II. Formamide in protostellar shocks: Evidence for gas-phase formation

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1. Introduction

One of the main open questions in astrochemistry regards the mechanisms leading to the formation of the so-called interstellar complex organic molecules (iCOMs), which are molecules with at least six atoms; iCOMs can be considered as the building blocks of more complex pre-biotic compounds (see e.g. Caselli & Ceccarelli 2012). This topic is even more important in regions around Sun-like protostars that will produce future solar-like systems. In particular, modern versions of the Urey-Miller experiment suggest that formamide (NH$_2$CHO) might be the starting point of metabolic and genetic macromolecules. Intriguingly, formamide is indeed observed in regions forming solar-type stars and in external galaxies. The reduced database is only available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/605/L3 (e.g. Garrod & Herbst 2006; Garrod et al. 2008), the latter through surface reactions or induced by energetic processing. Focussing on formamide, the gas-phase theory proposes that it is synthesised by the reaction of formaldehyde (H$_2$CO) and amidogen (NH$_2$), as suggested by Barone et al. (2015) and Vázart et al. (2016). Various mechanisms have been advanced for the formation of formamide on the grain surfaces including the combination of amidogen and formyl radical (HCO; Garrod et al. 2008; Jones et al. 2011); the hydrogenation of isocyanic acid (HNCO; Müller et al. 2013). Despite being so easily found, it is still hotly debated how this species and other iCOMs are formed (e.g. Herbst & van Dishoeck 2009).

The two current theories predict formation by reactions in the gas phase (e.g. Vasyunin & Herbst 2013; Balucani et al. 2015; Vasyunin et al. 2017) or on interstellar dust grains (e.g. Garrod & Herbst 2006; Garrod et al. 2008), the latter following surface reactions or induced by energetic processing. Focussing on formamide, the gas-phase theory proposes that it is synthesised by the reaction of formaldehyde (H$_2$CO) and amidogen (NH$_2$), as suggested by Barone et al. (2015) and Vázart et al. (2016). Various mechanisms have been advanced for the formation of formamide on the grain surfaces including the combination of amidogen and formyl radical (HCO; Garrod et al. 2008; Jones et al. 2011); the hydrogenation of isocyanic acid (HNCO; Müller et al. 2013). Despite being so easily found, it is still hotly debated how this species and other iCOMs are formed (e.g. Herbst & van Dishoeck 2009).

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Previous observations revealed that in B1 the jet impacts caused erosion of the grain cores and ices, producing large quantities of gaseous SiO ($\sim 10^{-7}$; Gueth et al. 1998), H$_2$O ($\sim 10^{-9}$; Busquet et al. 2014), and HCOOCH$_3$ ($\sim 10^{-8}$; Arce et al. 2008) among other species (see also LeFloch et al. 2017). Hence, L1157-B1 provides us with a perfect place to study the reactions occurring when previously frozen species are injected into the gas, as their relative abundance evolution depends on the relative efficiency of the various reactions. Previous studies have shown that any variation on the 1000 AU scale, such as that probed by our work, is due to the passage of shocks, rather than to differences in the composition of pre-existing, pre-shocked dust and gas (Benedettini et al. 2012; Busquet et al. 2014). To conclude, within the context of the study of iCOMs, the advantages of the L1157-B1 laboratory are twofold: (i) the source is not directly heated by the protostar, which is 0.08 pc away; and (ii) solid species in dusty icy mantles have been injected into the gas phase owing to a jet-induced shock and consequently sputtering (e.g. Bachiller et al. 2001).

L1157-B1 is one of the targets of the SOLIS$^1$ (Seeds Of Life In Space; Ceccarelli et al. 2017, hereafter Paper III) IRAM NOArTh Extended Millimeter Array (NOEMA) large programme to investigate iCOM formation during the early stages of the star forming process. In this Letter we report the first high spatial resolution NH$_2$CHO image and comparison with the acetaldehyde (CH$_3$CHO), which allow us to constrain how gas-phase chemistry matters for the formation of NH$_2$CHO.

