

EXISTENCE, SURVIVAL AND RECOGNITION OF ICY METEORITES ON ANTARCTICA WITH RESPECT TO PALAEOTEMPERATURES

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Összefoglalás - A Naprendszer kémiai kondenzációs modellje, valamint a meteoritek megfigyelt jellemző tulajdonságai alapján jégmeteoritok létezését, földi becsapódás utáni túlélését és megtalálhatóságát vizsgáljuk. Összegyűjtjük azokat az okokat, melyek alapján jégmeteoritek létezése igen valószínű, majd megvizsgáljuk jégmeteoritok túlélésének lehetőségét az Antarktiszon, ahol egyáltalán föllelhetők lehetnek a földi környezetben. Az Antarktisz paleohőmérsékleteire következtetéseket vonhatunk le a túlélő jégmeteoritek feltételezhető ammóniatartalma alapján. Az Appendixben fölidézünk egy föltételezhetően jégmeteorit kapcsolatú hullásról készült jelentést 1875-ből.

Summary - On the basis of characteristics of some meteorites (cold meteorites after falling, fragility), of the chemical condensation model of the Solar System, and also according to the main components of comets icy meteorites can be suspected to exist. Firstly, the reasons are listed which make it plausible that icy meteorites can indeed exist. Secondly, we enumerate arguments for their preservation on Antarctica, where they might be collected. The survival of an ammonia-bearing icy meteorite implies temperature constraints for Antarctic palaeotemperatures. An Appendix recapitulate and comment the scientific report on a possible icy meteorite fall in 1875.

Key words: icy meteorites, Solar System mineral belts, cometary contamination, paleoclimate on Antarctica.

1. INTRODUCTION

In general meteorites give a distorted but still characteristic sampling of the Solar System. Theoretical papers on the formation of the primordial system suggests substantial gradients of chemical concentrations, along with the thermal and pressure gradients; moreover observations on fallen meteorites as well as on asteroid spectra corroborate this expectation. However one of the theoretical predictions still remains without (direct) observations. While in the theoretical scheme (contaminated) ices are structural components of minerals from Jupiter outwards (*Lewis and Barshay, 1974; Larimer, 1967; Grossman, 1972*), and indeed astronomy observes ices at Iovian and Saturnian moons, in Saturn's rings, at Pluto and maybe Chiron, we do not observe ices in oncoming meteorites.

Nevertheless, it is easy to see that everywhere on Earth, except Antarctic interiors and maybe northern Greenland, the chances are nil for survival of extraterrestrial ice for a substantial time. So here we discuss two observations maybe suggesting an ice coating during fall (*Török, 1882*), and a possibility of permanent survival of recognisable icy meteorites on Antarctica.

By investigating extraterrestrial ice, one would get deeper insight into the structure of the Solar System, and could once more check the theories of its formation. We guess that icy meteorites would be almost as frequent as stony ones; only they melt and vanish rapidly on the main part of the globe.

2. IMPLICATIONS FROM THE CONDENSATION MODEL FOR THE SOLAR SYSTEM

Different calculations on the chemical equilibrium for minerals, condensed from the primitive Solar Nebula with cosmic (solar) chemical abundances, were published in the late 60's and early 70's (Larimer, 1967; Lewis and Barshay, 1974; Grossman, 1972). The main conclusion of such models was that three distinct material belts can be distinguished in the condensing solar nebula: the metal, the silicate and the ice ones (Fig. 1).

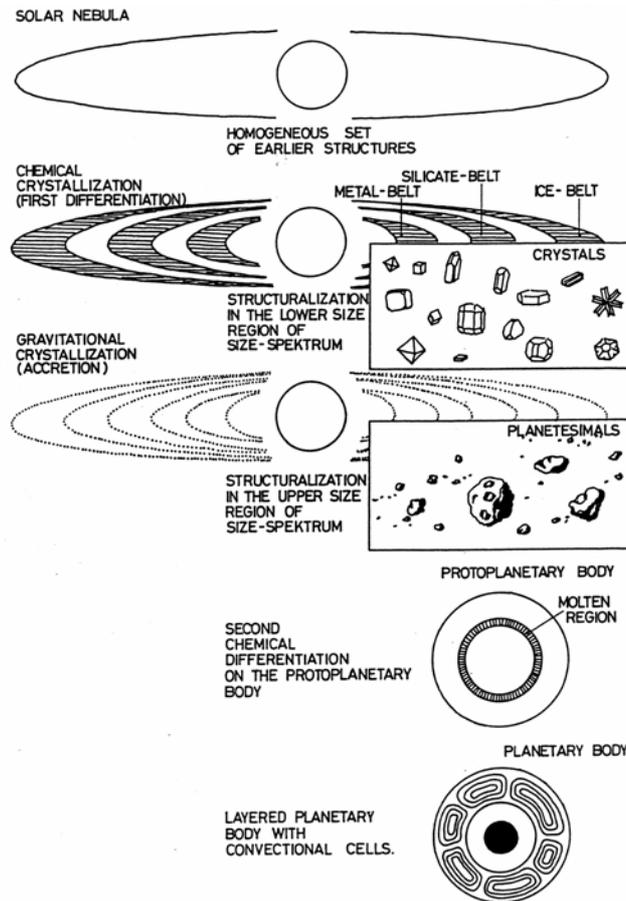


Fig. 1 Main steps of the evolutionary process of the Solar System from primordial solar nebula to global differentiation of planetary bodies. Central column: 3 stages of solar nebula. Right: events of planet formation.

For definiteness' sake we refer here to the work of *Lewis and Barshay* (1974). They calculated the sequence of precipitation of a gas nebula with solar elementary abundance when temperature decreases on to the Cameron adiabat. In their summarizing map of the p-T diagram of solar gas, the phase boundaries of solid phases in equilibrium with solar p-T conditions had been deduced by the intersection of these boundaries and the Cameron adiabat. The map shows that the temperature inhomogeneity differentiates the nebula. The temperature depends both on solar distance and time. Temperature, decreasing with solar distance, forms mineral belts around the Sun. Slow changes in the local temperature result in a time dependent precipitation sequence in the belts.

