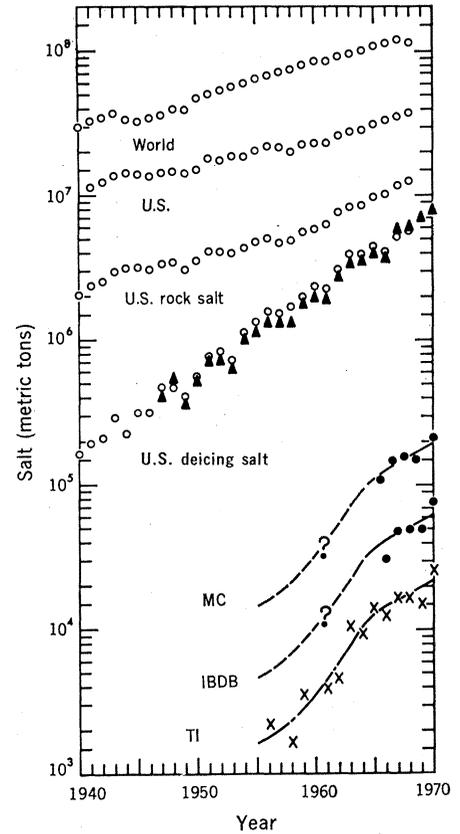
within the drainage basin required the use of large quantities of salt for deicing. (iii) The bay's outflow is restricted to a shallow channel into Lake Ontario. Therefore, there was little exchange of the deeper bay waters with the lake; thus, the bay acted as a sink to the various loads imposed on it.

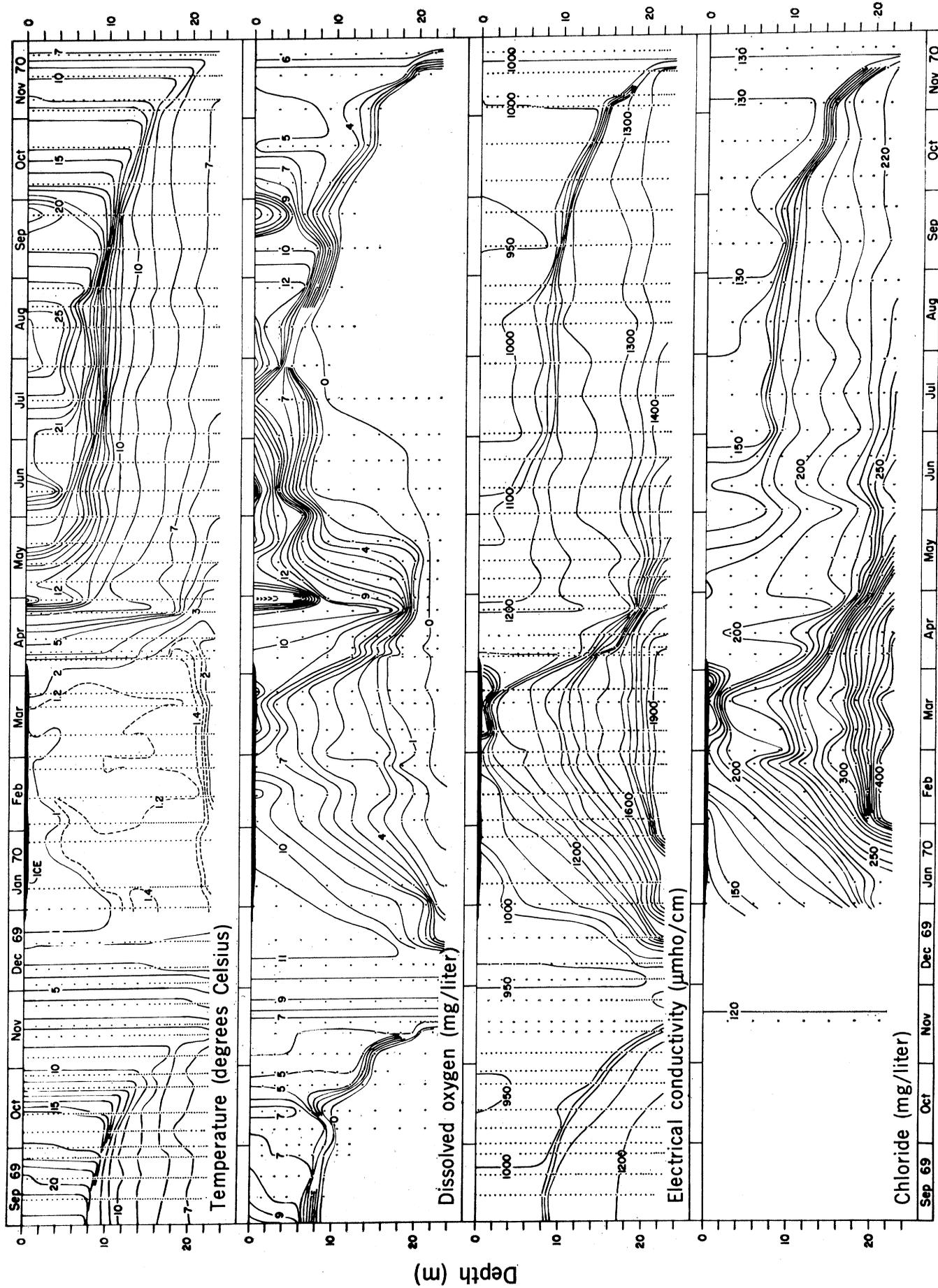
The chloride data for 1969–70 (Fig. 3) clearly indicate that a large amount