2. Observations

The L1157-B1 shock was observed at 3 mm with the IRAM NOEMA seven-element array during several tracks in July, October, and November 2015 using both the C and D configurations. The shortest and longest baselines are 19 m and 237 m, respectively, allowing us to recover emission at scales up to $\sim 17''$. The NH$_2$CHO ($4_{1,4}$--$3_{1,3}$) line ($E_u = 13$ K, $\Delta \mu^2 = 49$ D$^2$, $A_{\text{rot}} = 3.7 \times 10^{-5}$ s$^{-1}$) at 81693.45 MHz$^2$ was observed using 80 MHz backends with a spectral resolution of $156$ kHz ($\sim 0.57$ km s$^{-1}$). We recover about 60–70% of the emission observed by Mendoza et al. (2014) using the IRAM 30 m (see Fig. A.1 for the 30 m and NOEMA spectra). Calibration was carried out following standard procedures via GILDAS-CLIC$^3$. The bandpass was calibrated on 3C 454.3, while the absolute flux was fixed by observing MWC 349 and 0524+034; the latter was also used to set the gains in phase and amplitude. The phase rms was $\leq 50''$, the typical precipitable water vapor (PWV) was from 10 mm to 40 mm, and the system temperatures $\sim 80$–$100$ K (D) and $\sim 150$–$250$ K (C). The final uncertainty on the absolute flux scale is $\leq 15\%$. The rms noise in the 156-kHz channels was $2$ mJy beam$^{-1}$. Images were produced using natural weighting and restored with a clean beam of 5$''$$\times$$4''81$ (PA = $-94\%$).

3. Results and discussion

3.1. NH$_2$CHO spectra and maps

Formamide emission has been detected towards L1157–B1 with a $S/N \geq 8$, confirming the NH$_2$CHO identification by Mendoza et al. (2014) in the context of the ASAI IRAM 30 m spectral survey. Figure 1 shows the map of the NH$_2$CHO ($4_{1,4}$--$3_{1,3}$) integrated emission on top of the CO ($1$--$0$) image (Gueth et al. 1996), which well outlines the B1 and B2 cavities opened by the precessing jet driven by the L1157-mm protostar, located (in Fig. 1) at $\Delta \alpha = -25''$ and $\Delta \delta = +63''5$ from L1157-mm. The emission map of the NH$_2$CHO ($4_{1,4}$--$3_{1,3}$) line (integrated over the velocity range $-5$ to $+5$ km s$^{-1}$) is shown by the colour image. For the CO image, the first contour and step are $6\sigma$ ($1\sigma = 0.5$ Jy beam$^{-1}$ km s$^{-1}$) and $4\sigma$, respectively. The first contour and step of the NH$_2$CHO map correspond to $3\sigma$ (15 mJy beam$^{-1}$ km s$^{-1}$) and $1\sigma$, respectively. The dashed circle indicates the primary beam of the NH$_2$CHO image (64$''$). The magenta and white ellipses depict the synthesized beams of the NH$_2$CHO ($5_{1,7}$--$4_{1,6}$) and CO ($3_{1,2}$--$2_{2,1}$; PA = $-94'$) respectively, and the three dashed arrows indicate the directions (projected on the plane of the sky) of the episodic jet producing the shocks analysed in Sect. 3.2 and Fig. 2.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Southern blue-shifted lobe L1157 in CO (1--0) (white contours; Gueth et al. 1996). The precessing jet ejected by the central object L1157-mm (white star) excavated two cavities, with apices B1 and B2, respectively. The maps are centred at $\alpha(J2000) = 20h39m10, \delta(J2000) = +68'01''5$ ($\Delta \alpha = +25''$ and $\Delta \delta = +63''5$ from L1157-mm. $S_{\text{rms}}$ was fixed by observing MWC 349 and 0524+034; the latter was also used to set the gains in phase and amplitude. The phase rms was $\leq 50''$, the typical precipitable water vapor (PWV) was from 10 mm to 40 mm, and the system temperatures $\sim 80$–$100$ K (D) and $\sim 150$–$250$ K (C). The final uncertainty on the absolute flux scale is $\leq 15\%$. The rms noise in the 156-kHz channels was $2$ mJy beam$^{-1}$.

