References and Notes

1. W. W. Scott, *Standard Methods of Chemical Analysis* (Van Nostrand, Princeton, N.J., 1939), pp. 240–241.
2. K. R. Dawson, J. A. Maxwell, D. E. Parsons, *Geochim. Cosmochim. Acta* **21**, 127 (1960).
3. G. Boato, *ibid.* **6**, 209 (1954).
4. H. B. Wiik, *ibid.* **9**, 279 (1956).
5. ———, personal communication.
6. H. Craig, in *Isotopic and Cosmic Chemistry*, H. Craig, S. L. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1963).
7. J. Wood, in *The Moon, Meteorites and Comets*, B. M. Middlehurst and G. P. Kuiper, Eds. (Univ. of Chicago Press, Chicago, 1963).
8. G. W. Reed, K. Kogoshi, A. Turkevich, *Geochim. Cosmochim. Acta* **20**, 122 (1960).
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Crystallization of Clay-Adsorbed Water

Abstract. *The nature of crystalline water in frozen pastes made from representative clay minerals and water was studied by x-ray diffraction. Only the diffraction peaks corresponding to the normal hexagonal ice structure were detected. The relative intensities of the diffraction peaks revealed evidence of epitaxy in that the ice crystals appeared to be preferentially oriented with their* c*-axes perpendicular to the* c*-axes of the individual clay crystallites.*

The tendency of an advancing ice-water interface to exclude colloidal and silt-size soil particles has been demonstrated (*1*). Migration of particles and other foreign bodies ahead of an advancing freezing front was partially explained by postulating the existence of a submicroscopic layer of unfrozen liquid separating the particles from the ice. The existence of this unfrozen layer of water is also vital to current theories of ice segregation and frost heaving in frozen ground. Frozen soils and clays do in fact contain significant quantities of "unfrozen water" in equilibrium with an ice phase, and the mobility of this unfrozen water in response to thermal and electrical gradients is remarkable (*2*), but the nature and distribution of the two phases is still imperfectly understood. In a recent discussion of the latent heat of freezing of soil water, the thermodynamic argument employed required the assumption that soil water crystallizes as normal hexagonal ice (*3*); this assumption accords with field and laboratory observations of segregated ground ice and appears to have been verified by x-ray methods (*4*), but it is questionable in view of Brzhan's report of ice of unusual structure in frozen silica gel (*5*).

Crystallographic data are known for four of the nine generally recognized forms of ice: the normal, hexagonal, tridymite structure; a cubic structure stable apparently only below −80°C; and high-pressure cubic and tetragonal structures (*6, 7*). The first two are by far the best known. A completely amorphous form of ice that may appear when water vapor at a pressure of about 10^{-5} torr condenses on a substrate at or below −100°C and a vitreous form stable at higher temperatures also seem to be generally acknowledged. Therefore a form of ice in frozen soil or clay different from the normal tridymite structure would not be altogether surprising. As Brill (*7*) and others have pointed out, the geometry of the water molecule and its remarkable capacity for bonding make many configurations possible. Inasmuch as details of the study referred to by Martynov (*4*) have not become available and in view of the somewhat contradictory report of Brzhan (*5*), we have investigated the matter further.

X-ray diffraction patterns of frozen pastes of montmorillonite, kaolinite, and halloysite, in which the *c*-axes of the individual clay platelets were predominantly vertically oriented, were obtained with a Norelco x-ray diffractometer using copper $K\alpha$ radiation. During analysis the samples occupied a receptacle milled into an aluminum plate and were covered by a Mylar canopy to prevent changes in water content. Temperature of a sample was regulated by a thermoelectric module, in intimate thermal contact with the aluminum plate, in conjunction with a proportional-temperature controller actuated by a thermistor; sample temperatures were thus established at any desired values, ±0.05°C, between 0° and −40°C. Ambient room temperature was 5°C; this ensured no condensation of moisture on the inner surface of the Mylar canopy.

The samples were cooled rapidly to a selected temperature. Spontaneous nucleation occurred at about −5°C and the freezing front proceeded rapidly from the bottom upward and from the sides inward. Results obtained at −10°C are shown in Table 1, which also lists the data of Brzhan and the generally accepted *d*-spacings and diffraction intensities of powdered ice. The intensity data may be questioned; the difficulties in obtaining truly random crystal orientation have recently become known. However, we know of no more recent data; pending the determination of more reliable values, let us accept the ASTM data.

