5. S. E. Wanke and N. A. Dougharty, *ibid.* **24**, 367 (1972).
6. J. E. Benson, H. S. Hwang, M. Boudart, *ibid.*, in press.
7. W. G. Frankenburg, *J. Amer. Chem. Soc.* **66**, 1827 (1944).
8. R. B. Levy and M. Boudart, in preparation.
9. M. Boudart, M. A. Vannice, J. E. Benson, *Z. Physik. Chem.* **64**, 171 (1969).
10. M. Boudart, A. W. Aldag, L. D. Ptak, J. E. Benson, *J. Catal.* **11**, 35 (1968).
11. M. Boudart and L. D. Ptak, *ibid.* **16**, 90 (1970).

12. Supported by NSF grant GK 174 51X. We thank J. Voorhies for a sample of tungsten carbide used in this work.

30 April 1973

■

Ice Nucleation by Solid Solutions of Silver-Copper Iodide

Abstract. *The lattice misfit between ice and silver iodide can be reduced by partial substitution of copper atoms for silver atoms in the silver iodide lattice. The best crystal match is obtained with a composition of CuI-3AgI, which corresponds to the most active silver-copper iodide nucleation catalyst.*

Vonnegut and Chessin (*1*) showed that a solid solution of 30 mole percent AgBr in AgI causes nucleation in supercooled water at about half the supercooling required for nucleation by pure AgI. According to the nucleation theory of Turnbull and Vonnegut (*2*), this improved nucleation ability can be attributed to the fact that while the AgI crystal lattice is 1.5 percent larger than that of ice, the lattice of a solid solution with 30 mole percent AgBr in AgI is only 1.0 percent larger. Presumably AgI-AgBr solid solutions with even smaller lattice misfits should be even better nucleation catalysts. However, 30 mole percent is apparently the limit of solubility of AgBr in the AgI lattice, so 1.0 percent is the minimum lattice disregistry that can be obtained with AgI-AgBr solid solutions. The disregistry, δ, is defined as $(a - a_0)/a_0$, where a and a_0 are the respective lattice parameters of the catalyst and ice along similar low index planes.

In searching for solid solutions of AgI for which we could control the lattice parameter, our attention turned to CuI-AgI. We have prepared CuI-AgI solid solutions, each having a lattice parameter smaller than that of pure AgI by two techniques. The first was direct fusion at a pressure of 10^{-2} torr and a temperature of 20°C above the melting point of the solid solution, about 600°C. The second involved dissolving the proper proportions of reagent grade CuI and AgI in hydriodic acid and then boiling off the solvent. The crystal class of the resulting solid solutions is face centered cubic, but in the (111) plane the crystal structure is similar to that of ice in the (0001) plane. The lattice spacing in the (111) plane is given by $a\sqrt{2}/2$, where a is the edge of a unit cell in the cubic system. The x-ray data in Fig. 1 show that by varying the mole percent of CuI in AgI, a solid solution can be made to have any lattice spacing from 4.58 to 4.28 Å measured in the (111) plane. This range in lattice spacings corresponds to lattice disregistries with respect to ice ranging from 1.5 percent to − 5.2 percent. Since CuI and AgI are not appreciably soluble in water (10^{-5} and 10^{-8} mole/liter, respectively), they have a negligible effect in depressing the freezing point of the water.

To determine their relative effectiveness as nucleation catalysts, powdered samples of about 0.5 g of CuI-AgI were sealed in dilatometers containing approximately 1 g of distilled water, and the freezing temperature was observed when they were cooled in a vigorously stirred bath. The temperature was measured with a Beckman thermometer with an accuracy of 0.01°C and was lowered at a rate of 0.5°C min^{-1} (*3*). The water was singly distilled and had a conductivity of 3×10^{-6} ohm^{-1} cm^{-1}.

Figure 2 shows the observed threshold nucleation temperature as a function of composition for ten samples of both the fusions and the precipitates. The fusions were tested after having been in water for about 1 month. The precipitates were tested immediately after having been immersed in water. Reduction of the cooling rate from 0.05° to 0.01°C min^{-1} produced no observable differences in threshold nucleation temperatures.

