Pliocene-Pleistocene boundary" in the midcontinental United States is at least on the order of 2.2 × 10^6 years old.

The final chronologic placement of the Pliocene-Pleistocene boundary in its stratotype area (in Calabria, Italy) will dictate whether the first late Cenozoic glaciation in North America is to be considered Pliocene, Pleistocene, or spanning the Pliocene-Pleistocene boundary.

The working group of the International Geological Correlation Program (IGCP) Project N 41, "The Boundary Between the Neogene and Quaternary," and the Subcommission on the Plio-Pleistocene Boundary of the International Union on the Study of the Quaternary (INQUA) are considering a section near Vrica, about 4 km south of Crotone, Italy, as a potential stratotype for the Pliocene-Pleistocene boundary (*18*). Furthermore, these groups stated (*19*): "This boundary can be defined by the appearance of cold-water North Atlantic immigrants in the Plio-Pleistocene sequence of Calabria."

A layer of volcanic ash occurs near the middle of a sequence 60 m thick between definite Pliocene and definite Pleistocene sediments in the Vrica section and about 30 m above the recommended Pliocene-Pleistocene boundary as defined by the first appearance of cold-water forms. The presence of this ash makes the Vrica section extremely attractive as a stratotype for the Pliocene-Pleistocene boundary because the age of the ash provides a tool for recognizing the boundary in both marine and continental sequences elsewhere.

The Vrica ash has yielded dates of 2.5 ± 0.1 × 10^6 years [Ft-glass (*20*)], 2.1 ± 0.3 × 10^6 years [Ft-glass (*18*)], and 2.2 ± 0.2 × 10^6 years [K/Ar glass (*18*)]. The date of 2.5 ± 0.1 × 10^6 years is the age ash used herein for the Vrica ash and for the Pliocene-Pleistocene boundary (Fig. 2, column 1) because the sample yielding this date, as well as ash samples from the midcontinental United States on which Figs. 1 and 2 are based, were dated along with the Borchers ash, which is used as an intralaboratory standard (*13*). Thus, the age relationships of the Vrica and midcontinental United States ashes, as well as interpretations based on these ages, are more likely to be sound than those based on radiometric dates which are not tied together by an intralaboratory standard.

If the date of 2.5 ± 0.1 × 10^6 years is valid for the Pliocene-Pleistocene boundary, at least half of the time span of the North American Pleistocene is pre-Nebraskan in age and the oldest known late Cenzoic continental glaciation of North America probably spans the Pliocene-Pleistocene boundary. However, glacial deposits in eastern Nebraska and southwestern Iowa probably represent the maximum of this glaciation and may be Pleistocene.

As shown in Figs. 1 and 2, all of the currently used North American Pleistocene stage terms, except perhaps for the Wisconsinan, are in need of redefinition or revision. Such redefinition or revision is beyond the scope of this report. However, some alternatives are the following: (i) the establishment of chronozones based on radiometric dates, paleomagnetics, and paleontology for their recognition; (ii) the formulation of a revised stage terminology based on the chronology of major climatic changes and utilizing both the midcontinental United States and Gulf of Mexico records; and (iii) a system incorporating both chronozones and stages (*21*).

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References and Notes

1. G. F. Kay and E. T. Apfel, *Iowa Geol. Surv. 34th Annu. Rep.* (1929), p. 145.
2. E. C. Reed and V. H. Dreeszen, *Nebr. Geol. Surv. Bull.* **23**, 65 (1965).
3. J. H. Beard, *Trans. Gulf Coast Assoc. Geol. Soc.* **19**, 535 (1969).
4. D. B. Ericson and G. Wollin, *Science* **162**, 1227 (1968).
5. J. D. Boellstorff, final technical report on grant DES 74-23535, submitted to the Earth Science Section, National Science Foundation, Washington, D.C., 1977.
6. ——, *Kans. State Geol. Surv. Guidebook Ser. 1* (1976), p. 31.
7. ——, thesis, Louisiana State University (1973).
8. ——, *Isochron/West No. 8* (1973), p. 39.
9. ——, *Nebr. Acad. Sci. Trans.*, in press.
10. The legal description of Nebraska Geological Survey core hole 5-A-75 is NE$^1/_4$NW$^1/_4$NW$^1/_4$ section 33, T. 72 N., R. 29 W., Union County, Iowa.
11. J. D. Boellstorff and M. T. Te Punga, *N.Z. J. Geol. Geophys.* **20** (No. 1), 47 (1977).
12. J. D Boellstorff and P. L. Steineck, *Earth Planet. Sci. Lett.* **27**, 143 (1975).
13. All ashes were dated by J.B. along with samples of Borchers ash from Meade County, Kansas. The Borchers ash is used as an intralaboratory standard because it has been dated repeatedly by several investigators and by different methods, yielding an average date of 1.96 ± 0.22 × 10^6 years (*6*).
14. The legal description of the exposure at location 2 (Fig. 3) is SW$^1/_4$NW$^1/_4$ section 28, T. 72 N., R. 29 W., Union County, Iowa. The legal description of the exposure at location 3 (Fig. 3) is Cen. W$^1/_2$ section 27, T. 72 N., R. 29 W., Union County, Iowa.
15. G. F. Kay, *Geol. Soc. Am. Bull.* **35**, 71 (1924).
16. B. Shimek, *ibid.* **20**, 399 (1909).
17. J. D. Boellstorff, *Int. Union Quat. Res. 9th Congr. Abstr.* (1973), p. 31.
18. R. Selli *et al.*, in press.
19. Resolution of the joint meeting of the INQUA Subcommission on the Plio-Pleistocene Boundary and the IGCP working group on "The Boundary Between the Neogene and Quaternary," Birmingham, England, 1977. (Copies are available from J.B.)
20. J. D. Boellstorff, *Int. Union Quat. Res. 10th Congr. Abstr.* (1977), p. 27.
21. ——, in preparation; *Bull. Am. Assoc. Pet. Geol.*, in press.
22. I thank S. Anderson, G. Debus, H. DeGraw, J. Goeke, J. Spellman, and A. Zarins for their assistance in obtaining samples and in the analyses of tills and volcanic ashes. I thank D. Easterbrook for providing paleomagnetic information. This research was supported by the Conservation and Survey Division, University of Nebraska–Lincoln, and by the Earth Science Section, National Science Foundation (grant 74-23535).