Fig. 1 (top right). Salt production and salt usage for deicing. *World*: Total salt production including brine, evaporated, and rock salt; *U.S.*: total national production as above; *U.S. rock salt*: national production of rock salt; *U.S. deicing salt*: national use of salt for deicing; *MC*: deicing salt used in Monroe County; *IBDB*: deicing salt used in Irondequoit Bay drainage basin; *TI*: deicing salt used in the town of Irondequoit (included because it has the only accessible local data prior to 1965 and forms the basis for extrapolating the other local curves to earlier times). Open circles represent data from the U.S. Bureau of Mines (10); triangles, the Salt Institute; solid dots, the International Salt Company; and crosses, the town of Irondequoit. The records for the localities comprising the county and the drainage basin are not complete, but the data shown are probably low by no more than 5 percent.

Fig. 2 (middle right). Chloride concentration in the surface waters of Irondequoit Bay during the summer, near the mouth of Irondequoit Creek during the summer (11), and in Lake Ontario (12). The deicing salt tonnage curve is from Fig. 1 and involves the assumptions stated therein. Population is from the U.S. Bureau of the Census. Where a town straddles the basin boundary, salt and population were apportioned on an area basis. *IBDB*, Irondequoit Bay drainage basin.

Fig. 3 (bottom right). Chloride concentration in Irondequoit Bay and Irondequoit Creek during 1969–70. Concentration is given at depths of 3 and 21 m in the bay. Concentrations at other depths are shown in Fig. 4. The mean concentration was obtained by dividing total chloride in the bay by the volume of the bay; the equivalent in terms of NaCl is expressed by the scale on the right. The dashed curve through the creek data suggests the general trend but has no statistical significance. Fluctuations about this curve, especially during winter, are large and rapid depending on whether freeze or thaw conditions prevail. Bay data were obtained at the position where the bay is deepest. Creek data were obtained at two localities close to the mouth of the creek. Creek data prior to April are from the Federal Water Quality Administration (13). Snowfall was recorded by the National Weather Service at the Monroe County Airport.





of salt entered the bay, particularly during the winter. The data also show that there was little net accumulation of salt in the bay from November 1969 to November 1970 (that is, the bay got rid of the salt that it received). The average chloride concentration of the near-surface water during the year was about 160 mg/liter, and the flow rate out of the bay was about  $4 \pm 1$  m<sup>3</sup>/sec. Therefore, the amount of salt removed from the bay was about 32,000 metric tons. It thus appears that a little more than one-half of the 77,000 metric tons of salt used for deicing in the drainage basin during the 1969–70 winter remained stored in the soil and groundwater of the basin.

A part of this stored salt will be contributed to the streams during subsequent years. If allowance is made for the amount of salt from other sources (4), the estimate of deicing salt stored in the basin would be somewhat larger. On the other hand, if allowance is made for freshwater inputs such as periodic injections from Lake Ontario (5), the estimate of stored salt would be less.

The data in Fig. 3 also suggest that about two-thirds of the salt entered the bay from December 1969 through March 1970. (During this period, 10,000 metric tons was stored in the bay while 11,000 metric tons went out the outlet, if a mean surface concentration of 170 mg/liter of chloride and a flow rate of 4 m<sup>3</sup>/sec are assumed for the 4-month interval.) Despite uncertainties with the salt balance equations, it is clear that a large amount of additional salt enters the bay during the winter and that the only reasonable source for this salt is that salt spread on the streets.