The sequence of minerals, shown on *Fig. 2*, is the following:

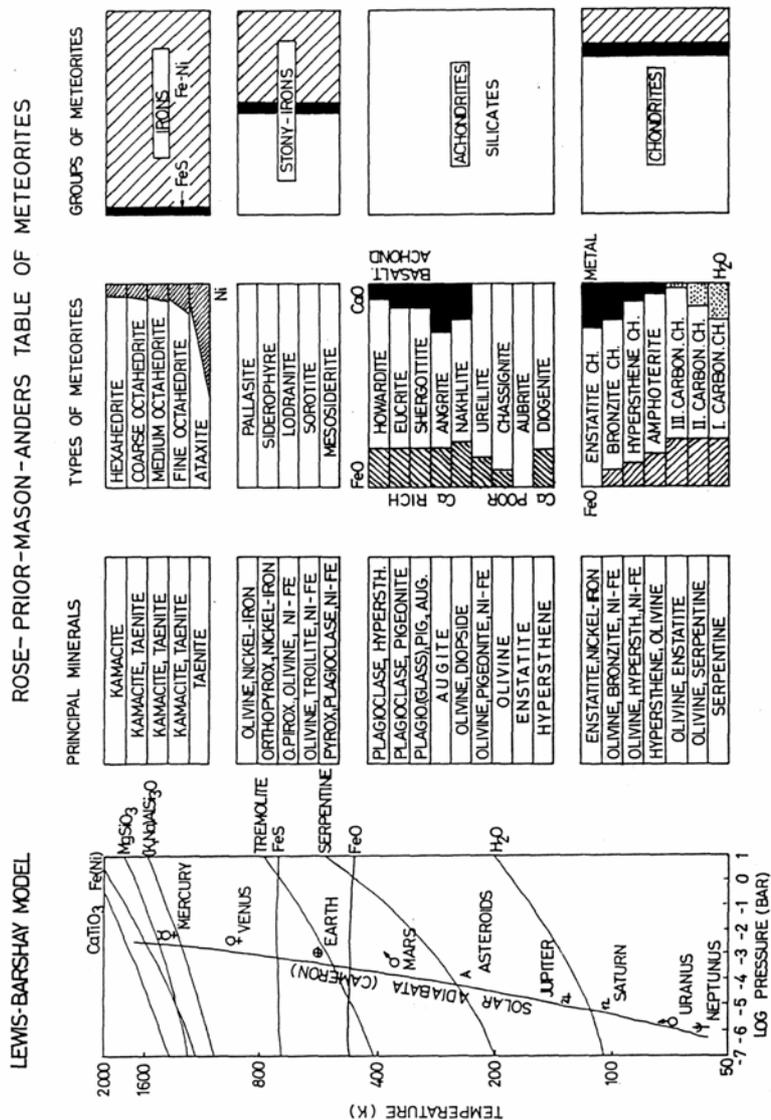


Fig. 2 Summary of the chemical crystallization in the Solar System according to *Lewis and Barshay* (1975) and meteoritic counterparts of these mineral bands. (The Rose-Prior-Mason-Anders table from *Bérczi, 1991*).

<i>Temperature</i>	<i>Elements, reactions</i>	<i>Mineral</i>
1600 K	CaO, Al ₂ O ₃ , REE oxides	Oxides (e.g. perovskite)
1300 K	Fe, Ni alloy metals	Fe-Ni
1200 K	MgO + SiO ₂ → MgSiO ₃	Enstatite (pyroxene)
1000 K	Alkal. oxid. + Al ₂ O ₃ + SiO ₂	Feldspar
1200-490 K	Fe + O → FeO, FeO + MgSiO ₃	Olivine
680 K	H ₂ S + Fe → FeS	Troilite
550 K	Ca-minerals + H ₂ O	Tremolite
425 K	Olivine + H ₂ O	Serpentine
175 K	ice H ₂ O crystallizes	Water-ice
150 K	gas NH ₃ + ice H ₂ O → NH ₃ .H ₂ O	Ammonia-hidrate
120 K	gas CH ₄ + ice H ₂ O → CH ₄ .7H ₂ O	Methane-hidrate
65 K	CH ₄ , Ar crystallizes	Methane, Argone ices

According to the presence of H₂O the sequence can be divided into groups. The two main belts (those with and without ice) are "separated" by the troilite belt.

The corresponding solar distances need reconstruction for the proto-Sun. However, from planetary compositions one may get roughly the double of the present temperatures (*Lewis and Barshay, 1974*). This means that the inner boundary of substantially hydrated minerals was cca. 1 AU and the innermost region for "pure" ice crystals was roughly 5 AU (Astronomical Unit).

Nevertheless, from the point of view of meteorite classification three main belts can be recognized: metal, stone (or silicate) and ice ones. Iron, stony-iron and stone meteorites are well-known, but, comparing the estimated mineralogy of these chemical models and the main types of meteorites, an important hiatus emerges. We summarize on *Fig. 2* the main meteorite types (*Anders, 1964*) and mineral belts in a form which clearly exhibit this hiatus. The correspondence between mineral belts of the condensing solar nebula and the main (and intermediate) meteorite types shows sharply that representatives of icy meteorites are missing.

Meteorites intermediate between the metallic and stone ones are well known. Of course, we should exclude pallasites and lodranites from this discussion, since they were, most probably, produced secondarily inside of planetesimals, asteroids etc.; however chondrites in themselves exhibit a wide range of metallic Fe content. Now, by analogy, one might look for icy-stone chondrites, and they indeed exist; carbonaceous chondrites contain volatile elements and structural water up to 15-20 weight % (*Yanai et al., 1995*).

Therefore it seems that the belt scheme of the theory is qualitatively correct and may be relevant for meteorites too; simply icy meteorites have not been collected for some reason. And indeed on the majority of the terrestrial surface local conditions are against the survival of an icy meteorite. On the other hand, there are places on the globe, which might preserve some pieces of them: especially Antarctica. The Antarctic meteorite collecting projects, and especially the Japanese one (*Yanai and Kojima, 1987; Yanai et al., 1993*), led to the recognition of new types; they may lead to the identification of this group too.

For some support we note that some descriptions of earlier meteorite falls may contain some important details referring somehow to the existence of volatile components, which later were not found at all. One such event happened in Hungary, when not only the intensity of the phenomenon suggests that there were missing masses, but the condition of

the found pieces (having been cold) is also in accord with supposed volatile components of the falling body.

Observe that icy-stones ought to be discriminated from the mixtures of ices and stones. In the first case the ice (water) would not percolate, so for first glance the meteorite would seem a stone one, only very fragile. However the fine distinction may wait until good specimens are found.

