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Title: New estimates of the production of volatile gases from ablating carbonaceous micrometeoroids at Earth and Mars during an E-belt-type Late Heavy Bombardment

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New estimates of the production of volatile gases from ablating carbonaceous micrometeoroids at Earth and Mars during an E-belt-type Late Heavy Bombardment

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Abstract. Heating and ablation of micrometeoroids during atmospheric entry yields volatile gases capable of altering atmospheric chemistry, surface climate and habitability. We have subjected powdered samples of the carbonaceous chondrites Orgueil (CI1), ALH 88045 (CM1), Cold Bokkeveld (CM2), Murchison (CM2) and Mokoia (CV3) to stepped pyrolysis-Fourier transform infrared spectroscopy to simulate the atmospheric entry of micrometeoroids and to quantify the yields of water, carbon dioxide and sulphur dioxide at various temperatures, offering insights into the nature of their source phases. We have incorporated these data into the recently-developed E-Belt model of the Late Heavy Bombardment (LHB) to estimate the production of volatiles from infalling micrometeoroids at Earth and Mars around four billion years ago. At the present day, the $4 (\pm 2) \times 10^{10}$ g yr⁻¹ of micrometeoroids arriving at Earth yield around $2.5 (\pm 1.3) \times 10^9$ g yr⁻¹ of indigenous water, $4.1 (\pm 2.2) \times 10^9$ g yr⁻¹ of total water, $1.9 (\pm 1.0) \times 10^9$ g yr⁻¹ of carbon dioxide and about $1.1 (\pm 0.6) \times 10^9$ g yr⁻¹ of sulphur dioxide, where “indigenous” water exclude water evolved at the initial pyrolysis step of 250 °C. For Mars, the infall of 6.8×10^9 g yr⁻¹ of micrometeoroids yields 3.6

(± 1.9) $\times 10^8$ g yr⁻¹ of indigenous water, 6.4 (± 3.4) $\times 10^8$ g yr⁻¹ of total water, 2.4 (± 1.3) $\times 10^8$ g yr⁻¹ of carbon dioxide and 1.5 (± 0.8) $\times 10^8$ g yr⁻¹ of sulphur dioxide. The LHB is associated with micrometeoroidal infall masses of 1.3 (± 0.8) $\times 10^{22}$ g at Earth and 2.3 (± 1.3) $\times 10^{21}$ g at Mars. For Earth, this mass is estimated to have produced 8.3 (± 4.9) $\times 10^{20}$ g of indigenous water, 1.4 (± 0.8) $\times 10^{21}$ g of total water, 6.3 (± 3.7) $\times 10^{20}$ g of carbon dioxide and 3.8 (± 2.2) $\times 10^{20}$ g of sulphur dioxide, with production rates in the peak 50 Myr of the LHB estimated at 5.1 (± 3.1) $\times 10^{12}$ g yr⁻¹ of indigenous water, 8.6 (± 5.1) $\times 10^{12}$ g yr⁻¹ of total water, 3.9 (± 2.3) $\times 10^{12}$ g yr⁻¹ of carbon dioxide and 2.3 (± 1.4) $\times 10^{12}$ g yr⁻¹ of sulphur dioxide. For Mars, total 4.1-3.7 Ga production of 1.3 (± 0.8) $\times 10^{20}$ g of indigenous water, 2.2 (± 1.3) $\times 10^{20}$ g of total water, 9.3 (± 5.5) $\times 10^{19}$ g of carbon dioxide and around 5.8 (± 3.4) $\times 10^{19}$ g of sulphur dioxide is estimated, with peak 50 Myr rates of 8.2 (± 4.8) $\times 10^{11}$ g yr⁻¹ of indigenous water, 1.4 (± 0.8) $\times 10^{12}$ g yr⁻¹ of total water, 5.8 (± 3.5) $\times 10^{11}$ g yr⁻¹ of carbon dioxide and 3.6 (± 2.1) $\times 10^{11}$ g yr⁻¹ of sulphur dioxide. The errors in these estimates for the present-day rates are dominated by $\pm 50\%$ uncertainty in the LDEF figure of 4 (± 2) $\times 10^{10}$ g yr⁻¹ of micrometeoroids while the errors for the ancient rates are dominated by the similarly large uncertainty regarding the mass ratio of micrometeoroids to asteroids. These errors indicate the need for improved understandings of infall rates and better models of solar system evolution. Current models of climate for early Earth and Mars focus on volcanic outgassing for greenhouse gases and aerosols, but pay less attention to extraterrestrial sources. Our data quantify an additional exogenous source of volatiles that augments the endogenous production.

1. INTRODUCTION

Every year, thousands of tonnes of micrometeoroids, typically around 200 μm in diameter and with a mass of around 10 μg (Love and Brownlee, 1993), arrive at the top of the atmosphere of Earth. These tiny bodies decelerate in the upper atmosphere, experiencing intense heating that causes the thermal degradation of mineral and organic phases, producing species including water, carbon dioxide and sulphur dioxide. It follows, therefore, that infalling micrometeoroids have the ability to release gases capable of altering the atmospheric chemistry and radiative balance of a terrestrial planet, with subsequent implications for the climate and habitability of the planetary surface beneath (Court and Sephton, 2009a, b, 2011; Greshake et al., 1998; Toppani and Libourel, 2003; Toppani et al., 2001). While the current rates of micrometeoroidal infall at Earth and Mars are too low for this process to influence atmospheric chemistry to a meaningful extent, application of this principle to the period of intense bombardment of the inner solar system around 4 Ga known as the Late Heavy Bombardment (LHB) has suggested that micrometeoroidal infall could be sufficient to add climate-changing quantities of volatiles to the atmospheres of Earth and Mars. For example, an LHB involving the delivery of about 3×10^{22} g of carbonaceous micrometeoroids to Earth, representing one-tenth of a total delivered mass of 10^{23} g (Gomes et al., 2005; Kring and Cohen, 2002), occurring over 200 Myr, would amount to individual rates of production of about $(1-2) \times 10^{13}$ g yr^{-1} for water, carbon dioxide and sulphur dioxide (Court and Sephton, 2009a, b, 2011).

However, recent advances in our understanding of the LHB have prompted a revision of these conclusions. The inclusion of the E-belt, an extension of the asteroid belt 1.7-2.1 AU from the Sun and dominated by enstatite chondrites (Bottke et al., 2012), rather than the carbonaceous asteroids more common in the outer main asteroid belt (Burbine et al., 2002;

Gradie and Tedesco, 1982; Grimm and McSween, 1993), in the Nice Model of the LHB (Gomes et al., 2005) led to the conclusion that the impactor flux at Earth was dominated by impactors from the E-belt, outnumbering main belt impactors by a factor of about three, with subsequent implications for volatile delivery to Earth (Bottke et al., 2012). Elsewhere, the current rates of micrometeoroidal infall, as calculated from the Long-Duration Exposure Facility (LDEF) (Love and Brownlee, 1993), have been reinterpreted to suggest a rate of micrometeoroidal infall around a tenth of the previously estimate (Cremonese et al., 2012), supported by radar observations (Mathews et al., 2001). Taken together, these data suggest the introduction of substantially fewer carbonaceous micrometeoroids during the LHB, and hence a greatly reduced potential for micrometeoroidal infall to influence the atmospheric chemistry, climate and habitability of Earth and Mars around the time of the origin of life on Earth.