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3.2. Formamide and acetaldehyde spatial anticorrelation

In Fig. 2, we report a zoom-in of the B1 structure, as traced by the line emission from formaldehyde and SiO (Gueth et al. 1998; Benedettini et al. 2013). The figure clearly shows the first important result of these observations: the formamide emission does not coincide with that from H$_2$CO and SiO, but only covers the southern portion of the B1 structure. Also, Fig. 2 reports the emission from another iCOM, acetaldehyde (CH$_3$CHO; Codella et al. 2015). Surprisingly, unlike formamide, it is mostly associated with the northern portion of B1. When the difference between these two species is considered, one can identify three zones as follows: SHOCK 1: the northern and youngest zone, where only acetaldehyde emits ($X$(CH$_3$CHO)/$X$(NH$_2$CHO) abundance ratio $> 8$; see Fig. 3); SHOCK 2: an intermediate zone, where both formamide and acetaldehyde are present ($X$(CH$_3$CHO)/$X$(NH$_2$CHO) = 2–8); and SHOCK 3: the southern and oldest region, where only formamide emits ($X$(CH$_3$CHO)/$X$(NH$_2$CHO) < 2).

The analysis of the SiO and HDCO distribution (Fig. A.2) confirms that B1 is composed by at least two different shocks and is not a single bow-like shock. Specifically, (A) the northern part, SHOCK 1, is associated with the youngest shock (within the B1 structure) at B1a, which is characterised by (i) the emission of HDCO, which is a selective tracer of dust mantle release (Fontani et al. 2014), and (ii) extremely high-velocity SiO emission that traces the current sputtering of the dust refractory cores. (B) The southern region, SHOCK 3, is associated with the oldest shock (within B1) because (i) no HDCO is observed, and (ii) SiO emission is only observed at low velocity and shows a “finger” pointing south (Gueth et al. 1998). This implies that either SiO molecules have been slowed down with time with respect to the high velocities (needed to produce gaseous Si) or that the shock incident angle has changed, so that the projected velocity is lower. In both cases this indicates that a unique shock structure for L1157-B1 is ruled out. (C) The central region, between SHOCK 1 and SHOCK 3, is characterised by the occurrence of the bulk of the low-velocity SiO molecules, which, once produced at high velocities, have plausibly slowed down with time. It is then reasonable to assume that this region is associated with a third, intermediate in time, shock event. However, the results and conclusions of the present paper are based on the occurrence of at least two shocks of different age (SHOCKs 1 and 3).

We notice that the difference in the three zones cannot be attributed to excitation effects, as the mapped formamide and acetaldehyde lines have similar upper level energies (11 K and 26 K), similar Einstein coefficients ($\sim 10^{-15}$ s$^{-1}$), and the derived excitation temperatures are also similar (i.e. 10 K against 15 K, for formamide and acetaldehyde respectively; Mendoza et al. 2014; Codella et al. 2015). Besides, there is no evidence of a monotonic volume density gradient across the B1 region from north to south (Benedettini et al. 2013; Gómez-Ruiz et al. 2015).
as in the case of CH$_3$CHO/NH$_2$CHO line intensity ratio (see Fig. A.2). Therefore, the difference between the three zones must be due to a difference in the chemical composition, thus indicating a clear evolutionary effect.

4. Chemical modelling

To understand what the observed chemical differentiation implies, we ran an astrochemical model (a modified version of Nahoon, Loison et al. 2014, see Appendix B) considering three possibilities: (i) formamide and acetaldheyde are grain-surface chemistry products, (ii) formamide and acetaldheyde are gas-phase chemistry products, and (iii) one of the two species is a grain-surface and the other one a gas-phase chemistry product. Briefly, we use a time-dependent gas-phase code that follows the chemical evolution of the gas. This code starts with the chemical composition of a molecular cloud and then simulates the passage of the shock by suddenly increasing the gas density and temperature to $10^5$ cm$^{-3}$ and 60 K, respectively, (i.e. the typical values measured for the B1 cavities, 20–80 K; Lefloch et al. 2012; 0.5–10 $10^5$ cm$^{-3}$; Gómez-Ruiz et al. 2015) and the gaseous abundance of grain mantle molecules. The abundances of the mantle molecules are assumed to be similar to those measured by IR observations of the dust ices (Boogert et al. 2005) or specifically constrained by previous studies on L1157-B1 (see Table B.1).

The chemical network is described in Appendix B. The results of the modelling are discussed for the three cases mentioned above.