3. METEORITES, FOUND IN COLD CONDITION JUST AFTER FALL

Accept, for a moment, an icy block with embedded stone fragments (just as in comets) to fall as a meteorite. That event would be more or less similar to the fall of a stone meteorite, except that

- the body can disintegrate into many pieces in the fall;
- ice fragments without stone core may vanish in mid-air, or on the ground, so less meteorites will be found than expected from the intensity of the shower ("missing mass");
- the stone cores will seem usual stone meteorites; but if the ice coating survived the fall then it is without surface melting;
- if, miraculously, the stones can be collected just after fall, then they are surprisingly cold.

Now one can see that indeed the reliable observation of an icy meteorite is difficult. Points 1 and 2 need observers reliable not to exaggerate, and without superstitious interpretations of shooting stars. Point 4 needs the fall to the immediate neighborhood of human habitat, together again with the reliability of the observers. This feature cannot be relied if the scientific investigation did not follow the fall in days. It is true that, Point 3 is a permanent feature, but stones without molten surface are rarely collected as meteorites. These factors in themselves may be responsible for the lack of our knowledge about icy meteorites.

Still there are rare events which might have been falls of icy meteorites. In his work "A Magyar Birodalom meteoritjei" (The Meteorites of the Hungarian Realm), *Török* (1882) describes a meteorite fall, when the pieces of the meteorite were found in cold condition. This was the Zsadány Meteorite.

The fall happened on 31st March 1875, in the vicinity of the village of Zsadány, in Temes County, Hungary. (Zsadány, now it is called Jadani, belongs to Romania.) Between 3 and 4 p.m. after a great thunder from the clear sky a swarm of rather small pieces of meteorites fell to the fields and gardens of the village. (For the locality, see e.g. *Herner*, 1987.)

It was very remarkable that when the pieces of the meteorites were taken into hands, they were found very cold. The author remarks, that there was another case, when a meteorite brought the "coldness of outer space to the surface". This event was in India, at Dhurmsala (or Dharmsala, Punjab), on 14th July 1860. There was found six pieces of meteorites and those were so cold, that, as reported, "people could not hold them for longer time in their hands".

The pieces of the Zsadány Meteorite are rather small like nuts; 9 pieces were found, representing chondrites. 3 pieces can be found in the Mineralogical Collection of the Eötvös University, Budapest, under the catalogue numbers L 376, 377 and 378, with

masses 14, 38 and 45 g, respectively. They are denoted in the catalogue as "spherical chondrites". It is worthwhile to note that the Zsadány event was well documented and investigated. The Lord Lieutenant of Temes County immediately reported the event to a scientific journal, enclosing two fragments. The meteorites fell in early afternoon to gardens, ploughfields and meadows, many eyewitnesses were present at this event. The Hungarian Academy of Sciences sent investigators to the site in 15 days, they questioned many eyewitnesses, and organized a systematic search with 30 persons after fragments in the area whither witnesses had seen several "stones" to fall, but only one tiny fragment was found. The eyewitnesses did not report light phenomena, and did report delayed falls in a period of 30 seconds. The results of the investigation were published immediately (*Krenner*, 1875). In the Appendix we recapitulate the relevant part of the report, never published in any other language than Hungarian.

We think that the data at least suggest that the Zsadány meteorites originated from an icy body with chondritic stony fragments embedded. (The Dharmasala event is impossible to reconstruct because local people collected the pieces and details are not known.) The probable story is that the parent body fragmented during the fall, most fragments were ices and partly evaporated in fall, partly liquefied before finding them, and the stony fragments were preserved from heating by their icy covers. We performed a preliminary visual investigation on one of the Zsadány meteorites; the results are not enough for publication but will be mentioned at the end of the Appendix.

We note at this point that the Tunguz event had a material source, of which only traces remained, but most of it seems to have evaporated.

4. ON THE POSSIBILITIES OF FALLING ICES AND THEIR OBSERVATION

In this Chapter we discuss the possibility of such events. As for probability, only very rough semiquantitative estimations would be possible at the present state of art. We can say that this probability is a product of factors describing the abundance and different survival chances of icy blocks. These points are treated separately below.

1) Origin

Ice is a substantial component in the outer Solar System (theoretical suggestions were given in Chap. 2.) Now, let us see the observational data. (*Francis*, 1981; *Encrenaz et al.*, 1990). Theory predicts that ices will be more and more dominant in the mineralogy of the bodies going outwards from the Sun. Indeed, some Iovian and many Saturnian satellites have icy surfaces. The same is true for satellites of Uranus but the composition seems to change: the Iovian moon, Europa, has mainly water ice, the Saturnian ones may contain ammonia too, but high ammonia content in the mixture is not expected, since for cosmic abundance N is no more than 1/8 of O (*Novotny*, 1973); and on those of Uranus observations suggest mixtures of water, ammonia and methane. Methane ice is abundant in the Pluto-Charon system, and sometimes the outer asteroid (?) Chiron is believed to represent a family of outer primary small icy bodies (to which Pluto also may belong). If so, then these objects may correspond to the ice belt of the scheme. From these planetary and satellite surfaces impacts may throw ices to interplanetary orbits in the same way as they throw fragments of inner bodies resulting in metallic and stony meteorites. Of course,

escape velocities are needed and this may be a problem for the Iovian and Saturnian satellites.

Obvious sources of meteorites are disintegrating comets; some observations suggest such origin for some "meteor swarms". Now, comet cores are believed to be stones cemented by ices.

So, as for origin, ices approaching the orbit of Earth may be as frequent as stones, and they may contain water, ammonia and methane.

2) Survival on orbit

At r solar distance the equilibrium temperature of a grey body is

$$T_{eq} = (R_S/2r)^{1/2} T_S \quad (1)$$

where R_S is the solar radius and T_S is the solar surface temperature. Hence, at 1 AU one gets 276 K, mere 3 degrees above the freezing temperature of water ice at very low pressures. In addition, ices are not grey because of high albedoes in the visible range dominant in solar irradiation, but definitely lower ones in the near infrared on which they radiate back. Therefore, a clean ice block could survive long on Earth's orbit, and indeed, comets survive the crossing although they lose some part of their ices.

