Reports

Influence of a Phase Transition of Ice on the Heat and Mass Balance of Comets

Abstract. *Differences in gas production rates of comets may be explained in part by the phase transition of ice in the comet nuclei.*

Recently, Smoluchowski (*1*) pointed out that the presence of amorphous ice may have an important influence on the heat and mass balance of particles of Saturnian rings.

According to Whipple (*2*), comet nuclei contain a large amount of water ice. This ice seems to have been condensed at temperatures lower than 100 K and must be amorphous [infrared data from interstellar clouds indeed suggest the presence of amorphous ice (*3*)]. If comet nuclei contain amorphous ice, the effect on heat and mass balance may be even more dramatic for comets than for the ice particles in Saturnian rings.

The heat conduction coefficient (K) of hexagonal ice is well known for absolute temperatures (T) between 0.5 and 273 K (*4–6*). For temperatures higher than ~ 25 K it can be expressed by the phenomenological law

$$K = \frac{5.67}{T} \qquad (1)$$

The solid line in Fig. 1 corresponds to this equation. Unfortunately, no measured data on the heat conduction coefficient of amorphous ice are available. According to Pohl (*7*), all heat conduction coefficients of amorphous dielectric solids measured up to now are confined to the shaded zone of Fig. 1. We can estimate the heat conduction coefficient of amorphous ice by using the classical formula (*8*)

$$K = \frac{1}{4} c v \lambda \rho \qquad (2)$$

where c is the heat capacity per unit of mass, v is the velocity of sound, λ is the mean free path of the phonon, and ρ is density. If we consider that the mean free path of the phonon is constant and about 5×10^{-8} cm [the order of magnitude of the elementary cell (*8*)], and take 2.5×10^{5} cm/sec as the mean value for the velocity of sound in ice, and then use for c the values measured for hexagonal ice by Giauque and Stout (*9*) [the difference between the specific heat of hexagonal and amorphous ice is less than 30 percent in the temperature range considered here (*10*)], we find that for temperatures higher than 20 K the heat conduction plot for amorphous ice obtained in this way (dashed line in Fig. 1) is situated in the shaded zone. We conclude for this reason that our estimation is not too bad.

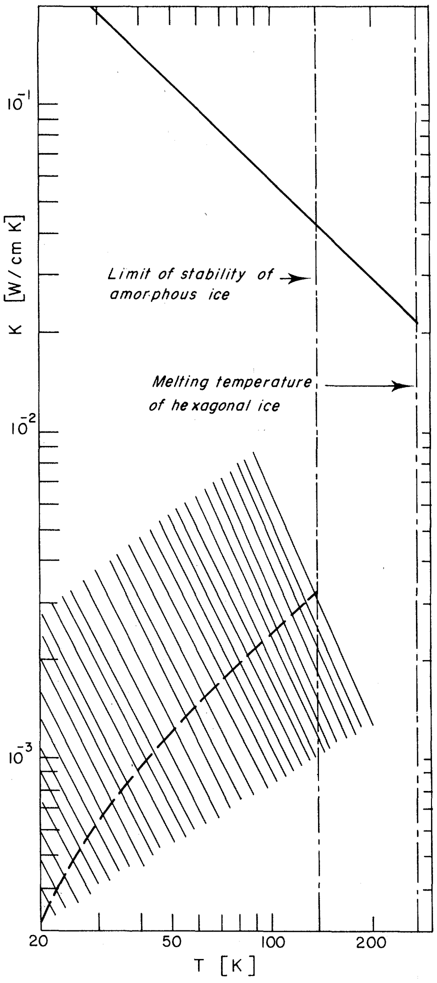

Fig. 1. Calculated heat conduction coefficient for amorphous ice (dashed line) compared to the heat conduction coefficient for hexagonal ice (solid line).

The heat conduction coefficient of hexagonal ice is at least ten times higher than that of amorphous ice. The value of K increases with temperature for amorphous ice. The heat conduction coefficient of cubic ice is not known, but as cubic ice is a crystalline form we expect that it is not very different from hexagonal ice. Amorphous ice is metastable with respect to crystalline ice. Transformation to cubic ice occurs within a few seconds at about 135 K, but for temperatures lower than 30 K amorphous ice is stable for more than 10^{27} years (*3, 11*).

Let us now consider a comet entering the solar system for the first time. The external crust of the nucleus will contain essentially amorphous ice. The upper limit of the "effective" heat conduction coefficient of the surface layer will be fixed by the heat conduction curve of amorphous ice. But because of the imperfect thermal coupling between individual grains, we expect very low values. At temperatures below 100 K the production rate of water vapor is low because of the low vapor pressure, and most of the absorbed solar radiation is either reradiated or used to heat the surface layer of the nucleus. Gas production will increase with increasing temperature. When a temperature between 130 and 140 K is reached, part of the water molecules in the surface layer will crystallize irreversibly in the cubic form. Since the phase transition is an exothermal process, the ice will release some excess heat (*10*), and the transformation of neighboring layers will be favored. The upper limit of the effective heat conduction coefficient will now be fixed by the heat conduction curve of crystalline ice. Because the recrystallization of amorphous snow is accompanied by a reduction of the specific surface area (*12, 13*), the coupling between grains may be better than it is for amorphous ice, and the value of the effective heat conduction coefficient may be closer to that of the compact material. We conclude that a larger part of the incoming heat will be transferred to deeper layers of the nucleus. A crust of crystalline ice will remain on the surface when the comet is leaving the neighborhood of the sun so that the heat conduction to the interior will be more important on the postperihelion branch of the orbit than on the preperihelion branch. The result will be asymmetric gas production with respect to the perihelion. Observations of the 18-cm radio spectrum of comet Meier (1978f) (*14*) seem to show an

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asymmetry of OH production with respect to the perihelion.

