Thermal decomposition of MgCO₃ during the atmospheric entry of micrometeoroids

G. Micca Longo[1] and S. Longo[1,2]

[1]*Department of Chemistry, University of Bari, via Orabona 4, 70126 Bari, Italy email: savino.longo@nanotec.cnr.it*
[2]*CNR-Nanotec, via Amendola 122/D, 70126 Bari, Italy*

Abstract: In this paper, a first study of the atmospheric entry of carbonate micrometeoroids, in an astrobiological perspective, is performed. Therefore an entry model, which includes two-dimensional dynamics, non-isothermal atmosphere, ablation and radiation losses, is build and benchmarked to literature data for silicate micrometeoroids. A thermal decomposition model of initially pure magnesium carbonate is proposed, and it includes thermal energy, mass loss and the effect of changing composition as the carbonate grain is gradually converted into oxide. Several scenarios are obtained by changing the initial speed, entry angle and grain diameter, producing a systematic comparison of silicate and carbonate grain. The results of the composite model show that the thermal behaviour of magnesium carbonate is markedly different from that of the corresponding silicate, much lower equilibration temperatures being reached in the first stages of the entry. At the same time, the model shows that the limit of a thermal protection scenario, based on magnesium carbonate, is the very high decomposition speed even at moderate temperatures, which results in the total loss of carbon already at about 100 km altitude. The present results show that, although decomposition and associated cooling are important effects in the entry process of carbonate grains, the specific scenario of pure $MgCO_3$ micrograin does not allow complex organic matter delivery to the lower atmosphere. This suggests us to consider less volatile carbonates for further studies.

Introduction

Inorganic carbonates play a very important role when meteor matter is considered in an astrobiological context (Fonti *et al.* 2001; Orofino *et al.* 2009; Blanco *et al.* 2013, 2014; D'Elia *et al.* 2016) and the knowledge of their physical and compositional properties in meteorites may also provide information about the presence of organic matter in their parent bodies (comets, asteroids, interplanetary dust). Indeed, carbonates are often associated with the presence of organic matter (Flynn *et al.* 2000; Pizzarello *et al.* 2006; Matrajt *et al.* 2012), so, in this perspective, they could be one of the keys to understand the complex chemistry of the Solar System (Flynn *et al.* 2003). In particular, they have been found in Mars meteorites (Borg *et al.* 1999; McKay *et al.* 1996), on the surface of Mars (Orofino *et al.* 2000; Boynton *et al.* 2009; Palomba *et al.* 2009), on the surface of Ceres and Vesta (Rivkin *et al.* 2006), as well as in cometary dust (Busemann *et al.* 2009). (Mg,Fe)CO₃ (the carbonate analogue of the Forsterite–Fayalite series) is common among phyllosilicate-rich micrometeorites and CI chondrites and has been reported as well in micrometeorites (Noguchi *et al.* 2002). Carbonates of II group elements (in particular aragonite and calcite) have been detected spectroscopically in cometary grain in close association to complex organic molecules (de LEUW *et al.* 2010; Yabuta *et al.* 2014). In the Martian meteorite ALH 84001, magnetite nanocrystals showing some analogies with those produced by magnetotactic Earth bacteria have been found into a carbonate matrix (McKay *et al.* 1996, 2003; Thomas-Keprta *et al.* 2009) refreshing the interest in panspermia theory, according to which life forms could spread from planet to planet carried by ice or mineral matter. In a weaker version of this theory, life templates (complex biomolecules, mineral catalysts to nucleic acid polymerization) might have survived during the atmospheric entry. In (Bisceglia *et al.* 2016), the facile decomposition of magnesium carbonate has been advocated as a possible cooling mechanism during delivery scenarios of organic matter to primordial Earth. The issue of complex organism survival during atmospheric entry has also been investigated in the STONE experiment series, where several rock materials, including sedimentary rocks, were subjected to real entry tests on the surface of the thermal protection systems of a FOTON capsule (Foucher *et al.* 2010; Parnell *et al.* 2011). These experiments, because of their nature, cannot however consider real entry speeds for comet grains (being limited to orbital speed) and microscopic particles, which need be addressed by computer simulations.

In spite of this state-of-the-art, there has been little attention to the thermal properties of carbonate minerals in the context of meteoritic studies, in particular to assess their behaviour when grains rich in carbonates enter Earth's atmosphere. It is

true that the thermal decomposition of carbonates is poorly characterized from a kinetic point of view (Rao 1996; L'vov 1997; Lvov 2002). While this difficulty is hardly overemphasized, times are mature to start a rigorous theoretical study of the behaviour of pure and mixed carbonates in atmospheric entry scenarios, in order to gather the essential information on which future evaluations will be grounded.

Therefore, in this paper a preliminary work for a specific material (pure magnesite), based on a rigorous dynamic and thermal model of the grain entry, is presented and a first-attempt model of the decomposition kinetics is proposed. The critical hypothesis, on which this first model is based, is as much as possible carefully described.

Theoretical background

Thermal effects experienced by micrometeoroids entering Earth's atmosphere have been intensively studied (Love & Brownlee 1991; Opik 2004) and these results have been preliminary reproduced by the authors assuming a silicate composition. Then, in view of the presence of Mg in carbonates and the predominance of Mg in silicates, pure magnesite ($MgCO_3$) is proposed as a mineral model. This mineral is much more sensitive to the high temperatures reached during an entry process, compared with silicates, due to facile decomposition into MgO and gaseous carbon dioxide.

Realistic entry conditions need be simulated in order to assess the contribution of chemical decomposition to the power balance of the grain. We have developed a dynamic-kinetic model, very close to that reported on (Love & Brownlee 1991) although improved in some minor details, and used it as a standard description of the entry process in order to evaluate the effects to carbonate evaporation kinetics. Actually we used the same set of entry parameters of the cited paper, since this allowed a benchmarking of our computer code for silicates and a clear, comprehensive comparison between carbonates and silicates.