How does the salt get into the bay? The chloride concentration in Irondequoit Creek, the principal input ( $\sim 3$  m<sup>3</sup>/sec) to the bay, reached and probably exceeded 360 mg/liter (Fig. 3)

Fig. 4. Temperature, dissolved oxygen, electrical conductivity at 25°C, and chloride isopleths for 1969–70 at the position where Irondequoit Bay is deepest. Temperature ( $\pm 0.002^\circ\text{C}$ ) and conductivity ( $\pm 3$  percent) were measured in situ. Dissolved oxygen ( $\pm 0.1$  mg/liter) and chloride ( $\pm 2$  mg/liter) were made on samples by the azide modification of the Winkler technique (9) and by the mercuric nitrate method (9), respectively. Data are plotted relative to water surface. Variation of water level during the period of observation was 0.7 m.

during the winter. A single winter sampling (18 February 1970) of ten small streams and storm sewers discharging directly into the bay ranged between 700 and 4000 mg/liter of chloride. If a mean flow rate from all sources of about 4 m<sup>3</sup>/sec is assumed, it is evident that the average chloride content of the waters entering the bay from December through March would have to be about 320 mg/liter in order to account for the 21,000 metric tons of salt that entered the bay during these months.

The winter influx of salt imposes a significant vertical density gradient upon the bay. During the spring of 1970, this gradient was sufficient to prevent the bay from completely mixing. This contention is supported by the fact that temperature, electrical conductivity, chloride, and dissolved oxygen isopleths remained continuous at depths greater than 18 m during the spring mixing (Fig. 4). Moreover, the bottom waters remained anaerobic. During 1939–40, the only previous period for which year-round data were acquired (6), the bay behaved like an ordinary deep lake in a temperate continental climate. It developed a strong summer and winter stratification and mixed completely to the bottom in both the fall and spring (6). The lack of spring mixing is far from unique, as many very small deep lakes do not mix completely in the spring (7, 8). However, the condition is rare for a lake as large and as shallow as Irondequoit Bay.

Another contrast is evident between the 1939–40 and 1969–70 data. In the fall of 1939, the bay mixed completely at a temperature of 12°C in early October, whereas in the fall of both 1969 and 1970, the bay mixed completely at about 8.5°C in early and mid-November, respectively. Thus, the period of summer stagnation appears to have been prolonged about a month as the result of the density stratification imposed by salt runoff. Of course, the 3.5°C difference in mixing temperatures does not necessarily correspond to a prolongation of a month. The time at which the mixing temperature is reached depends on the details of the autumnal cooling, which may vary from year to year.

The aforementioned changes are not viewed with alarm. The point is that the salt runoff has significantly changed the physical characteristics of the bay

and that similar conditions might be expected elsewhere, particularly in heavily salted areas that provide natural traps. Very small and relatively deep lakes are particularly susceptible to such conditions. Indeed, one tiny lake in Michigan has been prevented from completely mixing in the spring by salt runoff (8). More should be known about such lakes as it is likely that salt runoff will produce more of them.

The chloride levels are not presently critical. Although they exceed the U.S. Public Health Service recommended limit for human consumption of 250 mg/liter of chloride (1, 9) during parts of the year and are unsuitable for certain industrial processes (1), waters of much higher chloride content are utilized without processing in various regions (1). However, the fact that the chloride levels are rising rapidly suggests that they should be monitored carefully and that serious attention should be given to the fraction of deicing salt that is being stored in the groundwater. The need for more detailed statistics as to the local distribution of deicing salt is also evident.

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5. Both Irondequoit Bay and Lake Ontario exhibit surface seiches with unimodal periods of about 20 minutes and 5 hours, respectively. The interplay among these seiches, and longer-period atmospherically generated oscillations, results in frequent but small injections of relatively fresh lake water into the bay. Preliminary analysis of limited current and chloride data at the mouth of the bay suggests that the influx from Lake Ontario is probably small, but the problem requires further evaluation.