Figure 3 shows the smallest observed supercooling for the CuI-AgI fusions and precipitates, as a function of lattice disregistry with respect to ice. The disregistry is computed for the (111) plane of the CuI-AgI solid solution and the (0001) plane of ice. Vonnegut and Chessin's data for the AgI-AgBr solid solutions are also shown, along with Turnbull and Vonnegut's theoretical curve for coherent nucleation.

The fact that the temperature of − 2.5°C we measured for nucleation in the presence of pure CuI is appreciably higher than the value of − 15°C reported by Mason and Hallett (*4*) probably can be attributed to the very different conditions under which the observations were made. That the CuI-AgI catalysts precipitated from HI were generally more active than the fused CuI-AgI catalysts could be due to particle size, decay of the fused samples, or the effect described by Bigg (*5*) where small concentrations of HI can raise the nucleation temperature. Although the reasons for the difference are not clear, the parallel nature of the data in Fig. 3 suggests that the difference is uniform.

Turnbull and Vonnegut (*2*) advanced

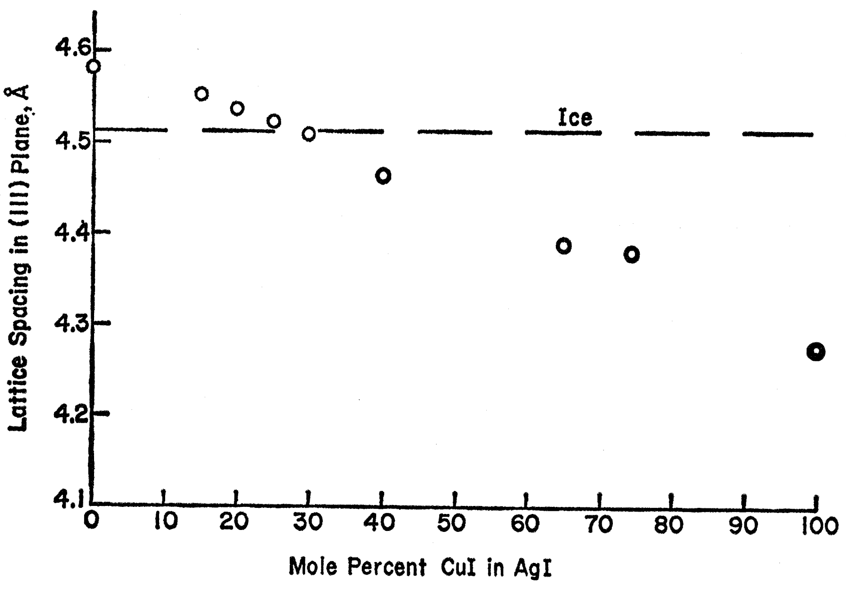

Fig. 1. Lattice parameter as a function of mole percent CuI in AgI.

a simple theory for nucleation catalysis based on the assumption that the interfacial energy between ice and a nucleation catalyst is a minimum when nucleation is coherent. Coherent nucleation occurs when the lattice of the forming crystal matches the lattice of the catalyst and can be likened to crystal growth. If the lattices are slightly mismatched, nucleation may still be coherent, but the resulting elastic distortion will increase the bulk free energy of the forming embryo. Consequently, the supercooling necessary for nucleation increases by an amount proportional to the square of the disregistry.