Here, we present new data revealing the production of volatile gases from micrometeoroids during atmospheric entry. We incorporate these data into the recent advances in our understanding of the LHB. We produce new estimates of the rates of generation of these volatiles from the micrometeoroid flux during the LHB and discuss the implications for atmospheric chemistry, climate and habitability on Earth and Mars.

2. MATERIALS AND METHODS

2.1. Selection of meteorite samples

Powdered samples of five carbonaceous chondrites are analysed here, covering a range of compositional and petrological types, following prior analyses (Court and Sephton, 2009b, 2011). These are Orgueil (CI1) (17.1 mg), ALH 88045 (CM1) (13.0 mg), Cold Bokkeveld (CM2) (19.9 mg), Murchison (CM2) (15.5 mg) and Mokoia (CV3) (12.4 mg). Orgueil was observed to fall in south-western France in 1864, ALH 88045 was collected from the Allan Hills in Antarctica in 1988 following prolonged exposure on the ice sheet, Cold Bokkeveld was observed to fall in South Africa in 1838, Murchison fell in Australia in 1969 and Mokoia fell in New Zealand in 1908. Previous analyses of carbonaceous chondrites have revealed a considerable degree of heterogeneity. For organic matter, samples of Murchison greater than 0.5 mm across are representative of the whole meteorite at a 99.9% level of confidence (Carter and Sephton, 2013). However, data for mineral distribution are less clear, with the abundance of sulphur in Orgueil having been reported at six values from 2.83 wt.% to 5.96 wt.% (Burgess et al., 1991, and references therein), while analyses of 200-400 µm samples of Orgueil, around 100-800 µg in mass, have revealed significant variations in the abundances of nitrogen and noble gases (Füri et al., 2013). The use of powdered samples, each around 10-20 mg, was intended to reduce the problem of sample heterogeneity.

2.2. The link between carbonaceous chondrites and micrometeoroids

We have used samples of carbonaceous chondrites as proxies for carbonaceous micrometeoroids, with the assumption that the two types of material are sufficiently similar to produce usable conclusions. Not only does this assumption need to be supported, but,

given the considerable mineralogical differences between Orgueil and Mokoia, it must be decided which chondrite or chondrites make the best proxy to the micrometeoroid flux.

Overall, the terrestrial micrometeorite collection is strongly enriched in carbonaceous material. Small interplanetary dust particles (IDP) retrieved directly from the stratosphere (Brownlee, 1985) are generally similar to CI chondrites in composition (Schramm et al., 1989), possessing a carbon content of about 12% (Thomas et al., 1994), while larger micrometeorites preserved in ice sheets more closely resemble CM chondrites (Kurat et al., 1994; Maurette et al., 2000). This observation is supported by the existence of a meteoritic component in the lunar maria soil that best resembles CM chondrites (Wasson et al., 1975). Carbonaceous chondrites such as Orgueil and Murchison have been regarded as sufficiently similar in composition to carbonaceous micrometeoroids to have been used previously as proxies (Greshake et al., 1998; Nozaki et al., 2006; Toppani et al., 2001). However, although $\geq 75\%$ of the present-day micrometeoroid flux is derived from fine-grained precursors compositionally similar to CI and CM meteorites (Taylor et al., 2012), about 18% is related to ordinary chondrites (Genge, 2008a). These figures indicate that carbonaceous meteorites can only be used as proxies to the approximately 80% carbonaceous component of the micrometeoroid flux.

The analysis of several carbonaceous chondrites allows the measured yields of volatiles to be averaged, further reducing the influence of sample heterogeneity. In particular, CM chondrites can have varying mineralogies, reflecting varying degrees of aqueous alteration on the parent body. The selection of three CM chondrites, ranging from the pervasively-altered ALH 88045 (CM1) to the less altered chondrites Cold Bokkeveld (CM2.2) and Murchison (CM2.5) (Rubin et al., 2007), allows data from across the range of CM-type material to be considered. Orgueil (CI1) was selected because of the similarity of the IDP flux

to CI chondrites (Schramm et al., 1989), and also on the basis of its abundant ferrihydrite, common in micrometeorites yet not found in CM chondrites. Mokoia (CV3) was included as an example of a carbonaceous chondrite that is dissimilar to the C1 and C2 chondrites, enabling the volatile yield from a chondrite less aqueously altered and less enriched in hydrated phyllosilicates to be assessed (Howard et al., 2010; Krot et al., 1998; Tomeoka and Buseck, 1990; Tomeoka and Ohnishi, 2010, 2011). While micrometeoroids resembling CV3 chondrites appear to be rare in the inner solar system (Genge et al., 2008), the inclusion of Mokoia (CV3) will enable the data presented here to be applied more easily in the future, should a significant CV component of past or present micrometeoroid fluxes be established. However, with CV3-type material currently not reported from the present-day micrometeoroid flux (Genge et al., 2008), it is appropriate to exclude the volatile yields from Mokoia (CV3) when applying these data to the carbonaceous micrometeoroid flux.

2.3. Stepped pyrolysis and quantification of volatile yields

This work builds upon previous investigations of the yields of volatiles from ablating micrometeoroids, as determined via laboratory simulation of the conditions of ablation by quantitative pyrolysis-Fourier transform infrared (py-FTIR) spectroscopy (Court and Sephton, 2009a, b, c, 2011). Our previous experimental simulations employed a simple pyrolysis regime, exposing samples of carbonaceous chondrite to a single heating event. While this is a sensible approximation that reflects the conditions experienced by a large proportion of infalling particles, a more sophisticated experiment would recognise that micrometeoroids are capable of experiencing a much more varied range of heating conditions for a range of durations. For example, large micrometeoroids that enter the atmosphere almost vertically at high speeds experience a brief period of very intense heating and ablation, whereas smaller particles entering at highly oblique angles experience up to a minute of less intense

heating, sometimes with no significant ablation (e.g., Love and Brownlee, 1991). Here, we use the more sophisticated process of stepped pyrolysis to investigate the temperature thresholds at which heating during atmospheric entry generates volatiles from mineral and organic phases present in carbonaceous micrometeoroids. Therefore, instead of a single heating event, of 15 s at 1000 °C, we have exposed samples to multiple incremental heating events, at 100 °C intervals up to 1000 °C.