Still some caution is needed. First, there is evaporation even under the freezing point; for this the same can be said as for the comets. Second, the surface may collect dust, which would increase the temperature to T_{eq} . However, then fast evaporation starts carrying away the dust particles, too. So ices may survive several crossings of Earth's orbit. More definite calculations are pointless now, since the survival rate/revolution depends more on the perihelion distance (which may be various) than on the details of the radiation balance at 1 AU.

3) Survival during fall

In the fall, the evolution of a meteoritic body is governed by 3 coupled differential equations whose approximate form for a sphere of radius R and mass density μ is as follows:

$$(4\pi/3)\mu R^3(dv/dt) = F_{drag} - (4\pi/3)\mu R^3 g \quad (2)$$

$$F_{drag} = F_{drag}(R, v, z) \quad (3)$$

$$(d(4\pi\mu R^3/3)/dt)cDT = \text{Wheat} = F_{drag} \cdot v \quad (4)$$

$$dz/dt = -v \cdot \cos\Theta \quad (5)$$

where F_{drag} is the drag force on the falling body, v is the velocity, z is the height, Θ is the angle to vertical, c is the specific heat, and DT is the difference of the evaporation temperature and the original one. Depending on the original dustiness of the surface, the latter is 200-270 K, so DT is comparable to 100 K. In addition, the latent heat of evaporation should be taken into account, which is again substantial. As for the drag force, the simplest approximation, (which must be corrected at high velocities), is the Stokes law

$$F_{drag} = 6\pi\Gamma(z)R(t)v(t) \quad (6)$$

where $\Gamma(z)$ is the viscosity of air, depending on $T(z)$.

Now observing that for ice DT is roughly 1 order of magnitude smaller than for silicates but c half an order higher, and the evaporation heat is high. Therefore the total mass loss of ices and silicates during fall is roughly similar. If stones can reach the surface, ices can either.

4) *Survival in the impact*

This is a rather obscure point. If a substantial part of the original velocity is retained, then at the impact the ice block breaks and some part liquefies. However fragments may survive in frozen state. We think that extraterrestrial ices could be recognized from composition; see later.

5) *Survival on the surface*

Now let us assume that an icy block survived the descent and landed in the interior of Antarctica. Then the next question is if it has a chance to survive until discovery. The survival is only necessary, not sufficient, condition for later observation, since a lot of interactions can be imagined between the icy meteorite and the ice and snow. (The meteorite can be buried by snow as well as stony meteorites can; it may be frozen to the surface, etc.) These interactions may be complicated. However the survival itself, i.e. the resistance to melting, depends on fundamental physical, chemical and meteorological facts.

First we list the melting points of possible icy meteorites, all for normal 1 atm pressure.

The melting point of the icy material strongly depends on chemical composition, which is expected to widely vary in the Solar System. So the survival chances depend on the place of origin. A complete analysis is not possible in the present status of our knowledge about the outer Solar System, but some possibilities can be discussed, according to the theoretical scheme and observational data mentioned in earlier Chapters.

Most obvious sources of icy meteorites are the cores of comets. There the possible constituents, according to cometary spectroscopy, are water ice, carbon dioxide, ammonia, methane and cyanides, with their mixtures, clathrates, etc. The best known such body is Halley's Comet, where the ice seems to be dominated by H_2O with some percents of CO and CO_2 and 0.1% of cyanides. Cometary ices may carry stony fragments with them.

As for planetary bodies, we are going outwards. The first great extraterrestrial store of ices is Mars. Note that the stony shergottites sometimes are believed of Martian origin (*McSween and Stolper, 1980; McSween et al., 1979*), either as direct products of a meteoritic impact on Mars, or helped to escape by water vapors deliberated from permafrost by the impact. In any case, if shergottites may come from Mars, ices may too; these ices would be contaminated by carbon dioxide and may contain stones. We note that the polar caps are believed to have water and carbon dioxide ices in comparable amounts, and the Viking probes observed H_2O-CO_2 clathrate rime.

As for the asteroid belt, no icy asteroid has been seen, so this source will not be discussed.

Some moons of Jupiter do have icy covers, most abundantly Europa. Of course, the escape from the Jovian system is difficult. For any case, the ice of Europa seems water-dominated.

Some moons of Saturn are icy, as well as the rings. Again, escape seems difficult from the system.

Going farther, one expects more and more ammonia and methane ices (*Bérczi and Lukács, 1995*). Oxygen is so abundant (*Novotny, 1973*) that water ice is probably not suppressed at any distance; but methane ice can be quite abundant at the outer fringes of the System. Such mixtures are seen on moons of Uranus on the surfaces of the Pluto-Charon double system. Also, the suspected asteroids outside Saturn (see e.g. Chiron) may be sources of mixture ices, and thence escape would be easy in an impact.

Now, dominantly methane ices cannot survive even in the neighborhood of the orbit of Earth, and dominantly ammonia ices cannot survive even on Antarctica; but we do not expect such ones anyway. So henceforth we concentrate on mixtures in which water ice is dominant. Water may form a variety of clathrates with the other molecules mentioned here; for that possibility the reader may consult the detailed chemical literature (*Berecz and Balla-Achs, 1980*). We deal here mainly with solutions or mixtures. For definiteness' sake we consider an environment permanently below -10°C .

Water can solve a substantial amount of CO_2 , still with melting point above -10°C .

Cyanides mean a variety of molecules. We discuss here the two simplest: dicyanide C_2N_2 and hydrogencyanide HCN.

Dicyanide freezes at -34.4°C . It can fairly be solved in water (some 1 weight% at room temperature; henceforth% means always weight%), and, due to the Raoult Law, this quantity would decrease the freezing point of the ice by less than 1°C . Therefore, dicyane-contaminated water ice can survive for long time.

Hydrogen-cyanide can be solved in water in any quantity, and, when pure, its freezing point is -15°C . So ices, even strongly contaminated by HCN, can survive for long time.

Methane freezes much below the Antarctic temperatures. Since water can solve only small quantities (0.001-0.01% in the relevant temperature ranges), only very lightly methane-contaminated ices can be formed; however these can survive indeterminably.

Finally we arrive at ammonia, and here we go into more details. Since ammonia freezes at -78°C , ammonia-dominated ices cannot survive. However, according to the Raoult Law 1% ammonia content decreases the freezing point to -1.1°C , therefore water ice can survive with several% of ammonia contamination for a long time. As for solubility, 0°C water-ammonia mixtures can go up to 47% NH_3 content. For more detailed phase diagrams see e.g. *Kargel (1992)*.