1. Grain-surface formation of CH$_3$CHO and NH$_2$CHO

First, we assume that both formamide and acetaldheyde are synthesised on the grain surfaces and that the passage of the shock injects these two species into the gas phase in quantities such that the measured abundances are roughly reproduced. The predicted abundances as a function of time are shown in Fig. 3. They decrease by approximately the same factor in a 2000 yr interval. Actually, the predicted [CH$_3$CHO]/[NH$_2$CHO] abundance ratio slightly increases with time, which is in contrast with the observations that show exactly the opposite trend. Therefore, the pure grain-surface hypothesis cannot explain the observed formamide/acetaldheyde segregation. In other words, our observations rule out the hypothesis that the bulk of the observed acetaldheyde and formamide in L1157-B1 are directly injected from the grain mantles into the gas phase.

2. Gas-phase formation of CH$_3$CHO and NH$_2$CHO

We then assumed that both acetaldheyde and formamide are formed in the gas phase from species previously on the grain mantles and injected into the gas phase during the shock passage. Acetaldheyde is assumed to be formed by the reaction of ethyl radical (CH$_2$CH$_2$) with atomic oxygen (Charnley et al. 2004): CH$_2$CH$_2$ + O $\rightarrow$ CH$_3$CHO + H. Formamide is assumed to be formed by the reaction of amidogen with formaldehyde (Barone et al. 2015; Vazart et al. 2016): NH$_2$ + H$_2$O $\rightarrow$ NH$_2$CHO + H. We ran various models with different values of ethyl radical, ammonia (mother of NH$_3$), and formaldehyde, to reproduce the observed abundances. We also ran alternative tests injecting ethane (CH$_3$CH$_3$), the fully hydrogenated so-called cousin of ethyl radical, and amidogen, a partially hydrogenated cousin of ammonia, into the gas. The best agreement with observations is obtained by injecting into the gas phase $4 \times 10^{-8}$ of ethyl radical, $2 \times 10^{-5}$ of ammonia, and $1 \times 10^{-6}$ of formaldehyde (see Appendix B for details). This model not only reproduces fairly well the observed abundances (see Fig. 3), it also fits the behaviour of the [CH$_3$CHO]/[NH$_2$CHO] abundance ratio, where acetaldheyde is more abundant in the younger northern SHOCK 1 and formamide is more abundant in the older southern SHOCK 3. The evolution timescale is sensitive to the cosmic ray ionisation rate $\zeta$. We find that the best agreement with the observations is obtained when $\zeta$ is $6 \times 10^{-16}$ s$^{-1}$, which is very close to that previously found (Podio et al. 2014) based on the analysis of the molecular ions in L1157-B1. Finally, a larger shocked gas density would result in speeding up the chemical evolution. As a consequence, the CH$_3$CHO/NH$_2$CHO abundance ratio curve would be shifted towards earlier times. For example, if the density were 10 times larger, namely $2 \times 10^6$ cm$^{-3}$, the curve would be shifted earlier by about 1000 yr. This just means that a substantial difference, by a factor 10, in the gas density at SHOCKs 1 and 3 would not change our major conclusions, but would just imply a slightly smaller cosmic ray ionisation rate.

3. Either acetaldheyde or formamide is a grain-surface and the other a gas-phase chemistry product

We checked the possibility that acetaldheyde is synthesised on the grain surfaces and formamide in the gas and we obtained results similar to the case (2). Hence, the gaseous CH$_3$CHO abundance evolution is rather independent on the formation route (surface chemistry or gas-phase chemistry). We finally checked the possibility that the gas-phase reaction NH$_2$ + H$_2$O is not efficient (Song & Kästner 2016). In this case, no model can reproduce the observations (both the abundance and the evolution).

In summary, the new SOLIS observations indicate that the formation of observed formamide in L1157-B1 is dominated by gas-phase reactions involving species previously hydrogenten on the grain surfaces, although we cannot exclude a minor contribution from mechanisms such as energetic processing of ices. The formamide abundance needs to peak when the acetaldheyde abundance has already started to decrease. This is only possible if formamide is mostly formed in the gas phase and the reaction between amidogen and formaldehyde (Barone et al. 2015; Vazart et al. 2016) successfully reproduces the observations. Although simple, our model captures the essential aspects of the chemical behaviour of formamide and acetaldheyde, namely their abundance as a function of time once the shock has passed. Indeed, the major uncertainties lie in the used chemical network more than in the detailed physical processes or the detailed gas-grain interactions (see Appendix B for more). In this context, it is encouraging that the age difference between SHOCK 1 and SHOCK 3 derived by our simple astrochemical model ($\approx 700$ yr) is the same order of magnitude of the one ($\approx 2000$ yr) independently derived by dynamical studies of L1157-B1 (Podio et al. 2016). A more detailed modelling including a more complex and realistic treatment of the shock will be necessary to confirm that this is not just a coincidence and to refine the present predictions.