Yields of sulphur dioxide, carbon dioxide and water were quantified using calibration curves (Court and Sephton, 2009a, b, c, 2011). The calibration curves of water and carbon dioxide were produced using the thermal decomposition of known masses of sodium hydrogencarbonate, while the calibration curve of sulphur dioxide was produced via the direct injection of known volumes of laboratory standard sulphur dioxide (99.9% purity, purchased from BOC) at atmospheric pressure through a septum into the Brill Cell using a gas syringe (Court and Sephton, 2009a). A complicating issue arises with the quantification of sulphur dioxide. The main absorption by sulphur dioxide is the doublet around 1375 cm⁻¹. However, absorption by water also occurs in this region. Accurate quantifications of the yield of sulphur dioxide require the separation of the absorptions of water and sulphur dioxide at 1375 cm⁻¹. This has been achieved by the subtraction of a weighted water spectrum from the spectra of the pyrolysis products of the meteorite samples, as used previously (Court and Sephton, 2011). This was accomplished by vaporising a series of masses of water in the Brill Cell using the Pyroprobe 5200 and measuring their FTIR spectra, using the same instrumental setup used for the analysis of the meteorite samples. A spectrum that possessed a water absorption band at 3853 cm⁻¹ similar in intensity to the 3853 cm⁻¹ water absorption bands in the spectrum of the pyrolysis products of a meteorite sample was selected, and a multiplication factor applied to the water spectrum such that the intensity of the 3853 cm⁻¹ band was the same in the spectra of both the water and meteorite pyrolysis

products. The modified water spectrum was then subtracted from the spectrum of the meteorite pyrolysis products, effectively eliminating the contribution of water absorption to the band intensity at 1375 cm^{-1} , leaving only the contribution of sulphur dioxide. The sulphur dioxide bands at 1375 cm^{-1} were quantified using their intensities; for the other volatiles, band areas have been used, but it was considered here that the broad dual sulphur dioxide absorption band was better suited to quantification by intensity (Court and Sephton, 2011). This process has a margin of uncertainty about $\pm 5\%$, resulting from uncertainties in the measured mass and purity of sodium hydrogencarbonate, and the measured volume and subsequent calculation of mass of sulphur dioxide. Hence, the data of Table 1 should be regarded as accurate to about $\pm 5\%$. The yields of volatiles quoted were calculated by comparing the masses of volatiles, as calculated using the calibration curves, to the mass of the original sample.

2.4. Selection of conditions of stepped pyrolysis

Infalling micrometeoroids can experience a wide range of conditions, reflecting variations in factors such as speed, mass, chemistry and angle of entry (Flynn, 1989a; Love and Brownlee, 1991). Here, we have chosen 15 s of heating in an atmosphere of helium up to a temperature of $1000\text{ }^{\circ}\text{C}$ to simulate the process of heating and ablation upon atmospheric entry. It must be asked whether these conditions are a reasonable simulation of those experienced by an ablating micrometeoroid, and how they compare to conditions employed by previous investigations in this area.

2.4.1. Atmosphere of helium

A micrometeoroid entering the atmosphere of Earth experiences peak ablation at an altitude of around 100 km (Love and Brownlee, 1991), under atmospheric pressure of around 10^{-5} bar. Inspection of Antarctic micrometeorites reveals that they commonly possess spinel rims, interpreted in terms of oxidation during ablation in the atmosphere of Earth, suggesting that an oxygenated atmosphere is desirable for experiments such as these (e.g., Genge, 2006a; Toppani et al., 2001). However, the abundance of oxygen at the altitude of peak ablation, around 100 km, is very low, reflecting the atmospheric pressure of about 10^{-5} bar. While the formation of a hydrodynamic bow shock in front of the ablating micrometeoroid (Genge et al., 1997) could increase the local air pressure, much of the gas in the vicinity of an ablating carbonaceous micrometeoroid, and particularly in its interior, would be derived from the breakdown of mineral and organic phases present with the micrometeoroid itself, thus arguing against the selection of an atmosphere rich in oxygen. The low-oxygen conditions at 100 km altitude can be recreated using a 1 bar atmosphere of helium, (Court and Sephton, 2009a, b, 2011). This approach has also been used by other investigations into ablation, either by using oxygen-free gases at atmosphere pressure, or by using air at low pressure (Nozaki et al., 2006; Toppani and Libourel, 2003; Toppani et al., 2001).

2.4.2. Maximum temperature of heating

The stepped pyrolysis technique employed here was limited to a maximum temperature of 1000 °C. However, modelling of the temperature experienced by infalling particles suggest that micrometeoroids commonly experience temperatures up to and beyond their melting points, around 1350 °C (Fraundorf, 1980; Love and Brownlee, 1991). The latter work assumed that particles smaller than 1 mm diameter would be unable to support internal thermal gradients during atmospheric entry and would therefore experience a homogenous

degree of thermal alteration, and that only about 1% of micrometeoroids would avoid melting into cosmic spherules (Brownlee, 1985). However, examination of Antarctic micrometeorites has suggested a modification of this viewpoint. For example, in the 50-100 μm size fraction, the observed micrometeoroid survival rate is 400 times greater than that predicted by modelling (Maurette, 1998). Furthermore, the presence of igneous rims and unaltered cores in many micrometeorites is clear evidence for the existence of significant internal temperature gradients, up to 950 $^{\circ}\text{C}$ across hydrated IDPs as small as $<30\text{ }\mu\text{m}$ diameter, between a melted rim around 1350 $^{\circ}\text{C}$ (Toppani et al., 2001) and a core containing partially dehydrated phyllosilicates around 400-800 $^{\circ}\text{C}$ (Genge, 2006a). This has been interpreted in terms of endothermic dehydration of silicates and the pyrolysis of carbonaceous materials, soaking up heat as it conducts into the micrometeoroid core (Flynn, 1995; Maurette, 1998; Szydlík and Flynn, 1992). This is supported by the rarity of phyllosilicates in fine-grained Antarctic micrometeorites, despite the textural and mineralogical evidence for their existence and the abundance of hydrated silicates in C1-2 chondrite matrices such as Orgueil and Murchison (Genge et al., 2001; Gounelle et al., 2002; Nakamura et al., 2001; Noguchi et al., 2002). Indeed, the existence of igneous rims on porous micrometeorites with textural evidence for only small amounts of phyllosilicates suggests that relatively little phyllosilicate or organic matter is required to support an internal temperature gradient (Genge, 2006a), while nuggets of ferrihydrite survive in about 10% of even the most heated cosmic spherules (Maurette, 1998).

These analyses of micrometeorites therefore give two important results. Firstly, they indicate that the temperatures modelled to occur during infall and ablation (Love and Brownlee, 1991) are frequently overestimates, with material in the core often experiencing much lower temperatures, and secondly that these temperatures are still normally sufficient to decompose hydrated phyllosilicates into anhydrous forms, releasing their water to the

atmosphere. This conclusion is supported by past stepped heating experiments on meteorite samples, and investigations into the thermal decomposition of volatile-releasing mineral phases. A peak heating temperature of 1000 °C is sufficient to decompose other volatile-producing phases such as phyllosilicates and carbonates, as summarised in Table 2. Even in the case of sulphur, heating of Orgueil (CI1) to 1000 °C for 15 s under air at 1 bar was sufficient to cause the evolution of almost all of the sulphur liberated at 1250 °C, with heating from 1000 °C to 1200 °C resulting in very little additional evolution of sulphur (Greshake et al., 1998). Data from Toppani et al. (2001) indicates a similar result, with samples of Orgueil heated at 1200 °C releasing about 85% of the sulphur released by heating to 1350 °C. Taken together, these data indicate that heating to 1000 °C is sufficient to release about 85% of the sulphur present in Orgueil, with only some thermally-resistant sulphur phases remaining, such as epsomite and anhydrite, possessing decomposition temperatures around 1100-1200 °C (Toppani et al., 2001). However, it should be noted that this problem is expected to be less pronounced in the other, less aqueously altered chondrites, relative to Orgueil, as they typically contain lower abundances of thermally-resistant sulphates. Hence, a maximum heating temperature of 1000 °C is expected to yield volatiles broadly similar to those released by additional heating to 1350 °C. Such a rationale has been used by previous investigations into the effects of atmospheric heating of micrometeoroids (Nozaki et al., 2006). In the context of estimating yields of volatiles from infalling micrometeoroid infall rates, partial decomposition represents a subordinate source of error, relative to uncertainties regarding bulk infall rates (e.g., Love and Brownlee, 1993), and can be addressed by the provision of appropriate error bars.