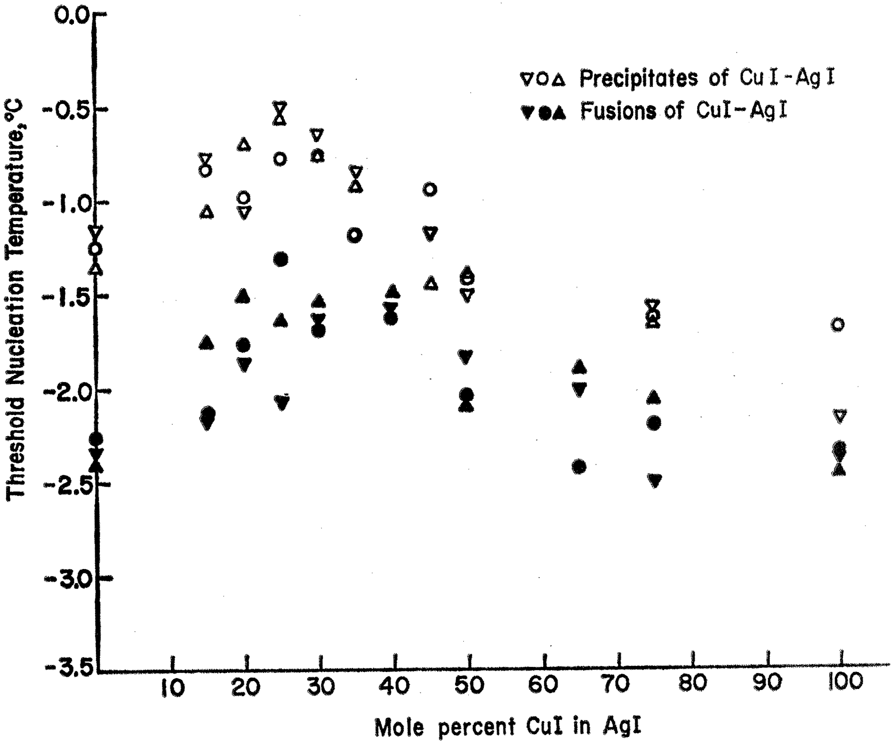

Fig. 2. Threshold nucleation temperature as a function of composition.

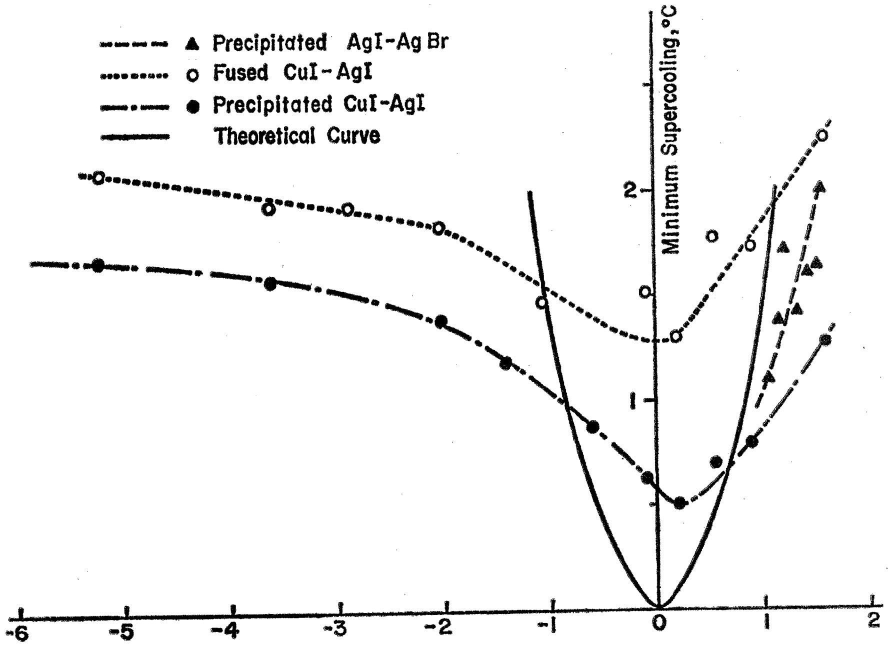

Fig. 3. Smallest observed supercooling as a function of percent lattice disregistry for CuI-AgI data and AgI-AgBr data (*1*), along with Turnbull and Vonnegut's (*2*) theoretical curve.