The model has two equations for two Cartesian components of velocity in the vertical entry plane xy (parallel to initial speed and through Earth's centre; v_y is assumed positive when moving towards the Earth) and includes the effect of gravity and drag forces, i.e.

$$m\dot{\mathbf{v}} = \mathbf{f}_D + \mathbf{g}. \tag{2.1}$$

Assuming hundred-µm-sized dust grains, the interaction of the grain with the atmosphere is always direct, with no effect due to hydrodynamics or shocks, and the radiation power from the atmospheric and evaporated components is negligible. Therefore, considering a spherical particle moving in a hypersonic molecular flux, the drag force can be estimated as usual by

$$f_{Dx} = -\pi r^2 \rho_{atm}(d) v_x v, \tag{2.2}$$
$$f_{Dy} = -\pi r^2 \rho_{atm}(d) v_y v, \tag{2.3}$$

where r is the grain radius, v is velocity magnitude and $\rho_{atm}(d)$ is the standard atmospheric density as a function of the distance d from the ground $d = (x^2 + y^2)^{1/2} - R_{Earth}$.

The gravitational acceleration is given by

$$g_x = -g \frac{x}{d + R_{Earth}}, \tag{2.4}$$

$$g_y = g \frac{y}{d + R_{Earth}}. \tag{2.5}$$

In this way, the Earth curvature is accounted as appropriate in the case of grazing entry. The initial values of v_x and v_y are given from the initial speed v and entry angle θ defined in such a way that

$$v_y(0) = v(0) \cos \theta.$$

Regarding the function $\rho_{atm}(d)$, this model uses an actual atmospheric density profile: a fit of the atmospheric density (from 600 to 10 km), as a function of the distance from Earth's surface, has been calculated; data have been collected from the empirical model in (Rees 1989) [equation (2.6) and Fig. 1].

$$\begin{aligned}
\rho_{atm}(d) = \exp[&-7.39 \times 10^{-1} - 2.63 \times 10^{-5} d \\
&- 3.03 \times 10^{-9} d^2 + 2.83 \times 10^{-14} d^3 \\
&- 1.16 \times 10^{-19} d^4 + 2.44 \times 10^{-25} d^5 \\
&- 2.62 \times 10^{-31} d^6 + 1.12 \times 10^{-37} d^7],
\end{aligned} \tag{2.6}$$

where d is in metres and $\rho_{atm}(d)$ in kg m^{-3}.

Concerning heating effects (Love & Brownlee 1991), air molecules give all their energy to the micrometeoroid entering Earth's atmosphere, so the power P_{in} delivered as heat to the particle is the rate at which the kinetic energy is deposited into it:

$$P_{in} = \frac{1}{2} \rho_{atm} \pi r^2 v^3. \tag{2.7}$$

The input power is balanced by radiation, vaporization and other mechanisms. In our case, radiative and evaporative energy losses are taken into consideration:

$$P_{in} = 4\pi r^2 (\epsilon \sigma T^4 + H_v C p_v \sqrt{m_{mol}/T}), \tag{2.8}$$

where ϵ is the body's emissivity, σ is the Stefan–Boltzmann constant, T is the temperature, H_v is the latent heat of vaporization, C is 4.377×10^{-5} (cgs units), p_v is the vapour pressure, and m_{mol} is the molecular weight.

Our numerical code is able to calculate the equilibrium temperature at which the sum of radiative and evaporative energy losses equals the input power by means of a binary algorithm: it starts from a 'guess temperature' of 1500 K and it adapts it with a 'jump' that is progressively halved until the best matching of the values of P_{in} given by the previous two formulae is obtained.

Temperature gradients and heat conduction are not important processes for micrometer particles considered here. In addition, we assume that evaporation takes place in vacuum.

Evaporation affects both particle's temperature and mass. In particular, it is possible to evaluate mass loss rate:

$$\dot{m} = 4\pi r^2 C p_v \sqrt{\frac{m_{mol}}{T}}. \tag{2.9}$$

The updated radius r is calculated from the mass using the known material density.

Evaporation kinetics

Silicates

Although this paper is devoted to the new case study of carbonates, the silicate evaporation law is included to provide a full compatibility with (Love & Brownlee 1991) for benchmarking and to provide a comparison of the cooling channels (Section 4).

Accordingly, following (Love & Brownlee 1991; Opik 2004), we assume that the vapour pressure of silicates follows the simple law:

$$\log p_v = A - \frac{B}{T}, \tag{3.1}$$

where A and B are constants and T is the temperature. Opik (2004) finds the values of A and B to be respectively 10.6 and 13 500, in cgs units. Mean molecular weight of the evaporate components for condritic micrometeoroids is 45.

Carbonates

Here we present the first attempt to explore, by means of a numerical model, the phenomena associated to carbonate grain atmospheric entry. Accordingly, the largest part of the development is connected to the thermochemical aspect: how to capture the main characteristics of a carbonate grain, which, in the course of the process, changes not only its temperature, but also its mass and average chemical composition.

As it is well known, carbonates undergo facile decomposition into CO_2 and oxide when heated in vacuum, due to the gain in lattice energy when the bulky carbonate ion is replaced by the small oxide ion. In the course of the entry process, the grain composition is therefore expected to be enriched in oxides at the expense of the initial carbonate content. In this respect, we have elaborated a model based on a well-mixed and ideal solid mixture, which is highly questionable, but allows a first evaluation of the grain behaviour. This model can be resumed into the following assumptions:

- pure $MgCO_3$ grain enters the atmosphere;
- the Langmuir law is assumed to be valid, based the vapour pressure calculated using thermodynamic data for $MgCO_3$, MgO and CO_2;
- the grain temperature is uniform; furthermore, the temperature is, at any time instant, equal to the stationary temperature of the equation (8) balance;
- the vapour pressure of the solid mixture $MgCO_3$/MgO follows Raoult's law;
- there is no limit for CO_2 diffusion inside the grain;
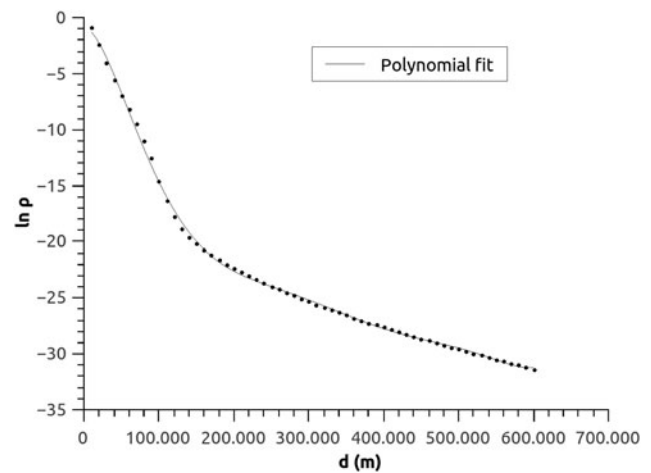

Fig. 1. Atmospheric density fit (kg m^{-3}), using equation (2.6) of data from (Rees 1989).