2.4.3. Duration and repetition of heating

The advantage of stepped heating as employed here is that it enables insights into the links between meteorite mineralogy, temperature of ablation and the composition of released volatiles. However, the programme of heating differs from that naturally experienced by an infalling ablating particle (Love and Brownlee, 1991). While a duration of heating of 15 s is broadly compatible with the modelled durations of ablation (Love and Brownlee, 1991), and is comparable with the choices of heating duration made by previous investigations (Greshake et al., 1998; Nozaki et al., 2006; Toppani et al., 2001), it may be considered that the repeated heating cycles involved in stepped pyrolysis would result in unnatural patterns of thermal degradation. However, comparisons of particles of the ungrouped C2 chondrite, Tagish Lake, heated for 10 s and 120 s indicate that bulk mineralogical changes are more strongly influenced by peak heating temperature, rather than heating duration, with a temperature difference of 100 °C being more influential than an order of magnitude difference in heating duration (Nozaki et al., 2006).

2.5. Application to Earth and Mars

A certain fraction of the micrometeoroid fluxes at both Earth and Mars, typically small particles entering at shallow angles and low speeds, are subjected to temperatures substantially lower than 1000 °C. It is possible that using the yields of volatiles measured after 15 s at 1000 °C might result in overestimation of the yields of volatiles from infalling micrometeoroids. In the case of Earth, the proportion of micrometeoroids failing to reach 1000 °C is relatively small and can be discarded without fear of unduly influencing results. For example, about 70-90% of micrometeorites in the 100-400 µm size fraction, encompassing the peak of infalling mass at 220 µm (Love and Brownlee, 1993), have experienced melting (Genge, 2008b; Maurette, 1998; Maurette et al., 1995), indicating that the mass fraction not experiencing 1000 °C is small. However, the case of Mars is more

challenging, as the weaker gravity and thinner atmosphere results in less pervasive thermal degradation of infalling micrometeoroids, and a different approach is required. The degree of alteration experienced by micrometeoroids entering the atmosphere of Mars was investigated by Flynn (1996), describing the fraction of micrometeoroid size ranges that experienced temperatures above 900 K (627 °C) and 1600 K (1327 °C). However, the masses in each size range reported by Flynn (1996) were produced using pre-LDEF data of Hughes (1978), summing to a total incident mass of micrometeoroids at Mars of $1.2 \times 10^{10} \text{ g yr}^{-1}$. It is desirable to maintain consistency with the LDEF data. We have therefore scaled the LDEF influx at Earth of $4 \times 10^{10} \text{ g yr}^{-1}$ to one at Mars of $6.8 \times 10^9 \text{ g yr}^{-1}$, a factor of 0.17 (Flynn and McKay, 1990), around 0.57 of the infall rate of $1.2 \times 10^{10} \text{ g yr}^{-1}$ used by Hughes (1978) and Flynn (1996). Application of this scaling factor of 0.57 to the masses in the micrometeoroid size ranges of Flynn (1996) yields the masses shown in Table 3. Further modification by a factor of 0.8, to $5.4 \times 10^9 \text{ g yr}^{-1}$, reflects the carbonaceous component of the micrometeoroid flux at Mars (Genge, 2008a; Taylor et al., 2012), as used for Earth.

Inspection of Table 3 shows that about 20% of the infalling carbonaceous mass at Mars, about $1.08 \times 10^9 \text{ g yr}^{-1}$, does not exceed a temperature of 627 °C and hence experiences a significantly reduced degree of thermal degradation. Similarly, about 29% of the flux, $1.58 \times 10^9 \text{ g yr}^{-1}$, reaches 1327 °C, experiencing thorough degradation, while the remaining 51% of the flux, $2.78 \times 10^9 \text{ g yr}^{-1}$, experiences a peak temperature between 627 °C and 1327 °C. A simple interpolation of these two temperature points suggests that about half of this material, 26% of the total flux, experiences a peak temperature in the range of 1000-1327 °C, taking the proportion of infalling material that experiences a temperature of 1000 °C or above to 55%, while the remaining 26% experiences a peak temperature in the 627-1000 °C range. Again, a simple interpolation results in this 26% being divided into three bins of about 8.7% each, one reaching 700 °C, another reaching 800 °C and the third reaching 900 °C. The

remaining 20% of the infall does not reach 627 °C and hence experiences relatively little degradation. These figures are summarised in Table 4. Given the skewing of the size-frequency distribution of micrometeoroids towards larger bodies around 220 µm diameter (Flynn and McKay, 1990), it can be concluded that very little micrometeoroidal mass would experience peak temperatures significantly below 600 °C. Hence, volatile yields from this 20% mass fraction will be calculated using the assumption of a peak temperature of 600 °C.

2.6. The problem of terrestrial contamination

The potential for terrestrial contamination is well known in meteorite studies. While often the problem is potential contamination by terrestrial biological organic matter, here the greater concern is mineralogical alteration resulting from exposure to the atmosphere and hydrosphere of Earth. In particular, the CM1 chondrite ALH 88045 was subjected to prolonged exposure to the terrestrial atmosphere and hydrosphere on the Antarctic ice, potentially resulting in oxidation of sulphides and organic matter, hydration of phyllosilicates and dissolution of sulphates and carbonates (Duprat et al., 2007; Kurat et al., 1994; Schultz, 1990; Sephton et al., 2004a; Velbel et al., 1991). Elsewhere, oxidation of sulphides to sulphates has been noted in Orgueil (Gounelle and Zolensky, 2001), potentially altering the yields of not only sulphur species, but also those of water, given the hygroscopic nature of many sulphates. It must be considered likely that a similar process has occurred, to some extent, in other chondrites that have experienced many decades on Earth, particularly when curation techniques were less well developed than today (e.g., Gounelle and Zolensky, 2001). An additional problem is one of sorption, with adsorption of atmospheric water to mineral surfaces capable of altering the water content of a chondrite, even without altering its mineralogy.