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Condensation of Nonequilibrium Phases of Refractory Silicates from the Vapor

Abstract. *Silicon monoxide solid was evaporated in a bell jar containing reducing, neutral, or oxidizing atmospheres at pressures of a few torr. The vapor invariably condensed as smoke-sized particles of silicon sesquioxide,* Si_2O_3. *The condensation of a solid whose composition differs from that of the parent gas and is apparently the least stable of the three solid species illustrates the importance of specific nucleation effects in the condensation process. This result has significant implications for theories of formation of grains in space.*

Fine grains occur in the interstellar medium, circumstellar dust shells, expanding nova shells, the primordial solar nebula, and comets (*1*). The grains have dimensions in the range from below 100 Å to a few micrometers. The origin of these particles has not yet been satisfactorily explained, although there appears to be a consensus that they condensed in a dense cloud (number of hydrogen atoms > 10^5 per cubic centimeter).

Some of the problems of particle formation arising from the characteristics of astronomical clouds as opposed to laboratory systems have been considered by Czyzak and Santiago (*2*) and Donn (*3*). Extensive laboratory experiments on the condensation of fine grains of many metals as well as some oxides, carbon, and silicon carbide have been carried out (*4*). Reference to recent Japanese work in this field may be found in Kamijo *et al.* (*5*). There are several significant differences between condensation processes in the laboratory and in space (*3*). The most important one for the present purpose is that particles observed in space are generally believed to be compounds of refractory oxides and silicates which do not exist in the gas phase.

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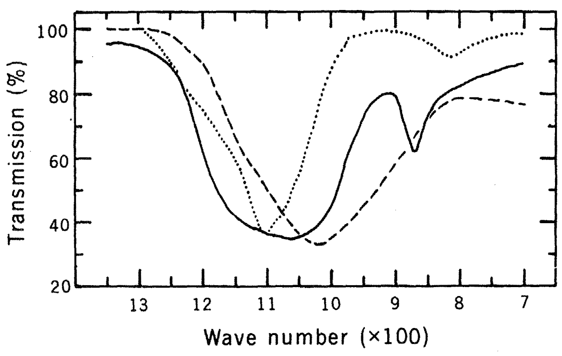

Fig. 1. Infrared spectra of three silicon oxides: (——) Si_2O_3 smoke; (- - -) SiO film condensed on a KBr pellet; (· · · ·) amorphous quartz particles (SiO_2) (diameter, 200 Å) on a KBr substrate.

We have studied the formation of silicate smokes as the initial step in an experimental investigation of condensation in astronomical systems. A description of the apparatus and results for magnesium silicates have been reported (*6*). We describe here the condensation of silicon monoxide (SiO) vapor.

Chunks of SiO (vacuum evaporation grade) a few millimeters in diameter were evaporated from a molybdenum basket at about 1500°C with an atmosphere of argon at a pressure of a few torr. A charge of about 0.5 g was evaporated in about 8 minutes. Smoke particles nucleated in the space near the crucible, drifted upward on convection currents, and deposited on a collecting plate. The particles of the condensate were examined by x-ray and electron diffraction and were dispersed in KBr for infrared analyses in the spectral region from 2.5 to 40 μm.

For the later experiments in the series we were able to control the condensation temperature by locating the SiO source about at the center of an auxiliary oven. The oven was a resistively heated alumina tube 10 cm in diameter and 20 cm high. Gas temperatures within the furnace were measured with a thermocouple, and these temperatures were adopted as the nominal condensation temperatures. The quantity of smoke produced with SiO and magnesium vapor, or with SiO vapor alone, had a high temperature dependence in the range between 20° and 500°C. Copious quantities of smoke were produced at room temperature, whereas at 500°C no smoke was collected for the same rate of vaporization. This result indicates that the condensation temperature was near the nominal temperature and only slightly perturbed by the SiO source.