Now, the original percents could be anything according to the parent body, so the subsequent fate on the Antarctic ice can be diverse. For more detailed statements the $\text{H}_2\text{O}-\text{NH}_3$ phase diagram would be needed, but this diagram is very complicated (note e.g. the wide variety of low temperature water ices) and belongs to low temperature chemistry. However, for our present purposes we do not have to go below moderately cold temperatures, and therefore a simple approximate scheme will suffice.

According to the Raoult Law, in dilute aquatic solutions 1% ammonia decreases the freezing point by 1.09°C . For liquid ammonia, solving water ice experiments are harder, but the van t'Hoff Law gives 0.53°C decrease to 1% water ice. So at both extremal compositions the mixtures freeze well below the simple linear interpolation of the freezing points of the pure liquids, as shown by *Fig. 3*. This is similar to the state diagrams of metals with eutectic alloys. We are not interested in the details around the crossing point of the Raoult lines because that state belongs to 80.5% NH_3 content and -88°C temperature, out of

the scope of our discussion; however, the simplified scheme makes the verbal argumentation easy.

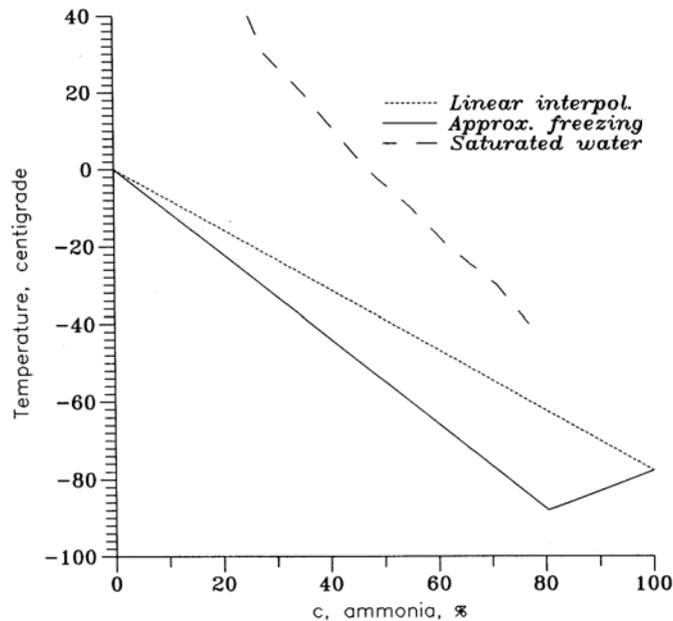


Fig. 3 Phase diagram of ice and ammonium. Melting points in the water-ammonia mixtures are somewhat simplified. Initial slopes are determined by the universal Raoult Law and suggest eutectic behaviour. For minor complications see Kargel (1992).

The dashed line is the solubility curve (for NH_3 solved in H_2O ; we are not interested here in the opposite case). For low temperatures we extrapolated the observations.

As an example consider the fate of an ice block with 20% ammonia content from winter to summer. The freezing point is some -22°C . In the winter the block remains frozen. However in some spring noon the block starts to melt. Then, as the diagram suggests, an ammonia-dominated component separates as liquid. Now, the temperature is above the boiling point of pure NH_3 , and above that of the "eutectic". Consequently, the separated liquid fastly evaporates. The result is a continuous depletion of the ice block in NH_3 at least on the surface. The process stops at the NH_3 content to which the freezing point is the summer maximum temperature. This is roughly 9% NH_3 at -10°C .

Now let us look for the possibilities of environments permanently below -10°C ; as we have seen, then even contaminated ices can survive. However, note that the main part of Antarctica lacks regular meteorological observations. Majority of stations are located near the shore with a mild climate, which is not hopeful for longer survival of icy meteorites. In the interior the conditions are better, but thence it is harder to collect meteorites, and the meteorology is less known.

In the Antarctic interior the meteorite is under cca. 1 atm pressure, and the summer mean temperature is well below 0°C . For the interior of the Dronning Maud Land, about 72° latitude, the January mean temperature seems to be $-16 - -20^\circ\text{C}$, while the July value somewhere around -40°C . From the observations of some regular stations the daily variations seem to be in the order of 10°C . So we would expect -10°C as upper boundary of

"normal" peak temperatures. Still, this value is doubtful: on some favored meteorite sites of the Dronning Maud Land Japanese expeditions observed traces of previous melting processes (Yanai *et al.*, 1993); nevertheless, not above 2000 m elevation. This suggests that there are occasional events of temperature increases. The neighborhood of the McMurdo station, where also some collection happened, is more southward, but at the station, on the shore, summer climate is mild. Maybe among all the sites where meteorite collection happened up to now, some in the Trans-Antarctic Mountains would be optimal for survival of contaminated ices.

Anyway, there are sites, not too remote for work, where moderately contaminated water ice remains frozen permanently in the present status of Antarctica. However, meteoritic falls are rare events, and the collected meteorites have been accumulated for a long period. So palaeotemperatures should be briefly discussed, which will be done in the next Chapter.

6) Chances of recognition

For pure water ice the meteorite cannot be identified. Stones covered by ices (as the Zsadány and Dharmasala meteorites) can be identified after collecting, but it is hard to find among similar terrestrial ice. A possibility of identifying NH₃-containing ices on site by reflection spectrum is under investigation by the authors. There exists a proposition for an electric (induction) measurement on ice fields (Földi *et al.*, 1995) to detect the presence of contaminating matter in water ice. However, we must admit that the outward similarity of the ice meteorite and the icy environment is a serious problem reducing the probability of collecting such meteorites.

However, assume that an ice block has been collected. Now, how can it be identified it as an icy meteorite?

A water ice block without stone core is of course hardly distinguishable from native Antarctic ice. Extraterrestrial origin, if suspected, can be checked by analysis of trace elements.

If it contains a stony core, then it can not be originated at the Antarctic interior, where native stone is absent. (True, some 10 of the more than 3000 analyzed Antarctic meteorites are (pre)classified as "terrestrial"; none has yet a bulk composition analysis (Yanai *et al.*, 1995). Their presence is unexplained up to now.) A possibility is some Antarctic ice coating of a stony meteorite. We cannot calculate the chances of such a process; however the fine chemical analysis of the water ice may help.

Contaminated ices need some attention according to the contaminant, as follows below.