When a periodic comet approaches the sun the surface of its nucleus will still contain cubic (and perhaps hexagonal) ice. This will be favorable to heat conduction to deeper layers, even at large solar distances, and gas production will be decreased by this mechanism. The gas production rate of "old" comets is indeed lower than that of "young" ones (*15*).

The mechanism proposed here will have as a consequence that some orbits may be favorable to gas production and others favorable to conduction of heat into deeper layers of the nucleus. Phase transition with an increase of thermal conduction will prevail when the temperature of the nucleus at the perihelion is close to the transition temperature. When the temperature is much higher, a large amount of the newly formed crystalline ice crust will evaporate. We see that two comets of comparable age, with comparable mean radiation intensity received during their revolutions, may have very different gas production rates. For this reason it seems that, disregarding the differences in age of the comets, the orbit of Halley may be intrinsically more productive than that of Tempel 2, even if we take into account that the mean radiation intensity received is lower for Halley than for Tempel 2.

The mechanism proposed here is obviously not able to explain all differences in gas production rates in comets, but it may be one factor among others. A space mission could give further information on heat transmission in the nucleus.

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Oscillatory Zoning in Plagioclase Feldspar

Abstract. *A kinetic mathematical model of crystal growth from the melt is used to describe quantitatively the phenomenon of oscillatory zoning in plagioclase feldspar. In this model, the functional dependence of crystal growth rate on both melt and crystal surface composition and the transport of material within the melt are explicitly considered. Oscillatory zoning is found to develop for a wide variety of such functional dependence and to be sensitive to the initial composition of the melt.*

Plagioclase feldspar, a common rock-forming mineral, consists of a solid solution between the end-members anorthite (An), $CaAl_2Si_2O_8$, and albite (Ab), $NaAlSi_3O_8$. Naturally occurring plagioclase frequently exhibits an oscillatory compositional zoning such that the mole fraction of the An end-member varies in a periodic fashion from the core to the rim of the plagioclase grain. The amplitude of this compositional oscillation is generally between 5 and 15 mole percent, and the wavelength is between 10 and 100 μm. Ten or more complete compositional oscillations may be observed in samples exhibiting this phenomenon (*1*).

Oscillatory zoning of plagioclase is commonplace in many geologically important and frequently occurring igneous rock types. An understanding of the cause of oscillatory zoning is essential for correct interpretation of the geologic history of such rock types as well as for the elucidation of the physicochemical processes of magma evolution. Numerous theories have been postulated to explain this phenomenon (*1, 2*), but none of them has led to a quantitative description of this patterning or the conditions leading to its development.

We present here a new crystal growth model based on the interaction of growth dynamics of a solid from a melt and diffusion of material within a melt (*3*). The chemical kinetic arguments that are introduced in this model account for the composition dependence of crystal growth rate and the formulation of the crystal growth process as a Stefan (moving boundary) problem. This model is the first to describe quantitatively oscillatory zoning and the range of control parameters over which it exists.

We consider the growth of plagioclase from a melt (magma) to be a kinetic process in which the layers at the crystal surface fill as a result of the construction of formula units of either the An or Ab end-member at a kink or other growth site. The melt from which plagioclase feldspars grow is a complex silicate liquid composed of various charged species (*4*). To simplify our considerations, we assume that the only relevant species for plagioclase growth are Na^+, Ca^{2+}, Al^{3+} (*5*), and $SiO_4{}^{4-}$; we ignore the possible participation of more complex Al- and Si-bearing species and polymers in the crystal growth process. This assumption leads to some loss of generality, but the results are essentially the same as for the case where other species such as $AlO_4{}^{4-}$ are considered (*3*).

We postulate that the reaction sequences for the construction of formula units of An or Ab are based on (i) the tendency for charge neutrality and (ii) structural considerations; that is, we expect that it is easier to put the first ion at the base of the growth site rather than at the top and then to build up from the bottom. We assume a macroscopically planar crystal–melt interface and assume that plagioclase grows by a layer-filling mechanism (*6*), although the method can be applied to other interface structures and growth mechanisms (*3*). Making the assumption of rapid equilibration for most intermediate reactions for the formation of formula units, we obtain an incorporation rate G_{An} (in moles per square centimeter per second). Typical results are

$$G_{An} = \tilde{K}_{An}[Ca^{2+}][Al^{3+}]^2[SiO_4{}^{4-}]^2 \quad (1)$$

$$G_{Ab} = [Na^+][Al^{3+}]\{K_{Ab}{}^{(1)}[SiO_4{}^{4-}] + K_{Ab}{}^{(2)}[SiO_4{}^{4-}]^2\} \quad (2)$$

Other rate laws of similar structure are also possible (*3*), and the correct law will not be known until experimental data have been collected. However, our general conclusions do not require a precise rate law.

The second postulate of our model is that the rate constants in Eqs. 1 and 2 depend on the surface composition of the growing crystal. There are several types of growth sites on the surface of a crystal, differing in the number of nearest An or Ab formula units already attached (*7*).