Low-temperature heating can drive off sorbed atmospheric water, and also dehydrate hydrated mineral phases such as sulphates. For example, Table 2 shows that the initial temperature step used in these experiments, of 250 °C, is sufficient to dehydrate phases such as ferrihydrite, epsomite and gypsum. It might be considered appropriate to exclude water yields at the initial 250 °C temperature step, given the potential for sorbed atmospheric water to evolve at this point. However, this would also exclude water produced by dehydrating phases, and it is not clear whether this water would be indigenous or a terrestrial contaminant. Analysis of micrometeorites recovered from the polar ice does not provide useful information regarding the original degree of hydration of sulphates, as these phases are absent, understood to have been destroyed by terrestrial alteration (Kurat et al., 1994). Elsewhere, while carbonates and sulphates are found in IDPs collected in the stratosphere, their degree of hydration is uncertain (Mackinnon and Rietmeijer, 1987; Zolensky and Lindstrom, 1991). The potential of terrestrial water to contaminate the water yields at 250 °C is common to the entire set of meteorite samples analysed here. Since it is not clear whether this water should be excluded from the calculated volatile yields, it is prudent to calculate water yields that both include and exclude the water released at this step, giving a range of water production rates. Similarly, it may be necessary to exclude data from ALH 88045 from consideration of the yields of volatiles from the micrometeoroid flux, if the data suggest that this chondrite has experienced significant aqueous alteration on the Antarctic ice.

3. RESULTS

FTIR spectra of the products of pyrolysis of the sample of Orgueil are displayed in Fig. 1, with bands attributed to absorption by water, carbon dioxide and sulphur dioxide indicated. Absorption bands produced by other volatiles, such as carbon monoxide, methane and sulphur-bearing species such as sulphur monoxide, sulphur trioxide, carbonyl sulphide and hydrogen sulphide, were not observed in these spectra, matching the observations of Court and Sephton (2011). Although the production of methane from the pyrolysis of concentrated meteoritic organic matter has been reported (Court and Sephton, 2009a), the masses of its source IOM involved in this study were much smaller and the detection of methane was not expected. The absorption bands of water, carbon dioxide and sulphur dioxide have been quantified using the calibration curves of Fig. 2, allowing the yields of these volatiles to be calculated, as ppm °C⁻¹ and wt.% relative to the original sample mass (Figs. 3-4, Table 1).

3.1. Orgueil (CI1)

Fig. 4A reveals a complex production profile of water, with a high production at the initial 250 °C step, possibly related to the volatilisation of sorbed atmospheric components (Court and Sephton, 2009b), followed by a second peak at 800 °C. The yield of carbon dioxide gradually increases from a very low level in the initial 250 °C step to a fairly well-defined peak at 900 °C. Low-temperature release of sulphur dioxide occurs at the 350 °C step, followed by a second peak in sulphur dioxide evolution between 500 °C and 700 °C, before decreasing at higher temperatures. Overall, total yields of 13.3 wt.% water, 7.3 wt.% carbon dioxide and 4.5 wt.% sulphur dioxide were determined. Disregarding the water produced at 250 °C reduces the yield of water to 7.6 wt.%

3.2. ALH 88045 (CM1)

The bimodal distribution of water production with temperature seen in Orgueil is again observed in ALH 88045 (Fig 4B), with a strong release at the initial 250 °C step and a second peak around 800 °C. For ALH 88045, however, the production of water at the higher temperature is more dominant than that at 250 °C, in contrast to Orgueil. The pattern of the carbon dioxide release matches that seen for Orgueil, with a similar peak at 900 °C, although the total yield is less. ALH 88045 produced much less sulphur dioxide upon pyrolysis, relative to Orgueil. The low-temperature release of sulphur dioxide observed from Orgueil is not present here, with sulphur dioxide instead starting to be released around 600 °C and peaking during the 1000 °C step. The pattern of the carbon dioxide release matches that seen for Orgueil, with a similar peak at 900 °C, although the total yield is less. Overall, total yields of 11.7 wt.% water, 3.4 wt.% carbon dioxide and 0.7 wt.% sulphur dioxide were determined for ALH 88045. Disregarding the water produced at 250 °C reduces the yield of water to 9.5 wt.%

3.3. Cold Bokkeveld (CM2)

The pattern of release of volatiles from Cold Bokkeveld (Fig. 4C) is similar to that seen from Orgueil. Abundant water is released by the first 250 °C step, with a secondary peak occurring at the 800 °C step. The production of carbon dioxide starts at low temperatures and increases to a maximum around 900 °C, while sulphur dioxide shows a bimodal distribution with a low-temperature peak around 400 °C and another peak around 700 °C. Overall, total yields of 15.9 wt.% water, 6.4 wt.% carbon dioxide and 3.9 wt.% sulphur dioxide were determined from Cold Bokkeveld. Disregarding the water produced at 250 °C reduces the yield of water to 7.9 wt.%

3.4. Murchison (CM2)

Strong release of water at the initial 250 °C temperature step is followed by a secondary peak in water production at 600 °C, behaviour similar to that seen among the other C1 and C2 chondrites here, but with the temperature of maximum water production being lower for Murchison (Fig. 4D). The yields of carbon dioxide follow a pattern similar to that of the other chondrites, with low yields at low temperatures gradually increasing to a maximum around 900 °C. However, the low-temperature production of sulphur dioxide seen from Orgueil and Cold Bokkeveld is absent from the Murchison data, with production not beginning until 600 °C and peaking at 800 °C. Overall, Murchison yielded 9.3 wt.% water, 3.9 wt.% carbon dioxide and 2.1 wt.% sulphur dioxide. Disregarding the water produced at 250 °C reduces the yield of water to 7.6 wt.%

3.5. Mokoia (CV3)

The yields of volatiles from Mokoia are much lower than those of the other chondrites analysed here (Fig. 4E). Loss of data at the 900 °C because of an instrument malfunction hinders the interpretation of results, but very little water was released, mostly at the initial 250 °C step, with some more at 300-500 °C, suggesting a dehydrated meteorite. Carbon dioxide shows a peak in production at relatively low temperature, 500 °C, before increasing again to another peak at 1000 °C, in contrast to the simple unimodal pattern shown by the other chondrites. Production of sulphur dioxide occurs mainly at high temperatures, 600-800 °C. Overall, total yields were 0.2 wt.% water, 0.7 wt.% carbon dioxide and 1.1 wt.% sulphur dioxide. Disregarding the water produced at 250 °C reduces the yield of water to 0.1 wt.%.

4. VOLATILE PRODUCTION DURING PYROLYSIS-FTIR

4.1. Bulk volatile yields

The overall yields of water, carbon dioxide and sulphur dioxide produced during stepped pyrolysis are illustrated in Fig. 3. These data can be compared with the bulk yields of volatiles produced by a single pyrolysis event at 1000 °C (Court and Sephton, 2009b, 2011). Good agreement exists for the yields of carbon dioxide between the data presented here and those of Court and Sephton (2009b). However, for water, some differences between the two data sets are apparent, with the total yields of water being higher than previously reported for all of the chondrites except Mokoia (CV3). A similar picture is apparent for sulphur dioxide, where yields produced by stepped pyrolysis as performed here are roughly double those produced by the single-pyrolysis event technique of Court and Sephton (2011).