Carbon dioxide of course contaminates all terrestrial waters, but its atmospheric concentration is 0.03%; therefore, only moderate CO₂ content is expected if the origin was terrestrial.

Free dicyan and hydrogencyanide are absent in natural terrestrial environment.

Methane can contaminate water in swamps, but the Antarctic interior lacks swamps in the last 5 million years. Hydrocarbon fuels may contain methane in small amounts, but previous spilling of oil-based fuels can be detected.

Ammonia is not totally absent in natural environments. E.g. some bacteria produce it from decaying organic matter. This situation is absent, however, in the Antarctic interior. The urine of lower animals contain a substantial quantity of ammonia; but higher animals convert it mainly to carbamide in urine, and in the Antarctic interior lower animals are

absent. True, mammal urine does contain some ammonia, but never without dominating carbamide. So if there was ammonia content without carbamide, then the ice cannot originate in the Antarctic interior.

5. ON ANTARCTIC PALAEOTEMPERATURES

Antarctica is in her southern polar position since Mesozoic (*Plumer and McGearry, 1991*). However after the mid-Permian glaciation (*Koppány, 1996a; Koppány, 1996b; Bérczi and Lukács, 1997*) Antarctica was free of permanent ice until mid-Pliocene, cca. 5.5 Ma ago. Antarctic icefields started with the Plio-Pleistocene glaciation. This period we survey retroactively.

We are in the Flandria interglacial after the Würm glacial. On large scale, the present temperatures are the highest at least after the start of Würm II, some 65,000 years ago. True, in Europe a temperature peak existed between 5500 and 3000 BC (*Clark, 1969*), but even then the temperature was higher in Western Europe by a mere 2.5°C.

Before Würm II we are out of the C14 horizon, so the chronology is obscure. Ice samples from NW Greenland (*Koppány, 1996b*) suggest, however, quite mild climate, comparable to present, between Würm I and II. Maybe so far the Würm was the coldest glacial period, so the Riss/Würm interglacial may well have been warmer than the present climate (*Zeuner, 1959*). So the present Antarctic temperatures are not representative before 65,000 BC. Note that the last melting obliterate all earlier ice meteorites (for irreversible processes see e.g. *Lukács, 1992*), and that time melting was possible except the very deep interior. Also, ice blocks are not supposed to have retained their identities in icy environment during long times and meteorological oscillations. So the beginning of the Würm is practically the absolute time horizon for the icy meteorites.

6. CONCLUSIONS

The aim of this paper is to call the attention to search for icy meteorites. By definition, an icy meteorite is a block of extraterrestrial ice in collision course with Earth which survives until the surface. We enumerated arguments:

- Such blocks on collision course may be frequent. Indeed, there are ices in the outer solar system (it is observed on moons and in comets); and they may survive some time even at 1 AU.
- During atmosphere crossing their relative mass loss is greater than that of stones but still comparable. So reasonable blocks can survive the deceleration.
- In the Antarctic interior the icy meteorites may remain frozen for a long time.
- A recovered piece can be identified by e.g. contaminants lacked in the Antarctic environment.

We cannot reliably estimate the finding probabilities since ice on ice is not too conspicuous, and also interactions may happen between terrestrial ice, snow as well as rime and the ice meteorite. However, until this factor undergoes detailed analysis, it is useful to keep in mind the suggested meteoritic class.

As for possible earlier observations, we listed two last century meteorite falls, at Zsadány and Dharmasala, when the stones just after fall were cold as if an ice coating had

preserved them from heating. In addition we mention that an original ice coating would be a possible interpretation for some doubtful pieces of the Asuka-87 meteorite collection (from the Asuka Station vicinity, Antarctica). We close the conclusion with this suggestion.

A review article (Yanai, *et al.*, 1993) tells that the Asuka-87 meteorite collection "also includes doubtful pieces which appear black or dark brown in color, like deeply weathered H chondrites. However, there is no distinct fusion crust on their surfaces". Now, if we look through the description of the collecting process, it is said that in the beginning of 1988 more than 100 pieces were collected around Mt. Balchen (Antarctica) "with or without fusion crust". Now, according to the map of the description, the Mt. Balchen area is between 1200 and 1800 m elevation, and the collecting party saw definite traces of melting in the area, mostly below 1500 m.

So assume that an ice block with embedded stones (just as in comets) landed in the Mt. Balchen area. Then the next melting process eliminated the ice cover and the stone remained, of course without fusion crust. If the meteorite came from a comet, then the stone is probably chondritic, just as found. A comparison of the doubtful Asuka-87 chondrites and the Zsadány fragments might be edifying.

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APPENDIX: THE CONTEMPORARY REPORT ON THE ZSADÁNY METEORITE FALL

Here we partially translate the scientific report on the Zsadány event immediately after the fall. The text is the paper of Krenner (1875), cited in the References. We, for the readers, give numbered notes in due course. Special attention will be given to the cultural background of eyewitnesses, because reports from stones falling from heavens may be colored by religion, superstition, etc. The time of the event was 7 years after introducing obligatory schooling in Hungary. This means that the middle age observers may or may not have got regular school education. Who had got, got it in a ground school of the local church because this was the general situation in last century Hungary in villages. Therefore the two main indicators of the cultural background of the Zsadány eyewitnesses are their religions (Temes County was a mosaic of religions) and profession. As for the latter one, the overwhelming majority of the village were farmers, not mentioned henceforth.

The investigation was made by the Royal Hungarian Society of Natural Sciences, not to be confused with the Hungarian Academy of Sciences. It was a scientific organization for propagating the science; the investigators were geologic experts. One of them, J. Krenner (1839-1920) was Professor of Mineralogy and Geology at the Pázmány University, Budapest, Chief Curator of the Mineral Collection of the National Museum, etc., Fellow of the Hungarian Academy of Sciences, discoverer of a string of minerals, as semseyite, kornelite, szomolnokite, andorite, lorandite, warthaite, fizelyte and schafarzikite. His name is commemorated by krennerite, a gold-telluride-sulfuride. So he was no doubt an expert mineralogist. The society had a monthly journal *Természettudományi Közlöny*, still in existence, in which they published the report.

The event happened on 31st March, 1875. The first report of the Lord Lieutenant of Temes County (*Fig. 4*), reached the Society on 14th, April, and the Society sent two investigators to the site on the same day. They arrived at Zsadány on 16th, April. Hence come the relevant parts of the original report (Krenner, 1875), orally given on 21st April in the Society. Some stylistic features of the text may be strange for the reader in English, but we wanted to give a translation as close to the original as possible.