- mass loss and evaporation can continue until complete stoichiometric conversion to MgO is reached.

In literature, carbonates in meteorites and micrometeorites account for a very small amount of the total volume, not for the entire bulk. Here we are considering a rough model for a carbonate micrometeoroid in order to assess its behaviour during the atmospheric entry. Actually, an 'artificial' bulk carbonate meteorite has been considered in the STONE experiment in (Brack *et al.* 2002). The weakest assumption of the model is that the diffusion of CO_2 is unhindered, corresponding to highly porous material. Under such hypothesis, however, the vapour pressure of the well-mixed solid based on Raoult's law is

$$p_{CO_2} = e^{-\frac{\Delta G_0(T)}{RT}} \chi_{MgCO_3}, \tag{3.2}$$

where χ_{MgCO_3} is the mole fraction of carbonate in the grain and $\Delta G_0(T)$ is calculated using polynomial fits of ΔH_f, ΔS_0 and c_p from (Chase 1986).

χ_{MgCO_3} is calculated using stoichiometry. After introducing m_{min}, the minimum mass in which all carbonate is turned into MgO:

$$m_{min} = \frac{M_{MgO}}{M_{MgCO_3}} m_0, \tag{3.3}$$

where M_{MgO} is the molecular weight of the pure oxide, M_{MgCO_3} is the molecular weight of the magnesite and m_0 represent the mass of the object when it is all composed by carbonate, χ_{MgCO_3} is given by:

$$\chi_{MgCO_3} = \frac{m - m_{min}}{m_0 - m_{min}}. \tag{3.4}$$

Results

The mathematical model described in the previous section has been implemented as a native Fortran code. We found that a solution of the coupled differential equations based on the
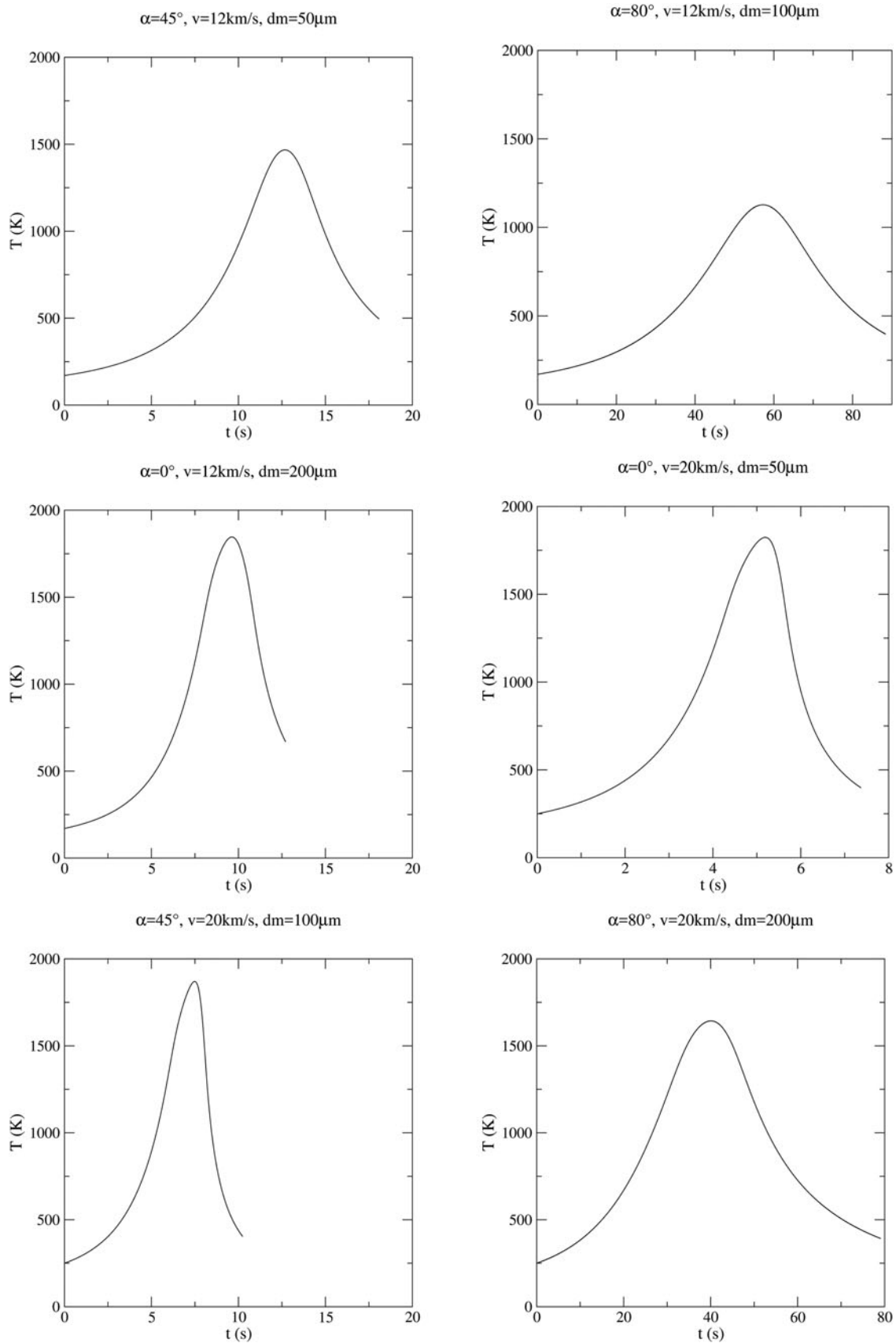
Fig. 2. Thermal curves for different entry scenarios (α is the entry angle, v is the entry velocity and dm is the meteoroid diameter) of a silicate micrometeoroid.
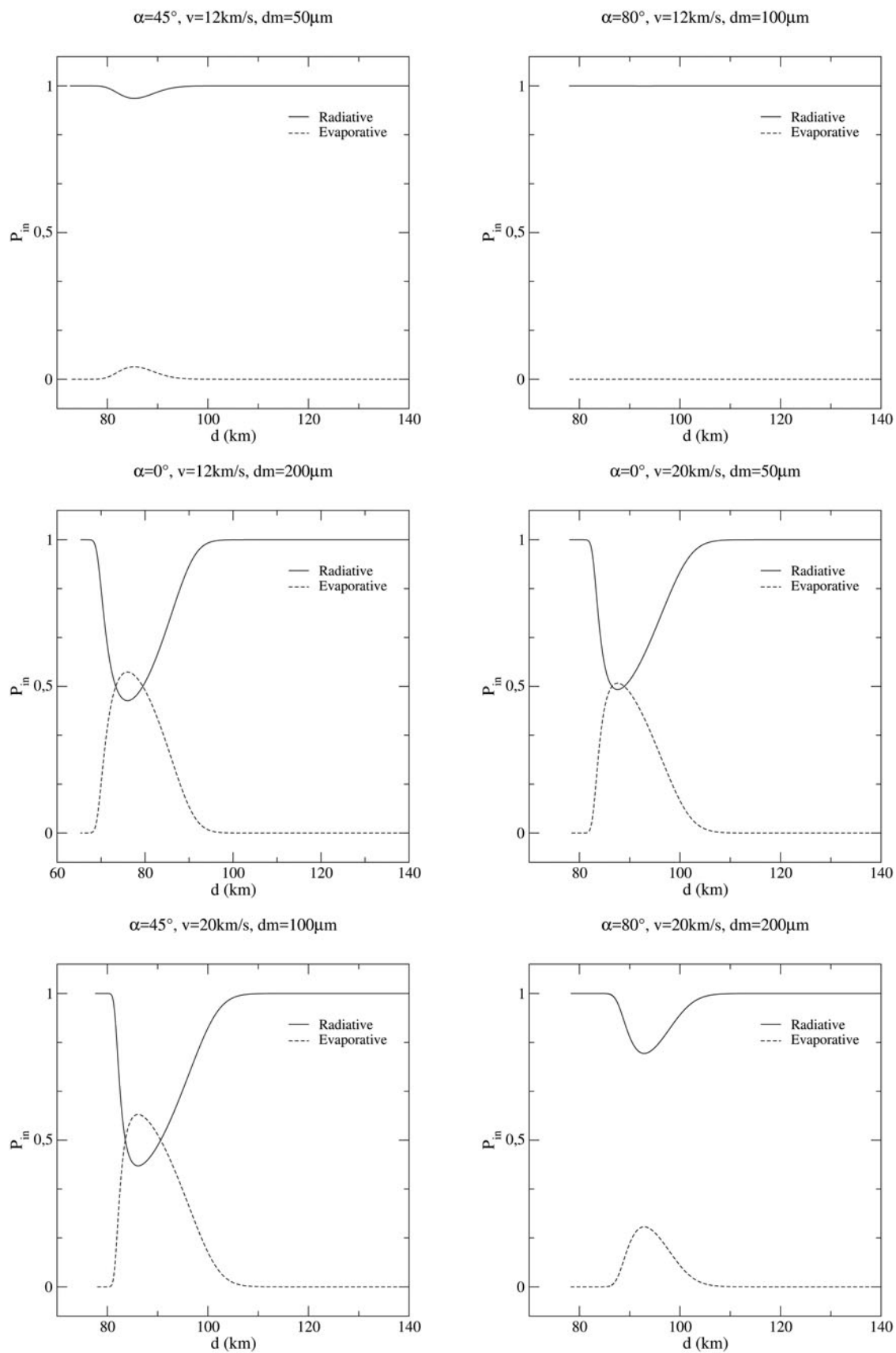