Interpretation of these variations in terms of sample heterogeneity is implausible, as these aliquots consisted of 10-20 mg of powdered chondrites, taken from the same larger powdered samples as the aliquots used by Court and Sephton (2009b) and Court and Sephton (2011). The possibility of significant terrestrial alteration (e.g., Gounelle and Zolensky, 2001) in the time gap between these sets of work also appears unlikely, as the powdered samples were stored under nitrogen in sealed glass vials. A more plausible explanation is that the repeated heating events of stepped pyrolysis have resulted in more pervasive degradation than would have been experienced during a single heating event, as used by Court and Sephton (2009b). However, it is notable that such behaviour is not clearly observed for the yield of carbon dioxide. While the tendency of volatile-producing phases to experience progressive degradation during repeated heating events is dependent on the chemistry and/or mineralogy of the material, this interpretation requires that the

carbonates and organic matter responsible for carbon dioxide production would not experience this behaviour. Furthermore, this behaviour would go against the observations of Nozaki et al. (2006), who noted that heating of samples of the C2 Tagish Lake chondrite for 15 s gave results that were broadly comparable with those obtained from 120 s heating, and that changes in mineralogy were more strongly influenced by the temperature attained, rather than by the duration of heating, with a temperature difference of 100 °C being more influential than an order of magnitude difference in heating duration (Nozaki et al., 2006). Nevertheless, it seems likely that the repeated heating events of stepped pyrolysis have resulted in some degree of additional degradation of phases capable of producing sulphur dioxide and water, relative to a single heating event. This suggests that our experiments are likely to be overestimating the yields of sulphur dioxide and water from ablating micrometeoroids by some degree. However, this uncertainty is expected to be small relative to the uncertainties in micrometeoroid infall rates, as discussed in Section 5.3.

4.2. The anomaly of ALH 88045

Inspection of Fig. 3 reveals that the yields of water, carbon dioxide, and sulphur dioxide generally increase with an increasing degree of aqueous alteration experienced by the meteorite. The most aqueously altered chondrite, Orgueil (CI1), produced high yields of all three volatiles, with yields generally diminishing for the less aqueously altered CM2 chondrites Cold Bokkeveld and Murchison, before falling to close to zero for the thermally metamorphosed Mokoia (CV3). The greater degree of aqueous alteration of Cold Bokkeveld (Browning et al., 1996; Rubin et al., 2007), relative to Murchison, is represented by greater volatile yields. Indeed, the data suggest that measuring the volatile yields produced by py-FTIR may be a quick and simple method of estimating the degree of aqueous alteration experienced by a chondrite, and hence its bulk mineralogy, although the small number of

532 samples of the chondrites analysed here, five compared to the twelve of Rubin et al. (2007),
533 indicates that a larger-scale study would be needed to investigate this properly.

534
535 One chondrite, however, strongly deviates from the general trend of Fig. 3. The Antarctic
536 CM1 chondrite, ALH 88045, produced a somewhat lower yield of water, and much lower
537 yields of carbon dioxide and sulphur dioxide, than might be expected from a C1 chondrite.
538 While this may reflect a certain degree of natural variability of chondrites, similar
539 anomalously low volatile yields were noted during the previous single-step py-FTIR
540 investigations of this chondrite (Court and Sephton, 2009b, 2011), and were interpreted in
541 terms of the alteration of this meteorite during the thousands of years of exposure to the
542 terrestrial atmosphere and hydrosphere typically experienced by Antarctic meteorites (e.g.,
543 Jull, 2006). Solar heating on calm days can raise the temperature of a dark carbonaceous
544 chondrite above 0 °C, (Schultz, 1990; Velbel et al., 1991), giving the opportunity for
545 terrestrial aqueous alteration to occur (Sephton et al., 2004a), resulting in lower volatile
546 yields via the oxidation of organic matter and elemental sulphur and the dissolution and loss
547 of carbonates and sulphates, a method of terrestrial alteration also invoked to explain the
548 paucity of sulphates and carbonates in Antarctic micrometeorites (Kurat et al., 1994).

549
550 Overall, this suggests that this chondrite has undergone significant mineralogical alteration
551 while on Earth, resulting in yields of volatiles dissimilar to those of a pristine sample. Hence,
552 ALH 88045 will not be used to infer the yields of volatiles produced by ablating
553 micrometeoroids. Since CV3 Mokoia was already excluded on the basis of the rarity of CV3-
554 type micrometeoroids, this means that averages of the volatile yields of Orgueil (CI1), Cold
555 Bokkeveld (CM2) and Murchison (CM2) will be used as proxies to the volatile yields of
556 carbonaceous micrometeoroids in general (Table 1).

4.3. Inferring the mineral origins of volatiles

Stepped pyrolysis has the considerable advantage over bulk pyrolysis in that the volatile release profiles visible in Fig. 4 can be related to mineral and organic phases present in the meteorite sample. The chondrites analysed here cover a range of compositions and petrologic types, so it is useful to briefly assess the phases capable of generating significant amounts of volatiles in each sample.

4.3.1. Volatile source phases in carbonaceous chondrites

Carbonaceous chondrites contain numerous phases capable of producing volatile gases upon thermal degradation, such as phyllosilicates, organic matter, carbonates and sulphates. The abundances of these phases are strongly influenced by the degree of aqueous alteration experienced on the meteorite parent body (e.g., Browning et al., 1996; Rubin et al., 2007; Zolensky et al., 1997). One further source is water adsorbed to mineral surfaces. The ability of a chondrite to adsorb water reflects its surface area and hence its porosity and mineralogy, with phyllosilicates being particularly able to adsorb water. Both of these factors favour increased abundances of adsorbed water on the more aqueously altered chondrites.

Phyllosilicates comprise as much as 70 wt.% of some chondrites (Bland et al., 2004). Sources of water are hydroxyl groups bound within the phyllosilicate mineral structure and molecular water trapped between phyllosilicate sheets. In CM chondrites, most phyllosilicates belong to the serpentine group, with a typical formula of $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$. Fe-rich serpentine phases are generally referred to as Fe-cronstedtite, while the more magnesian members are cited as Mg-serpentine (Howard et al., 2009). Progressive aqueous alteration of CM chondrites is understood to consume the hydrated iron-nickel sulphide

tochilinite, favouring the accumulation of Mg-serpentine at the expense of Fe-cronstedtite (Lauretta et al., 2000; Tomeoka et al., 1989). In CI chondrites, pervasive aqueous alteration has resulted in the formation of abundant saponite $(\text{Mg,Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, intergrown with serpentine and ferrihydrite. Previous work has offered insights into the behaviour of these phases at elevated temperatures, summarised in Table 2. Heating of saponite in air causes dehydration and loss of interlayer water around 400-600 °C, followed by decomposition and the loss of bound hydroxyl groups around 700-800 °C (Akai, 1992; Brindley and Hayami, 1965; Greshake et al., 1998; Nozaki et al., 2006). Serpentine, lacking the interlayer water of saponite, produces water only upon decomposition, which occurs around 400-500 °C for Fe-cronstedtite (Mackenzie and Berezowski, 1981) and around 500-600 °C for Mg-serpentine (Akai, 1992; Brindley and Hayami, 1965; Brindley and Zussman, 1957; Greshake et al., 1998; Nozaki et al., 2006).