"Zsadány¹ is a village on the Temesvár-Arad line², near Merczifalva, east of it. The houses are built on clay soil, covering sand and pebbles. The houses form a rectangle, whose eastern side goes northwest. The meteorites fell into the easternmost houses and on the neighboring meadows and ploughlands.

In the house of N° 202³, of Birejeszkú Paszku^{4,5} the owners' wife Birejeszkú Maricza and mother-in-law with Plesuné⁶ Djúla were working directly before the kitchen door, in the garden - this was between 3 and 4 o'clock p.m. - when sounded first a strong cannon boom, followed by musketry rattle and then by an uproar⁷ as if the whole sky were to boil. The frightened women looked up to north, whence the terrible noise came, and Mariucza stepped aside. Just then a stone fell to the soil, just to the place where Mariucza had stood before, and went into the tough clay soil. They instantly took the black stone, which emanated a strong sulfuric stench⁷. The stone was quite cold⁸, and Plesuné adds: icy cold. Later the sulfuric stench filled the whole garden, and became strong⁹. According to them the sky was quite clear with only a few small clouds. Fire phenomena were not observed on the sky. (The stone were sent to the Lord Lieutenant)

Márku Thoma, owner of the next house (N° 203) found later, on the 4th or 5th day after the fall, in his garden at the fence a stone which still had sulfuric odor¹⁰. The stone has been acquired by us. It fell 80 steps west of the previous one; half of it were in the soil.

Argyelánu Lázár, owner of house N° 128, was just working in his garden when became frightened by a very strong thunder above; this was followed by musketry roars, afterwards started a noise, which he can compare

best to the noise of railway train¹¹; then some steps from him a stone fell to the unhoed garden soil; a small dust cloud showed the place. Argyelánu Lázár instantly took the black stone of strong sulfuric odor; it was quite cold, which fact is corroborated by Szerbován Pével¹² as Szalka, and his wife Szanda, who had been just present and took also the stone into hands. This stone fell from the previous ones southwest, cca. 360 meters.

Spatario Constantin¹³, owner of house N° 145 and his son Péter¹⁴, both very open-minded and intelligent persons, tell that first happened a very strong cannon roar, then a musketry crack, followed in a little while by a special whistle; at the end of this a black stone fell into the garden on a chaff pile. Spatario Constantin and his son Péter instantly took the stone and it was quite cold as corroborated the housewife Spatario Florea¹⁵, present at the fall. In cca. half a minute a second, much smaller stone fell; taken also instantly, but it was not warm either. In both cases, there was a strong sulfuric odor. The chaff was not burnt or parched. We asked him¹⁶, if he had known, how long is half a minute, and he answered that he knew how long is a minute and between the two falls one could have counted roughly to 30¹⁷. The sky was clear, with rare white clouds, of which an oblong fleecy cloud was remarkable. But this cloud did not move and Spatario does not consider it to have been in connection with the meteorite fall. The fall happened between 3 and 4 o'clock¹⁸, nearer to 4. The daughter of the owner, Zsófia¹⁹, very intelligently mentioned that she had read a few weeks ago that sometimes stars fall to the earth, so when heard of the fall, she ran out asking her brother whither the star had fallen, and when he - with the stone in his hand - was just starting to show, fell the second piece, then Zsófia became so frightened that she ran into her room, was afraid to leave it during the afternoon, and being unable to dine anything.

The methodical investigation was made on 17th, Saturday, in a manner of a hunt, with some 30 men. We combed the vineyard, and also the northern and northeastern meadows and ploughlands. In spite of the statements of shepherds that they had heard there stones to fall, only a very small but complete meteorite was found by Gyuro Akim, on the meadow, 60 steps east from the Birejeszku house.

The thunder was heard in two neighboring villages, Szécsány and Orczyfalva²⁰, but not at Vinga²¹. Fire phenomena were not seen from these villages, as none of them from Zsadány.

In general, on the site, up to now²², the fall of nine meteorites have been verified. From them 6 have gone into the property of the Roy. Hung. Society of Natural Sciences, and 3 pieces are in property of other certain persons.

The stones found up to now are not too large, hardly nut sized; their shapes are either rough spheroids, wedge or tablet forms. Their material is grey, trachyte-like, with many scales of blinking white (probably nickel-iron), with a black crust, somewhere rugged somewhere shiny²³. The material is very similar to that of the Knyahinya meteorites²⁴. The big thunder, terrifying not only humans but the animals as well, makes it very probable that bigger blocks fell also, but they, just as at Knyahinya, went into the soil, whence they will reappear during plowing or hoeing²⁵.

The definitely verified fact that the falling bodies, at least at touching the earth, were cold, it is very remarkable. Not stressing the expression "icy cold", it can be regarded as an established fact that these meteorites, when entered Zsadány and became terrestrial, were not warmer than the air temperature, then still rather low²⁶. I do want to definitely stress this fact, in contrast to the cases when the higher temperature of the fallen meteorites were proven."

Here we stop with the text; the end contains mainly conclusions and acknowledgments, of which we only mention that of the helping activity of the village notary, Mosiescu Mózes²⁷, who seems to have escorted them in the village and who, by all probability, translated the Romanian answers²⁸.

We do not want to influence the readers. However, we state a few simple observations. The coldness of 4 meteorites is stated by 3 groups of eyewitnesses. It has nothing to do with Greek Orthodox popular religious ideas, it was reported by eyewitnesses of 3 different ethnic groups, and the reports were left without comment by the local clerk of different religious ideas. Therefore, it is either a fact, or a hoax in which the whole village participated, including the merchant, and, what is more, the notary. Now, the latter one was a member of the state administration, nominated by authorities well above village level, therefore he would have been afraid to misguide the emissaries of a nation-wide scientific society founded by a royal decree, who carried a recommendation letter from the Lord Lieutenant, and were accompanied by the local sheriff. In addition, the hoax would have been pointless. The village was not interested in tourism, and the population did not sell strange meteorites.

The observations clearly show missing mass, never found, and the lack of celestial fireworks suggests that the surface temperature during fall remained under 1000°C. The only fact contradicting the fall of ice-covered stones is the (partial) shiny crust of some meteorites, which may be fusion crust. So a reanalysis of the event would be useful; however, note that a fusion crust is incompatible with the coldness, corroborated by 4 groups of observers.