Fig. 3. Radiative and evaporative contributions during the atmospheric entry of a silicate micrometeoroid (α is the entry angle, v is the entry velocity and dm is the meteoroid diameter).
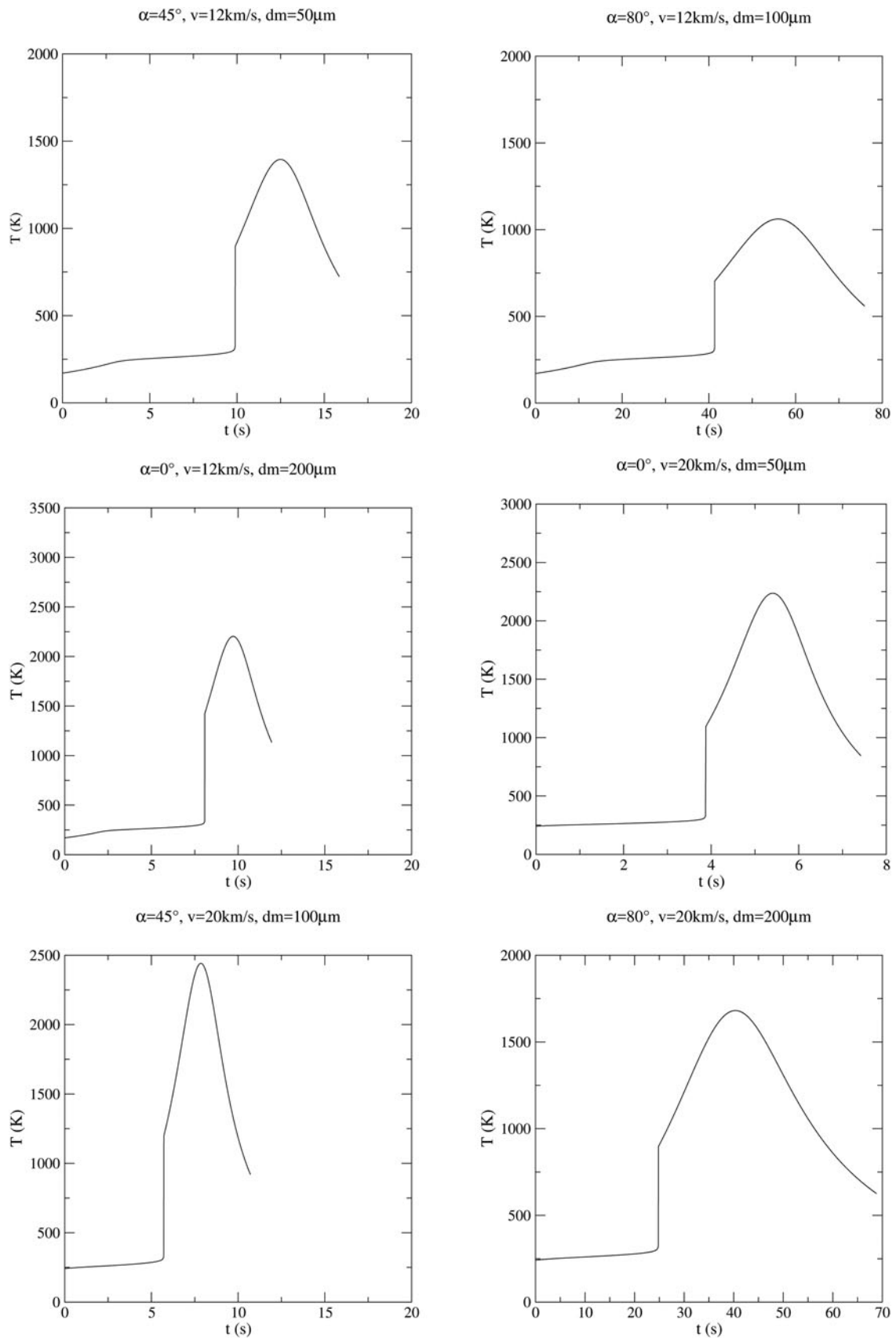
Fig. 4. Thermal curves for different entry scenarios (α is the entry angle, v is the entry velocity and dm is the meteoroid diameter) of a carbonate micrometeoroid.
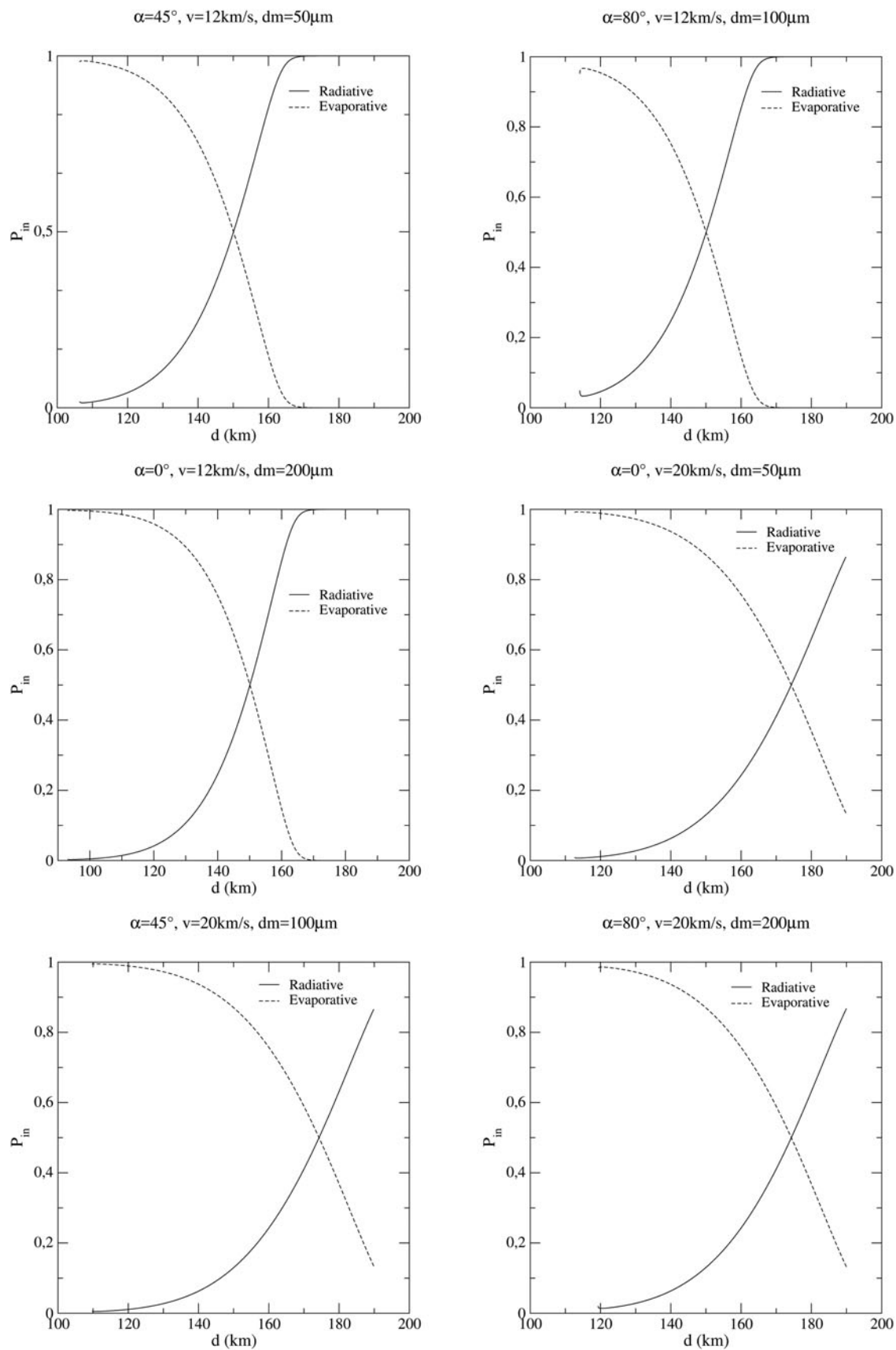
Fig. 5. Radiative and evaporative contributions during the atmospheric entry of a carbonate