Hydrated sulphates are a potent source of water. Sulphates are most abundant in CI chondrites, with reports of total abundances ranging from around 2 wt.% to up to 15 wt.% (Burgess et al., 1991; Gao and Thiemens, 1993), occurring in Orgueil as phases such as gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Ni-blödite $(\text{Na,Mg,Ni})(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Böstrom and Fredriksson, 1966; Bullock et al., 2005; Burgess et al., 1991; Fredriksson and Kerridge, 1988; Gounelle and Zolensky, 2001). The water of hydration in sulphates is released readily at low temperatures. For example, dehydration of gypsum to γ -anhydrite occurs around 180 °C, while epsomite loses water progressively until complete dehydration around 310 °C (Paulik et al., 1981). The temperature of dehydration of the Ni-blödite reported in Orgueil (Burgess et al., 1991) is unclear, but blödite $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ has been shown to dehydrate to its anhydrous form around 260 °C (Bish and Scanlan, 2006). The degree of hydration of some of these sulphates can be very variable, with magnesium sulphate capable of occurring as epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, hexahydrate $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Also, the

potential for hydration of sulphates by terrestrial water casts doubt on the indigenous nature of the water evolved at low temperatures, particularly in the more aqueously altered chondrites, more enriched in sulphates, and those that have experienced terrestrial alteration, such as Orgueil (CI1) (Gounelle and Zolensky, 2001).

Additional sources of water are ferrihydrite, tochilinite and organic matter. The poorly crystalline hydrated iron mineral ferrihydrite, understood as $\text{Fe}_5\text{O}_7\text{OH}\cdot\text{H}_2\text{O}$ (Bullock et al., 2005), is common only in CI chondrites, with a figure of 5.0 wt.% being reported for Orgueil (Bland et al., 2004). Ferrihydrite contains both bound molecular water and hydroxyl groups. Dehydration and loss of molecular water occurs around 100-200 °C; decomposition and production of additional water from the hydroxyl groups occurs around 500-600 °C (Mitov et al., 2002; Subrt et al., 1992). Tochilinite is a hydrated iron-nickel sulphide, understood as 1:1 layers of brucite $\text{Mg,Fe}(\text{OH})_2$ and mackinawite FeS (Mackinnon and Zolensky, 1984; Zolensky, 1984). This phase occurs in the matrix of CM chondrites but is rare or absent in CI chondrites (Burgess et al., 1991; Howard et al., 2009, 2011; Mahmood, 2013). It yields water at relatively low temperatures, <250 °C (Browning and Bourcier, 1997; Fuchs et al., 1973), or 300-400 °C (Nozaki et al., 2006). The organic matter present is capable of releasing water, carbon dioxide and sulphur dioxide. Pyrolysis of simple organic matter can produce volatiles at low temperatures, such as water from hydroxyl groups, carbon dioxide from carboxyl groups and sulphur dioxide from sulphonic acids, but the relatively low abundances of simple phases containing these groups (e.g., Sephton, 2002), means that they are a relatively unimportant source of volatiles. Much of the organic matter occurs instead in forms insoluble in common organic solvents, hence its description as insoluble organic matter (IOM). The IOM is interpreted as a complex, refractory organic heteropolymer, consisting of polycyclic aromatic cores bound by aliphatic and ether linkages (Hayatsu et al., 1977; Sephton et al., 2004b; Sephton et al., 1999), with an average composition in Murchison of

$C_{100}H_{48}N_{1.8}O_{12}S_2$ (Zinner, 1988). It has the potential to produce volatiles upon pyrolysis, but this process is hindered by its refractory nature and the paucity of oxygen during these pyrolysis experiments. IOM is generally more abundant in more aqueously altered chondrites, with abundances of 2.00 wt.% IOM carbon in Orgueil (CI1) and around 0.8 wt.% IOM carbon for the CM2 chondrites analysed here (Alexander et al., 2007). The heterogeneous, refractory nature of the IOM, along with the need for an external oxidant, means that a distinct peak in volatile production from IOM should not be expected. Instead, a gradual increase in the rate of production of volatiles with increasing temperature is more likely.

The other main source of carbon dioxide is carbonates, which most often occur as siderite $FeCO_3$, magnesite $MgCO_3$, calcite and aragonite $CaCO_3$ and dolomite $CaMg(CO_3)_2$, frequently as solid solutions between phases. These tend to be most abundant in the most aqueously altered chondrites, with CI chondrites being generally enriched in dolomite (Brearley and Jones, 1998; Endress and Bischoff, 1996; Fredriksson and Kerridge, 1988; Johnson and Prinz, 1993), while the CM chondrites contain some calcite (Howard et al., 2009, 2011; Zolensky et al., 1997). Mg-Fe carbonate is reported to decompose in the 400-650 °C temperature range, with Fe carbonates decomposing from 400 °C and Mg carbonate surviving until around 600-650 °C (Greshake et al., 1998; Nozaki et al., 2006; Smykatz-Kloss, 1974). Dolomite is more resilient, surviving to 700 °C (Nozaki et al., 2006), while calcite is most resilient, decomposing to yield carbon dioxide around 890 °C (Smykatz-Kloss, 1974).

Sulphur occurs at levels as high as 6-7 wt.% (Burgess et al., 1991; Gao and Thiemens, 1993), occurring as elemental sulphur, organic sulphur, sulphides and sulphates. Elemental sulphur is rare, not exceeding 1 wt.% in CI chondrites and 0.2 wt.% in C2 chondrites (Burgess et al., 1991). Organic sulphur is also not abundant, with sulphonc acids reported at 67 ppm and

with sulphur comprising about 4 wt.% of the IOM in Murchison, based on the bulk composition of $C_{100}H_{48}N_{1.8}O_{12}S_2$ (Sephton, 2002; Zinner, 1988). Important sulphide phases are troilite FeS, pyrrhotite $Fe_{1-x}S$, pentlandite $(Fe,Ni)_9S_8$ and tochilinite $FeS \cdot (Mg,Fe)(OH)_2$ (Mackinnon and Zolensky, 1984). Tochilinite occurs in the matrices of CM chondrites, hindering quantification; matrix is frequently described as intergrowths of phyllosilicate and tochilinite (Bland et al., 2004; Tomeoka and Buseck, 1985; Zolensky and McSween, 1988). Tochilinite contents of CM2 chondrites were originally estimated to be up to 10 wt.% (McSween, 1987), but later work revised this down to around <2% (Howard et al., 2009; Zolensky et al., 1993). Troilite and pyrrhotite are most abundant in CI chondrites while pentlandite is more abundant in the CM chondrites (Bland et al., 2004).

The nature and abundance of sulphate phases are discussed above in the context of their ability to evolve water of hydration. However, discerning the decomposition temperatures of the sulphur-bearing phases is much more challenging. Sulphides lack the necessary oxygen within their chemical compositions to evolve sulphur dioxide upon thermal decomposition in a fashion analogous to that of water from phyllosilicates, instead requiring an external source of oxygen. Furthermore, the chemistry of sulphides and sulphates at high temperatures can be quite diverse. For example, calcium sulphate decomposes to calcium oxide and sulphur oxides in air around 1200 °C (Colussi and Longo, 1974; Ingo et al., 1998; Smykatz-Kloss, 1974), or as low as 900 °C under oxygen (Burgess et al., 1991), yet it can also undergo other reactions, such as reduction to calcium sulphide by carbon, yielding carbon dioxide, around 700-850 °C in air and 950-1000 °C under nitrogen. To further complicate matters, the calcium sulphide formed in this fashion can itself react with calcium sulphate to yield calcium oxide and sulphur dioxide, around 900-1000 °C (Strydom et al., 1997; van der Merwe et al., 1999). As such, the attribution of the sources of sulphur dioxide will be performed with caution. More broadly speaking, the order in which groups of sulphur-

bearing phases reacted with oxygen in the work of Burgess et al. (1991), with elemental sulphur oxidising first below 200 °C, followed by sulphides at 400-600 °C and the decomposition of gypsum and epsomite around 900 °C and 1100 °C respectively, offers insights in the likely relative thermal stability of the phases present.