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15 March 1971

## Sintered Diamond Compacts with a Cobalt Binder

**Abstract.** *Diamond powder can be successfully cemented with cobalt. At 62 kilobars the sintering occurs over the temperature range from 1570° to 1610°C. The maximum microhardness of the compact (>3000 kilograms per square millimeter on the Knoop scale) is obtained with a mixture of 20 percent cobalt (by volume) and a diamond particle size of 1 to 5 micrometers.*

Recently Stromberg and Stephens (1) and Hall (2) have reported the synthesis of a polycrystalline diamond compact, carbonado, at high pressures and temperatures. We have discovered a method for sintering diamond powder (also at high pressures and temperatures) in which cobalt is used as a binder, analogous to its role in cemented tungsten carbide. In comparison with synthetic carbonado (1, 2), it appears that this new material is easier to make and can be made in larger, more nearly uniform specimens. It is harder than cemented tungsten carbide and thus may be a useful replacement in many scientific and industrial applications. We describe here the sintering conditions used and some of the properties of the cemented compacts obtained.

The starting materials were commercially available diamond powder of either 0- to 2- $\mu\text{m}$ , 1- to 5- $\mu\text{m}$ , or 10- to 20- $\mu\text{m}$  size and cobalt powder of 0- to 5- $\mu\text{m}$  size and 99.9+ percent purity. The powders were dried, weighed, and mixed and then packed into tantalum containers for sintering. Pressure was generated in a piston-cylinder appara-

tus with appropriate modifications to allow us to work in the 60- to 65-kb range (3). The samples were heated by means of an internal graphite heater, and the temperature was monitored with a Pt-Pt (10 percent Rh) thermo-

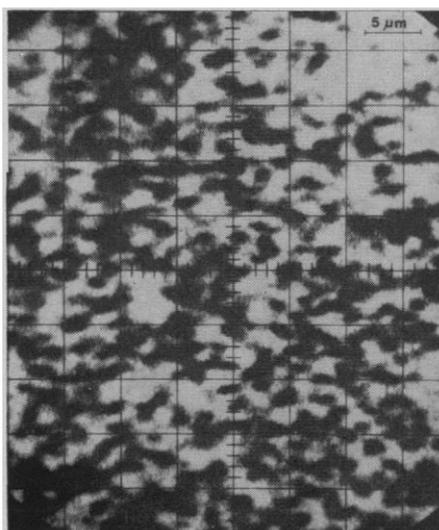


Fig. 1. Electron microprobe photograph of a sample containing 20 percent cobalt (by volume) and 1- to 5- $\mu\text{m}$  diamond grains. The darker areas are cobalt, and the lighter ones are diamond.

couple. The electromotive force of the thermocouple was corrected for the effect of pressure (4), and the correction corresponded to an addition of 15°C to the temperature values obtained directly from the standard tables.

We chose 62 kb as a convenient pressure at which to work and then determined experimentally the temperature range in which the sintering occurred. Samples had to be heated above the cobalt-diamond eutectic temperature, but not so high as to graphitize the diamonds. At  $62 \pm 1$  kb the samples showed partial graphitization when heated above  $1610^\circ \pm 10^\circ\text{C}$ . This temperature is well below  $1700^\circ\text{C}$ , which is the diamond-graphite equilibrium temperature at 62 kb reported by Bundy *et al.* (5) and calculated by Berman (6). Recently Haygarth (7) has used a piston-cylinder apparatus similar to ours to determine a diamond-graphite equilibrium point at  $51.8 \pm 0.2$  kb and  $1335^\circ\text{C}$ . Using this point and Berman's slope (6) of  $30.4^\circ\text{C}/\text{kb}$ , one can calculate an equilibrium temperature of  $1645^\circ\text{C}$  at 62 kb, which is much closer to the value that we find. Both Stromberg and Stephens (1) and Hall (2) report work on the sintering of diamonds at higher temperatures and at pressures close to those used in our study, but, since no cobalt was present in either case to dissolve and reprecipitate the metastable diamonds as stable graphite, higher temperatures could be used. Below  $1570^\circ \pm 10^\circ\text{C}$ , which is apparently the cobalt-diamond eutectic temperature at 62 kb, no strong compacts were formed.

Therefore,  $1590^\circ\text{C}$  and 62 kb were chosen as the sintering conditions. The samples were maintained at these conditions for about 20 minutes and were then cooled to room temperature in about an hour. As the samples were cooling, the pressure was slowly released in order to minimize the residual strains in the product but care was taken so that the samples were always kept within the diamond stability region.

The sintered samples were grayish, metallic-looking, slightly ferromagnetic cylinders,  $\sim 6.3$  mm in diameter and 2.5 to 9.0 mm long. Their properties were determined by x-ray diffraction, scanning electron microscope, electron microprobe, density, and Knoop microhardness measurements.

The microhardness results are shown in Table 1 for various sintered samples.