5. Conclusions

The present work demonstrates that the formamide observed in L1157-B1 is dominated by gas-phase chemistry and that the reaction NH$_2$ + H$_2$O $\rightarrow$ NH$_2$CHO + H explains the observations. Although we are unable to place constraints on the acetaldheyde formation route, we note that quantum chemistry computations have shown that the simple combination of the methyl radical (CH$_3$) and formyl radical (HCO) is an inefficient channel on water ice surfaces (Enrique-Romero et al. 2016), so that it is possible that CH$_3$CHO is also a gas-phase product. The recent detection of iCOMs in cold objects (e.g. Vastel et al. 2014) has already challenged a pure grain-surface chemistry paradigm for their formation (e.g. Vasyunin & Herbst 2013, and references therein). These new observations add evidence that gas-phase chemistry plays an important role in the game of iCOM formation.
Figure A.1. (upper panel) shows the comparison in flux density scale between the NH$_2$CHO ($4_{1,4}$–$3_{1,3}$) spectrum as observed using the IRAM 30 m antenna (Mendoza et al. 2014) and that extracted from the present NOEMA map from a circular region equal to the IRAM 30 m HPBW (30′′). $F_\nu$(Jy) = 4.9493 $T_B$(K). The NOEMA spectrum has been smoothed to match the IRAM 30 m velocity resolution. Lower panel: emission (in $T_B$ scale) extracted at the peak of the formamide spatial distribution (see Fig. 2). Horizontal dashed line indicates the 1σ noise level (13 mK).

Appendix A: Additional line spectra and maps

Figure A.1 (upper panel) shows the comparison in flux density scale between the NH$_2$CHO ($4_{1,4}$–$3_{1,3}$) spectrum as observed using the IRAM 30 m antenna (Mendoza et al. 2014) and that extracted from the present NOEMA map from a circular region equal to the IRAM 30 m half power beam width (HPBW) of 30′′. The lines are blue-shifted ($v_{sys}$ = +2.6 km s$^{-1}$; Bachiller et al. 2001). Between 60% and 70% of the emission observed using the IRAM single dish is recovered by the NOEMA interferometer, which filters out emission structures larger than 17′′.

Figure A.1 (lower panel) also shows the NH$_2$CHO ($4_{1,4}$–$3_{1,3}$) emission line (in brightness temperature scale, $T_B$) observed at the peak of the formamide spatial distribution (Figs. 1, 2).

Figure A.2 shows how different shocks are present within the L1157-B1 structure. The northern region (see the B1a position) is associated with both SiO emitting very high velocities (up to ~18 km s$^{-1}$ with respect to $v_{sys}$), as well as with HDCO, which is a selective tracer of dust mantle release. On the other hand, the southern region is characterised by no HDCO and by low-velocity SiO emission producing the so-called “finger” pointing towards south (Gueth et al. 1998).

Appendix B: Sensitivity to the model parameters

In order to understand the origin of the observed spatial segregation between the acetaldehyde and formamide emission, we ran a chemical model with the aim to simulate the passage of the shock. To this end, we used a modified (to make it more flexible) version of Nahoon (Loison et al. 2014), and a chemical network consisting of 511 species and 7792 reactions. The base of the chemical network is KIDA.2014$^4$, which has been augmented and corrected with updated reactions (Loison et al. 2014; Balucani et al. 2015; Barone et al. 2015). To simulate the passage of the shock, we followed the strategy used in previous works (Podio et al. 2014; Codella et al. 2015), namely a two-step modelling. In the first step, we ran a model assuming the conditions of the gas before the passage of the shock, namely a gas cloud of 2 $\times$ 10$^4$ H-nuclei cm$^{-3}$ and a temperature of 10 K.