In every instance the *d*-spacings due to water in the frozen clays corresponded to those of normal ice, ±0.02 Å; moreover, no anomalous, unidentifiable peaks were detected. The results in Table 1 were obtained with clays of low water content. If we assume the specific surface of montmorillonite to be 800 m^2/g of clay, the calculated thickness of the water films distributed over the total surface of the clay is of the order of 5 to 10 Å. When it froze, this adsorbed water evidently collected at nucleation sites where, in spite of adsorption forces, it crystallized in the normal hexagonal configuration. Numerous determinations at higher water contents and lower temperatures gave similar results; *d*-spacings detected were always attributable to hexagonal ice.

The observed relative intensities of the diffraction peaks showed consistent deviations from the random powder pattern; this fact is best explained by postulating a preferred orientation of the microscopic ice crystals in the frozen clay. During preparation of the sample, we tried to obtain preferential orientation of the individual clay platelets by repeatedly remolding the sample with a spatula. Subsequent observation of greatly enhanced (001) diffraction peaks of the montmorillonite and kaolinite clays proved that the *c*-axes of the clay platelets were preferentially oriented in the direction perpendicular to the plane of the goniometer stage.

The data of Table 1 indicate that a significant majority of the ice crystals were so oriented that their *c*-axes were in the plane parallel to that of the goniometer stage. The fact that the relative intensities of the (101), (102), (103), (112), and (203) spacings did not diminish consistently, together with the fact that relative to the (002) the (101) reflection intensified in most instances, suggests that there may be some tendency toward parallel orientation of this face; however, the main effect is still the relative intensification of the (100) reflection. On this basis one may postulate that the orientation of the clay particles was significantly effective in determining the orientation of the ice crystals in the frozen clays.

Hendricks and Jefferson, Macey, and Mathieson and Walker (*8*) have suggested various ways in which the configuration of the hexagonal network of oxygen atoms at the surface of silicate-clay minerals could provide both the foundation and a template on which an ice-like, hydrogen-bonded structure of the adsorbed water might be built up. If this were in fact the case, clay particles might be expected to act as effective ice-nucleating agents in the atmosphere. Kumai and Francis (*9*) have shown that clay particles do indeed function in this manner, and Schaefer and Mason and Maybank (*10*) among others have reported systematic studies of the relative nucleating efficiency of various silicate-clay minerals. The adsorbed-water structures of Hendricks and Jefferson, Macey, and Mathieson and Walker (*8*) have *c*-axes that are aligned with the *c*-axis of the clay lattice. If the clay and an adsorbed-water hull of this configuration were to act as a nucleating agent, the ice formed would most logically be expected to crystallize with its *c*-axis similarly aligned; the data in Table 1 do not support this conclusion.

Table 1. X-ray diffraction intensities, I/I_{002}, for crystalline water in various frozen (−10°C) clay-water pastes. Brzhan's qualitative data on silica gel and the generally accepted *d*-spacings and diffraction intensities of powdered ice are included. Weight of water (gram) per gram of clay appears in parentheses.

Paste	Relative intensities							
	Indexes							
	100	002	101	102	110	103	112	203
	d-*Spacings*							
	3.93	3.68	3.45	2.68	2.26	2.069	1.92	1.52
Hexagonal ice, powder *	10	100	20	15	10	50	10	15
Silica gel †	S	VS			S		M	
Hydrogen-bentonite (0.54)	68	100	24	14	1	38		
Lithium-bentonite (0.74)	64	100	32					
Sodium-bentonite (0.99)	294	100	144	33	95	50	33	
Potassium-bentonite (0.60)	76	100	35	23	17	29		
Calcium-bentonite (0.33)	200	100	80	40	80	60		
Kaolinite (0.40)	92.5	100	70.3	38.6	56.6	58.4	21.1	
Halloysite (0.90)	106	100	104	31	60	43	40	

* ASTM card 1-0509 [Dennison, *Phys. Rev.* **17**, 20 (1927)]. † From Brzhan (*5*): S, strong; VS, very strong; M, medium.

It has been established by dilatometric, calorimetric, and conductance techniques that frozen-clay pastes contain significant amounts of unfrozen water, and an x-ray technique recently revealed that in bentonite–water pastes most of the unfrozen water is located immediately adjacent to the interlamellar clay surfaces (*11*). This fact tends to refute the type of epitaxial ice-crystal growth most easily visualized in terms of the various hydrogen-bonded adsorbed-water structures that have been proposed. Moreover, although it is generally conceded that some sort of water structure develops at the clay-water interface, it is also generally thought that, since it must accommodate the various exchangeable ions, hydratable oxides of iron and aluminum, and any free electrolytes present, the water structure must be relatively transitory, rather highly disordered, and of limited extent and stability. The exchangeable ions, and presumably to a great extent also the oxides of iron and aluminum, are constrained to regions close to the clay surface except insofar as their hydration shells permit them to dissociate from the surface. Thus, since solutes and foreign bodies tend to be excluded from a growing ice crystal, the finding that there exists an unfrozen, structured layer of water separating the clay surface from the ice is perfectly plausible.