micrometeoroid (α is the entry angle, v is the entry velocity and dm is the meteoroid diameter).
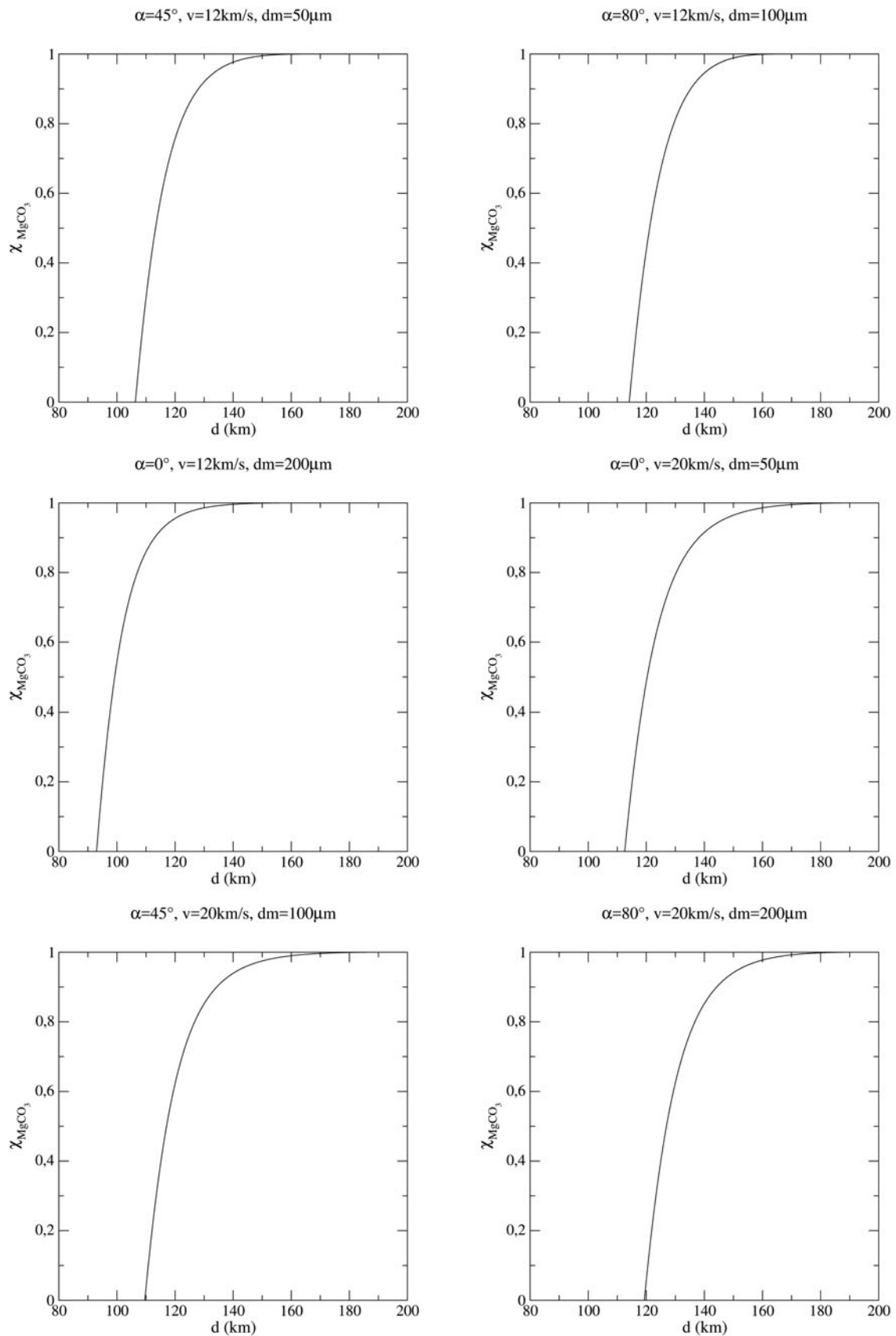
Fig. 6. Amount of MgCO$_3$ during the atmospheric entry (α is the entry angle, v is the entry velocity and dm is the meteoroid diameter).
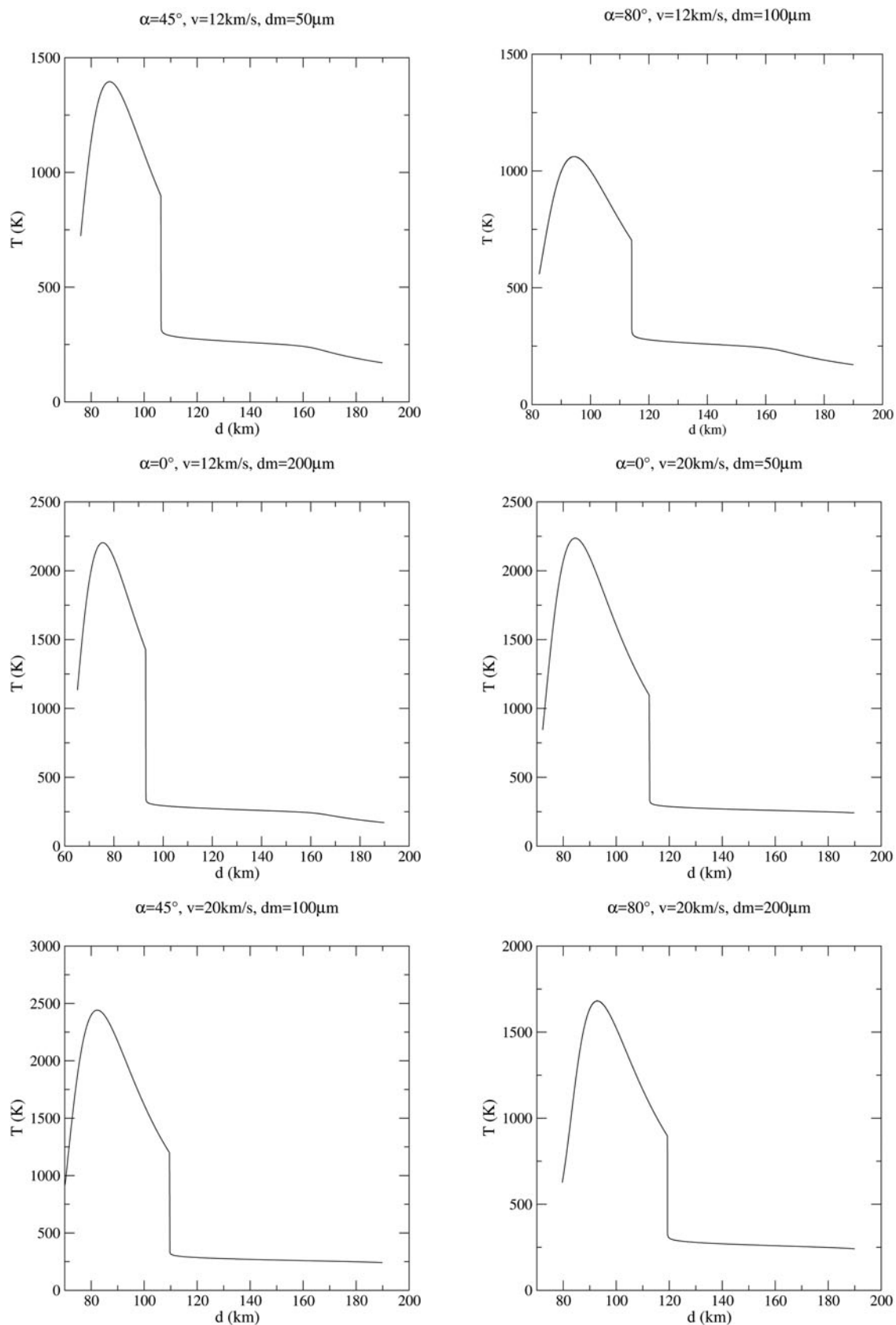
Fig. 7. Thermal curves, as a function of the quota *d*, for different entry scenarios (α is the entry angle, *v* is the entry velocity and *dm* is the meteoroid diameter) of a carbonate micrometeoroid.