The symmetry of the data in Fig. 3 suggests that catalysts with a positive disregistry have about the same nucleating ability as those with an equal negative disregistry. This result agrees with Turnbull and Vonnegut's prediction that $\Delta T = k\delta^2$, where ΔT is the supercooling, δ is the disregistry, and k is a constant. However, for our data the supercooling does not approach 0°C as the disregistry tends to zero, but instead reaches a minimum of about 0.5°C. In their derivation Turnbull and Vonnegut neglected other factors, such as particle size and adsorption, which could cause additional supercooling. When other nucleation parameters are taken into account, as suggested by Fletcher (*6*), the equation for coherent nucleation can be written as

$$\Delta T = k\delta^2 + \Delta T_1$$

where ΔT_1 is the supercooling due to the combined effect of any nucleation parameters independent of the disregistry. The parallel nature of the data in Fig. 3 tends to confirm this type of relation.

Coherent nucleation theory predicts that nucleation will become incoherent for large disregistries where the bulk free energy of ice formation is less than the free energy required to distort the ice lattice to fit the catalyst lattice. If nucleation is not coherent, Turnbull and Vonnegut predict a linear relation between the disregistry and the supercooling. The data for the CuI-AgI catalysts in Fig. 3 show a sharp dip in supercooling between lattice disregistries of ± 1.5 percent. This region could correspond to coherent nucleation. The region between − 1.5 and − 5.2 percent disregistry could correspond to incoherent nucleation, as the supercooling is a fairly linear function of the disregistry.

RICHARD E. PASSARELLI, JR.
Department of Atmospheric Science,
State University of New York
at Albany, Albany 12222
HENRY CHESSIN
Department of Physics, State
University of New York at Albany
BERNARD VONNEGUT
Atmospheric Sciences Research Center,
State University of New York at Albany

References and Notes

1. B. Vonnegut and H. Chessin, *Science* **174**, 945 (1971).
2. D. Turnbull and B. Vonnegut, *Ind. Eng. Chem.* **44**, 1292 (1952).
3. R. E. Passarelli, Jr., H. Chessin, B. Vonnegut, *J. Appl. Meteorol.* **12**, 416 (1973).
4. B. J. Mason and J. Hallett, *Nature* **179**, 357 (1957).
5. E. K. Bigg, thesis, University of London (1953).
6. N. H. Fletcher, *The Physics of Rainclouds*

(Cambridge Univ. Press, Cambridge, England, 1962), p. 210.

7. We thank E. Barreto, D. C. Blanchard, N. R. Gokhale, and C. W. McCutchen for their helpful comments and suggestions, and E. Nagle for making the dilatometers. Supported in part by Office of Naval Research contract N00014-71-C-0156; in part by Air Force Cambridge Research Laboratories, Office of Aerospace Research, contract F19628-68-C-0057; and in part by National Science Foundation grant GI-34732.

9 February 1973; revised 16 April 1973 ■

Lead Pollution: Records in Southern California Coastal Sediments

Abstract. *The present anthropogenic lead fluxes into sediments from the Santa Monica, San Pedro, and Santa Barbara basins of Southern California are, respectively, 0.9, 1.7, and 2.1 micrograms of lead per square centimeter of sea bottom per year; the natural (prepollution) rates for these three basins were, respectively, 0.24, 0.26, and 1.0 microgram of lead per square centimeter per year. Studies of isotopic composition indicate that lead pollutants in coastal sediments are derived mainly from the combustion of lead additives in gasoline.*

The sedimentary deposits of coastal areas may well constitute historical records of the atmospheric burden of particulates, such as the lead-containing species produced from the combustion of lead alkyls in gasoline. The basins off the coast of Southern California are especially promising for such studies. Their sediments accumulate at rates of millimeters per year, annual layers are occasionally available for analysis, and there is a very rapid removal of lead to them from the overlying waters (*1*). These basins (Fig. 1), situated near an area of substantial leaded gasoline combustion (*2*), are the basis for several recent models of the sources and dispersion of pollutants introduced to the atmosphere (*2, 3*). The investigation presented here is aimed at the development of the sedimentary records of lead accumulation over the past century, similar to those held in the Greenland snow strata (*4*). Since sedimentation rates vary from place to place along the California coast, the absolute concentrations of man-generated materials in the deposits are often less useful than their fluxes. The time parameter is readily introduced into these sediments (*1*), and thus the rates of deposition of lead can be sought as well as the absolute concentrations.