$^4$ http://kida.obs.u-bordeaux1.fr

The cosmic ray ionisation rate was previously constrained to be $\sim$ 3 $\times$ 10$^{-16}$ s$^{-1}$ (Podio et al. 2014). The steady state abundances are then used as initial abundances for modelling the second step, with exceptions of the species that are injected into the gas phase because of the shock passage. In this second step, the density is set at 2 $\times$ 10$^3$ H-nuclei cm$^{-3}$ and the temperature at 60 K (Leffoch et al. 2012; Gómez-Ruiz et al. 2015). The shock passage is accompanied by the sputtering of several species from the grain mantles into the gas phase, which corresponds to a sudden increase of their abundance. Again, following previous works, we increased the abundances of these gaseous species to simulate the sputtering. Table B.1 lists the species injected into the gas and their assumed abundances. The injected species have abundances similar to those measured by IR observations of the interstellar dust ices (Boogert et al. 2015). Specifically, they were constrained to match the abundances derived through direct observations of the 1100 years old L1157-B1a shock (Tafalla et al. 1995; Benedettini et al. 2013; Busquet et al. 2014). For some injected species, we chose the values derived by comparison of observations with model predictions. In addition, we slightly changed the values to fit the observed acetaldehyde and formamide abundances. The final model also reproduces the observed abundances of the species reported in Table B.1. When possible, we report the observed gas-phase abundances towards L1157-B1a, i.e. the youngest (1100 yr) shocked region within the B1 structure. Finally, we use a pure gas-phase model with no freeze-out included, since the involved timescale is too short for freeze-out to have any impact on the results. In the following, we
Table B.1. Abundances (with respect to H-nuclei) of the species injected into the gas in the second step of the model and previously observed towards L1157-B1a.

<table>
<thead>
<tr>
<th>Species</th>
<th>Injected ([H])</th>
<th>Observed ([H])</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>$3 \times 10^{-8}$</td>
<td>$\leq 3 \times 10^{-4}$</td>
<td>Ices L1157-B1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$2 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$1-3 \times 10^{-4}$</td>
</tr>
<tr>
<td>OCS</td>
<td>$2 \times 10^{-6}$</td>
<td>$\approx 10^{-6}$</td>
<td>3</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$4 \times 10^{-6}$</td>
<td>$5.5 \times 10^{-6}$</td>
<td>4</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>$1 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-6}$</td>
<td>4</td>
</tr>
<tr>
<td>NH$_3$</td>
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<td>$2 \times 10^{-7}$</td>
<td>6</td>
</tr>
</tbody>
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Notes. (a) These values have been indirectly derived by comparison of observations and model predictions.


In order to test the robustness of the results showed in Fig. 3 and discussed in the main text, we also ran a case where 1% of ammonia is directly injected as amidogen (namely $2 \times 10^{-7}$), which is possibly analogous to the ethyl radical. In this case, we obtain almost exactly the same results shown in Fig. 3, with differences of a few % within the first 2000 yr, confirming that the important mother species in the formamide formation is indeed ammonia. To summarise, the comparison between the observations and the model predictions leads to ammonia and ethyl radical as being the two needed previously frozen mother species of acetaldehyde and formamide, respectively, with frozen-and-injected amidogen and ethane being minor actors.

Finally, it is possible that before equilibrating at 60 K, the shocked gas passed through a high-temperature period. In order to verify whether this period would affect the results reported in Fig. 3 and our conclusions, we ran two models with the gas temperature equal to 1000 K in case (1) and case (2). We found (1) acetaldehyde and formamide are grain-surface chemistry products: during the first 2000 yr of a possible high-temperature period the predicted abundance ratio of acetaldehyde and formamide remains practically the same, as they are destroyed by the same molecular ions (H$_3$O$^+$, H$_3^+$, and HCO$^+$), such that it does not affect the output of Fig. 3 and our conclusion that this case does not reproduce the observed behaviour. (2) Acetaldehyde and formamide are gas-phase chemistry products: at 1000 K, the formamide rate of formation in the gas is very low, as it decreases with a power of 2.56 in temperature (Vazart et al. 2016), such that no formamide is appreciably synthesised during the high-temperature period. On the contrary, the predicted acetaldehyde abundance is almost the same as that at 60 K during the first 2000 yr. Therefore, a high-temperature period preceding the 60 K period would lean towards the same direction of our conclusions. The region with only acetaldehyde is younger (and possibly also warmer), while the region with formamide identifies an older shocked region and formamide is synthesised via the gas-phase reaction NH$_3$ + H$_2$CO. In summary, even if a high-temperature period, not included in our simple model, preceded the present 60 K equilibrated gas temperature, the effects would not change our main conclusion, namely that formamide has to be a gas chemistry product.