Examination of the smoke by x-ray and electron diffraction showed only broad halos, indicating an amorphous structure, which was of no help in chemical identification. However, when the smoke was dispersed in KBr and examined in the infrared, the results were quite surprising. In every case the spectrum observed was that of silicon sesquioxide (Si_2O_3). Figure 1 shows the spectrum of the experimental smoke compared with infrared spectra of small particles of SiO_2 and an SiO film. The 880-cm^{-1} signature of Si_2O_3 is most distinctive, but the principal peaks between 1200 and 1000 cm^{-1} are also easily distinguished. Our Si_2O_3 spectrum is in good agreement with others found in the literature (*7, 8*). Condensation at nominal room temperature and 300°C produced similar particles.

It seemed possible that some oxidation of the SiO vapor by residual oxygen in the chamber could be taking place. To reduce this possibility, the chamber was backfilled with 99.99 percent argon, reevacuated to 10^{-5} torr, and then filled with argon to a pressure of 2 torr once more. Once again, only Si_2O_3 particles were observed. Next, we carried out the experiment in a purified hydrogen (highly reducing) atmosphere. As before, Si_2O_3 was the predominant product; the infrared spectrum looked no different from those produced when the ambient atmosphere was argon. The same result was obtained in H_2O. Thus, the choice of a neutral, reducing, or oxidizing environment had no effect, and reactions between the vapor of the source material and the ambient atmosphere did not influence the condensates. We carried out a final check for system anomalies by evaporating SiO under vacuum conditions (~ 10^{-5} torr). The thin film deposited on the collecting plate was scraped off and dispersed in KBr for infrared analysis; it proved to be SiO, as expected.

Under our experimental conditions, the predominant condensate from a vapor of SiO was invariably Si_2O_3. The question of why this happens is most intriguing and not altogether answerable from our data. As far as we know, Si_2O_3 has never been recorded in the vapor state, although Si_2O_2, SiO_2, and Si_3O_3 all have (*9*). However, it has been shown (*10*) that the higher oxides make up only 10^{-3} to 10^{-4} of the vapor over heated SiO; the rest is monomeric SiO. Therefore, the production of smoke grains through repetitive reactions of the form

$$SiO + SiO_2 \rightarrow Si_2O_3$$

seems quite unlikely. Furthermore, one would expect the percentage of the vapor in the form SiO_2 to be even smaller when the experiment was carried out in a hydrogen atmosphere.

The properties of Si_2O_3 appear to be the result of a defect SiO_2 structure (*8*) consisting of SiO_4 tetrahedra with excess silica distributed within the amorphous lattice. The structure of SiO is generally similar with a higher silica concentration and a smaller Si–Si bond distance.

When we simultaneously evaporated magnesium and SiO, we obtained an amorphous, nonstoichiometric smoke. Pure SiO also yielded an amorphous smoke, of Si_2O_3 grains. Neither material condensed to the thermodynamically most stable form. In each case a metastable grain condensed. This result appears to be an illustration of Ostwald's law of stages (*11*), according to which the most stable phase of a compound is not generally the one to nucleate.

These results on the nature of the condensate forming from the gas phase have major implications for situations where such phenomena occur (*12*).

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References and Notes

1. G. W. Field and A. G. W. Cameron, *The Dusty Universe* (Neale Watson, New York, 1974).
2. S. Czyzak and J. Santiago, *Astrophys. Space Sci.* **23**, 443 (1973).
3. B. Donn, *Mem. Soc. R. Sci. Liege Ser. 6* **9**, 44 (1976).
4. J. Turkevich, in *Fundamental Phenomena in the Materials Sciences*, L. J. Bonis, P. L. de Brune, J. J. Duga, Eds. (Plenum, New York, 1966), vol. 3, p. 195; M. Gen and Y. Petrov, *Russ. Chem. Rev.* **38**, 12 (1969).
5. F. Kamijo *et al.*, *Icarus* **26**, 102 (1975).
6. K. L. Day and B. D. Donn, *Astrophys. J. Lett.* **222**, L45 (1978).
7. Y. Nishimura, K. Inagaki, K. Sasaki, *Fujitsu Sci. Tech. J.* **2**, 87 (1966).
8. E. Ritter, *Vak. Tech.* **21**, 42 (1972).
9. J. S. Anderson and J. S. Ogden, *J. Chem. Phys.* **51**, 4189 (1969).
10. R. F. Porter, W. A. Chupka, M. G. Inghram, *ibid.* **23**, 216 (1955).
11. W. J. Dunning, in *Nucleation Phenomena*, A. C. Zettlemoyer, Ed. (Dekker, New York, 1969); W. Ostwald, *Lehrb. Allg. Chem.* **2**, 2 (1896).
12. We are investigating this process to determine how it applies to grain formation in a variety of astronomical clouds.
13. One of us (K.L.D.) acknowledges the support of the NASA Goddard Space Flight Center, where the work was performed while he was on leave from the University of Arizona. This work was also partially supported by the National Science Foundation. We thank J. Nuth for carrying out several SiO condensation experiments.

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