simple second-order Leapfrog method is accurate enough. A time step of 1 ms is used in all simulations.

All simulations begin at 190 km altitude, with velocity and entry angles as free parameters. The micrometeoroid material density is set at $3 \, \text{g cm}^{-3}$, both for silicates and carbonates.

Silicates

Different entry scenarios are plotted for a silicate micrometeoroid, in order to focus on the duration of the peak temperature (Fig. 2).

Both radiative and evaporative contributions during the atmospheric entry of a silicate micrometeroid are proposed in Fig. 3, for few entry scenarios.

Carbonates

In Fig. 4, different entry scenarios for a carbonate micrometeoroid are plotted.

These results show that the thermal behaviour of a carbonate grain, at least at the early stage of the entry process, is markedly different from that of the corresponding silicate. Because of the very low evaporation enthalpy of $MgCO_3$ in particular, the evaporation process soon becomes the most important energy dissipation process, thermal radiation being negligible in comparison (see Fig. 5).

Figure 6 reports χ_{MgCO_3} as a function of the quota and shows that CO_2 fully evaporates until the grain becomes pure oxide.

In Fig. 7, the equilibration temperature is plotted as a function of the quota d, under the assumption of unlimited gas diffusion in the grain and full decomposition.

Discussion

Silicates

Our results, on the scale of the plots, are the same as those originally reported by Love & Brownlee (1991) for the same scenarios, showing that our dynamic model is appropriate to provide a comparative study. In the case of silicates, high-peak temperatures of the order of 1500 K are preceded by a steady temperature increase already at early stages of the entry trajectories. This monotonous behaviour is due to the fact that most of the energy is dissipated via black-body radiation at any stage of the entry, as shown in Fig. 3. Evaporation of silicates requires in fact quite high temperatures even in vacuum and can play a significant role only at the temperature peak.

Carbonates

As can be seen from Figs. 4 and 5, the global composition of the original $MgCO_3$ grain changes very fast as the carbonate grain, while entering the atmosphere, gradually release CO_2 and it becomes a solid mixture of carbonate and oxide. When CO_2 is completely evaporated and the grain becomes a pure oxide (Fig. 6), the grain mass does not change anymore and the temperature increases dramatically, only mitigated

by black-body radiation, since MgO is actually much more refractory even than silicate.

As can be seen from Fig. 7, $MgCO_3$ grain will be converted into oxide at altitudes between ~ 90 and ~ 130 km, depending on entry conditions and grain size.

Of course, this result can be affected by a revision of the hypotheses of the model. Nevertheless, as soon as $MgCO_3$ is the material under consideration, the general conclusion of our simulation can hardly be modified substantially. The high volatility of magnesium carbonate produces this thermal scenario.

The approximations made in the simulation, in particular the description of the very poorly known decomposition kinetics, could be replaced by different ones in the future, leading to different results. The weakest one is probably the hypothesis of well-mixed solid, which is hardly actually fulfilled at the low temperatures envisaged by these calculations. Changing this hypothesis would shift the evaporation peak at later times and higher temperatures.

Conclusions

In this paper, we have studied, by using a comprehensive numerical method, several scenarios for the entry into Earth's atmosphere of magnesite grains, in order to evaluate the additional thermal protection offered to organic matter, to which they are frequently associated. The present study assumes microsized grains since this scenario allows a rigorous study on physical basis even without considering fluid dynamics effects, and additionally it makes possible a full validation of the dynamic and thermal part of the model by comparing results on silicate grains with literature.

At the same time, it must be recognized that this scenario is the harshest possible one for this material, since under these conditions the kinetic energy needs to be dissipated fully by the grain surface. Even so, we found that chemical decomposition of magnesite provides so much additional cooling, with respect to silicate grains, to keep very low temperatures at early stages of the entry process, compared to silicate grains. This very strong effect is actually a weakness of the specific material ($MgCO_3$), since a lower volatility would allow thermal radiation to dissipate more energy, while this material exhaust its capability to offer additional cooling quite early, having been completely converted into oxide. Although pure magnesite provides an encouraging perspective for the study of carbonates in space, on the other hand it is not able to guarantee thermal protection throughout the whole Earth atmosphere, considering in particular microsized meteoroids in an astrobiological context.

Future studies should therefore consider less volatile carbonate, like calcite and aragonite. Different scenarios, including fragmentation of a larger body into smaller meteoroids at a lower quota, could be taken into consideration. Finally, the inclusion of a true fluid dynamic treatment will illustrate more realistic results: the air cap (Opik 2004) provided by air fluid dynamics could be one of the key point for offering a thermal protection during the atmospheric entry.

Acknowledgements

References

Bisceglia, E., Micca Longo, G. & Longo, S. (2016). Thermal decomposition rate of $MgCO_3$ as an inorganic astrobiological matrix in meteorites. *International Journal of Astrobiology* 1–7.

Blanco, A., Orofino, V., DElia, M., Fonti, S., Mastandrea, A., Guido, A. & Russo, F. (2013). Infrared spectroscopy of microbially induced carbonates and past life on mars. *Icarus* **226**(1), 119–126.

Blanco, A., Orofino, V., Mancarella, F., Fonti, S., Mastandrea, A., Guido, A., Tosti, F., Russo, F. & D'Elia, M. (2014). Microbialites vs detrital micrites: degree of biogenicity, parameter suitable for mars analogues. *Planetary and Space Science* **97**, 34–42.

Borg, L.E., Connelly, J.N., Nyquist, L.E., Shih, C.-Y., Wiesmann, H. & Reese, Y. (1999). The age of the carbonates in martian meteorite alh84001. *Science* **286**(5437), 90–94.