Sediments from three inner basins near the Los Angeles area were obtained with box-coring equipment which retained the uppermost strata. These three shallowest basins of the group (core water depth at San Pedro, 890 m; at Santa Monica, 930 m; and at Santa Barbara, 575 m) were selected because their sediments are anoxic and thus relatively free from biological disturbances. In the case of the Santa Barbara Basin annual varves can be recognized. A similarly anoxic deposit in the Soledad Basin (520 m) off the coast of Baja California (25°13.8′N, 112°40.6′W) was used as a control. This more southerly sample, remote from the prevailing wind patterns off Southern California and free from its waste discharges, is intended to provide a base-line set of samples. A fifth core was taken off the Los Angeles County waste outfall (75 m) at Whites Point to provide sediments containing domestic and industrial wastes. These Whites Point deposits are accumulating so rapidly that only a recent age can be assigned to them on the basis of both ^{210}Pb and ^{228}Th/^{232}Th chronologies.

The lead isotopic compositions and concentrations were determined by mass spectrometry on all samples except those from the Santa Monica Basin. The lead concentrations were also determined by atomic absorption. In different subsections of the cores at equivalent depths where both mass spectrometry and atomic absorption determinations were carried out, the results usually were in agreement to within 10 percent. The atomic absorption lead values (Fig. 2) are given for the Santa Monica and Santa Barbara samples; the other lead data are isotopic dilution results. The aluminum values were obtained by atomic absorption. The aluminum was used as a normalization factor that reasonably represents a measure of the detrital minerals that are assumed to have had a uniform input over the past century. The ages of the sedimentary levels were determined by ^{210}Pb and ^{228}Th/^{232}Th geochronologies. In Fig. 2, the lead values are given both as concentrations on 110°C dry-weight basis and as the lead/aluminum ratios. In general, both the lead values and lead/aluminum ratios give similar curves as a function of depth in the sediments. The exceptions involve the surface sediments which contain high water and high salt contents because these sediments are subject to less compaction than the deeper deposits. As a result, the absolute concentrations of lead in surface sediments are diminished.

The isotopic compositions of the leads in these sediments are indicative of their sources (*5*). The surface deposits of the Soledad Basin contain lead with isotopic ratios similar to those of the weathering products from the Baja California province (*6*). The Whites Point deposits contain lead with isotopic ratios comparable to those found in gasoline sold in Southern California (*7*). The isotopic compositions of lead in the surface sediments of the inner California basins (*5*) are distinctly less radiogenic than those in the deep sections of the cores which

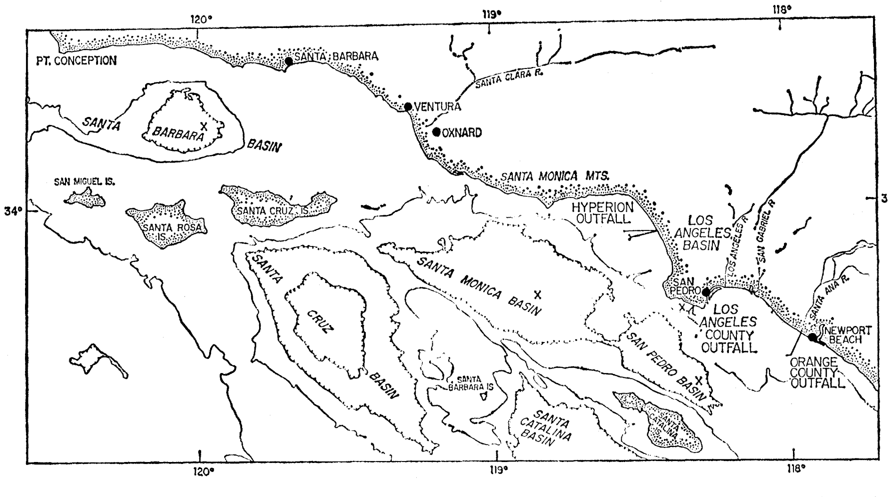

Fig. 1. The inner basin region off the coast of Southern California; X, coring site.