To our knowledge, no results of new investigations about the Zsadány meteorites were published since 1882. We have performed a preliminary visual study of the piece L 377. It is an average-looking small meteorite. The crust is rather dark, nearly black, but only partial, covering cca. 2/3 of the surface. The stone is rather shapeless, and its surface is not smooth, unlikely to river pebbles. A number of protuberances appear on its surface.

Now, the crust is thin, and quite uniform in width. It closely follows all the protuberances of the surface, and no trace of flow of molten material can be seen. Therefore, it seems as if the surface had not been molten for longer times. Either we see the result of a very superficial melting, or that of oxidation in solid state, or that of some chemical processes in the prehistory. As for the areas, not covered by crust, they might have been formed by fragmentation. However i) the meteorites were reported to have fallen to earth or to vegetation; ii) no irregularities of the material are seen on the supposed breakup surfaces. So the fragmentation would remain without explanation.

No more can be told without a detailed reanalysis which needs time. Note that even if the crust of the L 377 piece was fusion crust, the matter would not be settled. Namely, the contemporary report does not say that all the Zsadány meteorites were cold. It reports 9 pieces to be found and mentions 4 cold at fall: one in the Birejeszkú, one in the Argyelán, and two in the Spatario gardens. The report mentions 2 stones found days after in the soil: one in the Márku garden, and one found by Gyuro on the meadows. These two may or may not have been hot at the fall; and we do not know anything about the remaining 3 pieces. In addition, no document exists to state which one has been catalogued as L 377. So, even if 4 pieces had thick ice coatings, nothing can be told against such a scenario in which the coating of the future L 377 was thin, completely evaporating during fall and so leaving the stone exposed to friction heating for a short time.

We close by drawing attention to a point in the narration of Argyelánu. He saw the stone falling, and instantly took it. Now: it was cold, sulfurous in odor and black. Either the eyewitness remembered falsely, or the stone had got its black color earlier than the fall at cca. 3.30 p.m., on 31st March, 1875.



Fig. 4 Map of Hungary in 1875, when the Zsadány Meteorite fell. Five other famous meteorite sites are also marked, namely Knyahinya: the most massive, Nyírábrány: the most recent, Mocs: the most numerous, Mezömadaras: the most cited and Kaba: the most organic.

NOTES TO THE APPENDIX

1. Present official name is Jadani, Romania. The pronunciation is the same, only the orthography has been Romanised.
2. Present official names Timisoara and Arad, Romania.
3. In small villages the houses were simply numbered for postal and administrative identification.
4. The names mentioned in the village are predominantly Romanian. In Temes County that meant to belong to the (Romanian) Greek Orthodox Church, whose administration shifted in those years from Cyrillic to Latin letters. So, for all probability the names are Hungarian transliterations of the original forms by Cyrillic letters. Also, we may expect that the overwhelming majority was educated in Greek Orthodox ground schools, if at all.
5. In Hungarian the first name is the family name. As an example, present Romanian texts would write the names of the Birejeszkú's as Pascu and Mariuta Bireiescu.
6. The suffix means that she was the wife of a Plesu.
7. This sulfuric stench will be repeated in the reports of eyewitnesses. It is not detailed. It may mean brimstone stench of something originated from Hell (but see the next Note), but the farmers may simply remember to sulfur vapors using for cleaning wine barrels.
8. So she could not believed it coming from Hell. Then the "sulfuric" stench was a real stench.
9. Sulfuric volatile deliberated? No explanation has been found up to now which is compatible with the coldness reported.
10. Again the "sulfuric" odor. Suggestions are welcome.
11. Railway lines reached the region some years before.
12. This name is clearly Serb. It means to be Greek Orthodox. Generally the Romanian and Serbian Greek Orthodox Churches were separated in Hungary, and Greek Orthodox churches used native languages in the rites even in the last century. We do not know, however, if there were a separate Serbian Church or school in Zsadány. The village was rather small.
13. This name is Greek. It is transliterated to Latin, not to Hungarian. According to the economic structure of the region he was probably the local merchant, and his family was literate. The Greek Greek Orthodox Church was quite separate from the Serbian and Romanian Greek Orthodox Churches.
14. The son's second name is written in Hungarian form.
15. Her second name is Romanian.
16. I.e. Spatario Constantin.
17. This definite statement suggests an extended source or a complicated fragmentation.
18. P.m.
19. The Hungarian form of the Greek name Sofia. The Hungarian forms of the children' names indicate that the interview with them happened in Hungarian. Greek and Armenian merchants of the region were multilingual.
20. The distance from Zsadány is 6 and 10 km, respectively.
21. 12 km from Zsadány. All 3 villages lie at north or northeast from Zsadány. The big city Temesvár with newspapers, journalists etc. was nearer than 20 km on the south, and nothing was reported.
22. I.e. 21st April, 1875.
23. This statement is not detailed any further. The shiny crust may or may not be fusion crust, but the rugged one may hardly be.
24. Ung county, now in Ukraine. The biggest observed meteorite event in Hungary, in 1866. Some 900 kg of fragments were found.
25. They did not reappear. No further meteorite was reported from the site, in spite of the attention. In the 1882 review article (*Török*, 1882) the new pieces should have been mentioned and they were not.
26. At the beginning of spring.
27. From the name probably of Israelite religion, which, according to this and to his office of a schooling, differs from that of the village people. Village notaries were nominated by higher authorities on the ground of being able to administrate, both on local language and on Hungarian, for communication with the county offices. Some moderate knowledge of law was needed too.

28. The linguistic problems involved are nontrivial. The text never mentions translation. However it must have happened. Temes County is an ethnic mosaic, and Zsadány was predominantly Romanian. The emissaries' passable Romanian is highly improbable. Romanian is Neo-Latin after a fashion (with more Latin words in Greek Catholic villages, due to the linguistic reforms of Bishop Samuel Micu-Klein of Balázsfalva), but cannot be understood via Latin, and contemporary popular Greek (Dimotiki) is very hardly understood via Classical Greek. But the male population of the village may have had a partial ability in Hungarian and German, from military service and because of the big city Temesvár at 20 km (where the dominant languages were German, Hungarian and Serbian). Probably the notary (whose family name indicates Romanian as first language) translated, but the subjects were possible to follow the translation partially. If they did not correct, the translation was considered exact.