Although these arguments tend to rule out the possibility that ice crystals may propagate directly on clay surfaces, two alternate conceptions of nucleation and subsequent epitaxial growth are easily visualized. Nucleation may occur at a favorable site on the clay surface, and the growing ice crystal, except for sporadically distributed points of attachment, may remain largely separated from the clay surface by a film of unfrozen structured water containing the exchangeable ions, hydrated oxides, and any electrolyte present; or nucleation may occur at a point remote from the clay surface and may remain entirely separated from the surface by films of unfrozen water. The evidence in Table 1 does not permit a distinction.

Since the possibility of ice propagation directly on the mineral surface has been ruled out, it is necessary to suggest an alternate hypothesis. The probability that long-range clay-water forces act to enhance the ordering of the water structure at distances greater than 50 Å from clay surfaces has been suggested and is gradually being accepted (*12*). The exact arrangement of the water molecules probably cannot be known, but, assuming that it is different from that of the adsorbed-water structures discussed above, it is possible that epitaxy in this instance is controlled not by the atomic configuration of the clay surface but by long-range clay-water interaction.

Brzhan's data (*5*) do not support his contention that an unusual form of ice existed in his frozen silica gel. As is evident in Table 1, all the diffraction peaks reported by him can be attributed to hexagonal ice; in fact he detected no anomalous peaks. He did find, however, that in terms of relative intensities the (100) and the (110) diffraction peaks seemed to be unusually strong. In the absence of evidence to the contrary, this also is most reasonably explained in terms of a preferential orientation of the ice crystals in the frozen silica gel and does not warrant the postulation of a new crystallographic form of ice.

In conclusion, our results can be accounted for satisfactorily by postulating the presence, in the frozen clays of microcrystals, of hexagonal ice having a preferred orientation determined at least in part by the orientation of the clay lamellae. Contrary to deductions based on an ice-like configuration of the clay-adsorbed water, the *c*-axes of the microcrystals of ice tend to lie in planes perpendicular to the *c*-axes of the platey-clay crystals.

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References

1. A. E. Corte, *J. Geophys. Res.* **67**, 1085 (1962); P. Hoekstra, thesis, Cornell Univ. (1963).
2. Z. A. Nersesova and N. A. Tsytovich, *Proc. Intern. Conf. Permafrost Frozen Ground, 1st* (NRC-NAS, Washington, D.C., in press); P. Hoekstra and E. Chamberlain, *Nature* **203**, 1406 (1964).
3. D. M. Anderson, *Proc. Intern. Conf. Permafrost Frozen Ground, 1st* (NRC–NAS, Washington, D.C., in press).
4. G. A. Martynov, *Principles of Geocryology*, translated from the Russian edition (Academy of Sciences, Moscow) by E. R. Hope (Canadian National Research Council, Ottawa, tech. transl. 1065, 1959), pp. 153–92.
5. V. S. Brzhan, *Colloid J. USSR English Transl.* **21**, 621 (1959).
6. K. Lonsdale, *Proc. Roy. Soc. London* **247A**, 424 (1958).
7. R. Brill, *Angew. Chem. Intern. Ed. Engl.* **1**, 563 (1962).
8. S. B. Hendricks and M. E. Jefferson, *Amer. Mineralogist* **23**, 863 (1938); H. H. Macey, *Trans. Brit. Ceram. Soc.* **41**, 73 (1942); A. McL. Mathieson and G. F. Walker, *Amer. Mineralogist* **39**, 231 (1954).
9. M. Kumai and K. E. Francis, *J. Atmospheric Sci.* **19**, 474 (1962).
10. V. J. Schaefer, *Bull. Amer. Meteorol. Soc.* **29**, 175 (1948); B. J. Mason and J. Maybank, *Quart. J. Roy. Meteorol. Soc.* **42**, 723 (1958).
11. D. M. Anderson and P. Hoekstra, *Soil Sci. Soc. Amer. Proc.*, in press.
12. P. F. Low, *Advan. Agron.* **13**, 269 (1961); D. M. Anderson, G. F. Leaming, G. Sposito, *Science* **141**, 1040 (1963).

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