Boynton, W.V. *et al.* (2009). Evidence for calcium carbonate at the mars phoenix landing site. *Science* **325**(5936), 61–64.

Brack, A. *et al.* (2002). Do meteoroids of sedimentary origin survive terrestrial atmospheric entry? the ESA artificial meteorite experiment stone. *Planetary and Space Science* **50**(7), 763–772.

Busemann, H., Nguyen, A.N., Cody, G.D., Hoppe, P., Kilcoyne, A.L.D., Stroud, R.M., Zega, T.J. & Nittler, L.R. (2009). Ultra-primitive interplanetary dust particles from the comet 26p/Grigg–Skjellerup dust stream collection. *Earth and Planetary Science Letters* **288**(1), 44–57.

Chase, M.W. (1986). JANAF thermochemical tables. *JANAF thermochemical tables, by Chase, MW Washington, DC: American Chemical Society; New York: American Institute of Physics for the National Bureau of Standards, c1986. United States. National Bureau of Standards.* 1.

D'Elia, M., Blanco, A., Galiano, A., Orofino, V., Fonti, S., Mancarella, F., Guido, A., Russo, F. & Mastandrea, A. (2016). SEM morphological studies of carbonates and the search for ancient life on mars. *International Journal of Astrobiology* 1–6.

De LEUW, S., Rubin, A.E. & Wasson, J.T. (2010). Carbonates in CM chondrites: complex formational histories and comparison to carbonates in ci chondrites. *Meteoritics & Planetary Science* **45**(4), 513–530.

Flynn, G.J., Keller, L.P., Feser, M., Wirick, S. & Jacobsen, C. (2003). The origin of organic matter in the solar system: evidence from the interplanetary dust particles. *Geochimica et Cosmochimica Acta* **67**(24), 4791–4806.

Flynn, G., Keller, L.P., Jacobsen, Ch., Wirick, S. & Miller, M.A. (2000). Organic carbon in interplanetary dust particles. In *Bioastronomy 99*, vol. **213**.

Fonti, S., Jurewicz, A., Blanco, A., Blecka, M.I. & Orofino, V. (2001). Presence and detection of carbonates on the martian surface. *Journal of Geophysical Research: Planets* **106**(E11), 27815–27822.

Foucher, F., Westall, F., Brandstätter, F., Demets, R., Parnell, J., Cockell, C.S., Edwards, H.G.M., Bény, J.-M. & Brack, A. (2010). Testing the survival of microfossils in artificial martian sedimentary meteorites during entry into Earth's atmosphere: the Stone 6 experiment. *Icarus* **207**(2), 616–630.

Love, S.G. & Brownlee, D.E. (1991). Heating and thermal transformation of micrometeoroids entering the earth's atmosphere. *Icarus* **89**(1), 26–43.

L'vov, B.V. (1997). Mechanism of thermal decomposition of alkaline-earth carbonates. *Thermochimica Acta* **303**(2), 161–170.

Lvov, B.V. (2002). Mechanism and kinetics of thermal decomposition of carbonates. *Thermochimica Acta* **386**(1), 1–16.

Matrajt, G., Messenger, S., Brownlee, D. & Joswiak, D. (2012). Diverse forms of primordial organic matter identified in interplanetary dust particles. *Meteoritics & Planetary Science* **47**(4), 525–549.

McKay, D.S., Gibson, E.K. Jr., Thomas-Keprta, K.L., Vali, H., Romanek, C.S., Clemett, S.J., Chillier, X.D.F., Maechling, C.R. & Zare, R.N. (1996). Search for past life on mars: possible relic biogenic activity in martian meteorite ALH84001. *Science* **273**(5277), 924.

McKay, C.P., Friedmann, E.I., Frankel, R.B. & Bazylinski, D.A. (2003). Magnetotactic bacteria on earth and on mars. *Astrobiology* **3**(2), 263–270.

Noguchi, T., Nakamura, T. & Nozaki, W. (2002). Mineralogy of phyllosilicate-rich micrometeorites and comparison with Tagish lake and Sayama meteorites. *Earth and Planetary Science Letters* **202**(2), 229–246.

Opik, E.J. (2004). *Physics of Meteor Flight in the Atmosphere.* Courier Corporation, New York.

Orofino, V., Blanco, A., Blecka, M.I., Fonti, S. & Jurewicz, A. (2000). Carbonates and coated particles on mars. *Planetary and Space Science* **48**(12), 1341–1347.

Orofino, V., Blanco, A., DElia, M., Fonti, S. & Licchelli, D. (2009). Time-dependent degradation of biotic carbonates and the search for past life on mars. *Planetary and Space Science* **57**(5), 632–639.

Palomba, E., Zinzi, A., Cloutis, E.A., DAmore, M., Grassi, D. & Maturilli, A. (2009). Evidence for mg-rich carbonates on mars from a 3.9 μm absorption feature. *Icarus* **203**(1), 58–65.

Parnell, J., Bowden, S.A., Muirhead, D., Blamey, N., Westall, F., Demets, R., Verchovsky, S., Brandstätter, F. & Brack, A. (2011). Preservation of organic matter in the Stone 6 artificial meteorite experiment. *Icarus* **212**(1), 390–402.

Pizzarello, S., Cooper, G.W. & Flynn, G.J. (2006). The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. *Meteorites and the Early Solar System II* **1**, 625–651.

Rao, T.R. (1996). Kinetics of calcium carbonate decomposition. *Chemical Engineering & Technology* **19**(4), 373–377.

Rees, M.H. (1989). *Physics and Chemistry of the Upper Atmosphere*, vol. **1**. Cambridge University Press, Cambridge.

Rivkin, A.S., Volquardsen, E.L. & Clark, B.E. (2006). The surface composition of Ceres: discovery of carbonates and iron-rich clays. *Icarus* **185**(2), 563–567.

Thomas-Keprta, K.L., Clemett, S.J., Mckay, D.S., Gibson, E.K. & Wentworth, S.J. (2009). Origins of magnetite nanocrystals in martian meteorite ALH84001. *Geochimica et Cosmochimica Acta* **73**(21), 6631–6677.

Yabuta, H. *et al.* (2014). X-ray absorption near edge structure spectroscopic study of hayabusa category 3 carbonaceous particles. *Earth, Planets and Space* **66**(1), 156.