4.3.2. Orgueil (CI1)

The prominent low-temperature release of water from Orgueil, of 6.5 wt.% at 300 °C and lower (Table 1), can be ascribed to sorbed water, the dehydration of sulphates and ferrihydrite. Orgueil has sulphate contents reported at 1.5-3.5 wt.% gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 5.1 wt.% epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 7.24 wt.% Ni-blödite $(\text{Ni,Na,Mg})(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Burgess et al., 1991; Fredriksson and Kerridge, 1988). Complete dehydration of these phases could yield up to about 5 wt.% water, but magnesium sulphate in particular is capable of lesser degrees of hydration, such as hexahydrite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ and kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, suggesting that this figure of 5 wt.% may be an overestimate. Stoichiometry of the dehydration of the 5.0 wt.% ferrihydrite $\text{Fe}_5\text{O}_7\text{OH} \cdot \text{H}_2\text{O}$ content (Bland et al., 2004; Bullock et al., 2005) implies a yield of water of around 0.2 wt.%. Oxidation of hydrogen in the IOM can also contribute, to a maximum of about 1 wt.%, using an IOM atomic H/C ratio of 0.673 and an abundance of carbon in the IOM of Orgueil of 2.00 wt.% (Alexander et al., 2007), but this water would be released across a wide range of temperatures, not just at ≤ 300 °C. Hence, it is likely that some of the water released at 300 °C is terrestrial water adsorbed to mineral surfaces. The release of water at high temperatures, above 400 °C, can be attributed to phyllosilicates, with ferrihydrite and IOM being of limited importance. X-ray diffraction (XRD) studies of the matrix of Orgueil indicate 64.2 wt.% disordered interstratified saponite-serpentine in roughly equal proportions, 7.3 wt.% serpentine and 5.0 wt.% ferrihydrite (Beck et al., 2010; Bland et al., 2004; Bullock et al., 2005; Cloutis et al., 2011; Tomeoka and Buseck, 1988). Stoichiometry

indicates that complete decomposition of 40 wt.% serpentine of composition $\text{Mg}_2\text{FeSi}_2\text{O}_5(\text{OH})_4$ and of 32 wt.% saponite of composition $\text{Mg}_2\text{FeSi}_3\text{AlO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ (Bland et al., 2004; Howard et al., 2010) would result in a water yield around 17 wt.% in the range 400-1000 °C, while the decomposition of the 5 wt.% ferrihydrite (Bland et al., 2004), having already lost its molecular water of hydration, would yield just 0.4 wt.% water. However, Table 1 indicates that a water yield of about 7 wt.% occurs across this region, suggesting either that the phyllosilicate abundance is lower than reported or that phyllosilicate decomposition is incomplete. Literature data (Table 2) suggests that the release of water at the lower end of the high-temperature range, around 400-600 °C, can be assigned to the dehydration of saponite. Also contributing around 600 °C is the decomposition of Fe-rich serpentine and of ferrihydrite. The observed peak of water release around 800 °C is consistent with the decomposition of saponite.

Production of carbon dioxide from Orgueil (CI1) rises with increasing temperature, peaking during the 800-900 °C step, for a total carbon dioxide yield of 7.3 wt.%. The carbonate phase most vulnerable to thermal decomposition is breunnerite ($\text{Mg}(\text{Fe,Mn})(\text{CO}_3)_2$) in the 500-600 °C range (Nozaki et al., 2006), suggesting that carbon dioxide production below 500 °C is derived from organic matter. Above 500 °C, decomposition of breunnerite is followed by dolomite around 700 °C (Nozaki et al., 2006) and then calcite around 900 °C (Smykatz-Kloss, 1974). Carbonate abundances of <5 vol.% dolomite accompanied by some breunnerite, 1.79 wt.% magnesium carbonate and 1.30 wt.% calcium carbonate have been reported in Orgueil (Endress and Bischoff, 1996; Fredriksson and Kerridge, 1988). Decomposition and oxidation of IOM occurs across a broad temperature range because of the heterogeneous nature of the IOM and the requirement for an external oxidant. Assuming that the carbonate abundance is broadly similar to 5 wt.% dolomite enables a maximum yield of carbon dioxide from carbonates of about 4 wt.% to be calculated, implying a need for a significant

contribution of carbon dioxide from organic matter. Complete combustion of the 2.00 wt.% IOM carbon content (Alexander et al., 2007) could produce about 7.3 wt.% carbon dioxide, similar to the observed yield of 7.3 wt.%. Taken together, the data indicate that partial decomposition of both organic matter and carbonate is occurring; the decomposition temperatures of carbonates indicate that carbonate decomposition is occurring (Table 2), but carbonates alone cannot produce the observed carbon dioxide yield.

An initial release of sulphur dioxide at 400 °C is followed by a another peak in the 500-800 °C region, followed by a slight further rise at 1000 °C (Fig. 4). Stoichiometry and the order in which sulphur-bearing phases released sulphur dioxide in the work of Burgess et al. (1991) offer insights in the processes operating here. Oxidation of the elemental sulphur content of Orgueil of about 0.5 wt.% (Burgess et al., 1991) would yield about 1.0 wt.% sulphur dioxide, compatible with the observed production of about 1 wt.% at 400 °C and below (Table 1). Simple organic sulphur species are also liable to release sulphur dioxide at relatively low temperatures, but their abundance is much lower than that of elemental sulphur. Sulphur in the IOM, occurring with an atomic S/C ratio of 0.028 (Alexander et al., 2007) could yield up to 0.3 wt.% sulphur dioxide. The relative weakness of carbon-sulphur bonds indicates that sulphur dioxide produced in this fashion would evolve at relatively low temperatures, likely contributing to the peak at 400 °C. Sulphur dioxide production at intermediate temperatures, 400-700 °C, has been interpreted in terms of sulphides (Burgess et al., 1991; Greshake et al., 1998), although elsewhere pyrrhotite has been assigned a rather higher range, 700-900 °C (Nozaki et al., 2006). The oxygen source required to generate sulphur dioxide from these sulphide phases is not clear, but reaction of hot sulphides with water evolving from phyllosilicates has been noted to be capable of producing elemental sulphur (Böstrom and Fredriksson, 1966), readily oxidised at these temperatures. Stoichiometry indicates that complete oxidation of the 2.1 wt.% troilite and 4.5 wt.% pyrrhotite present in

Orgueil (Bland et al., 2004) could yield about 5 wt.% sulphur dioxide. This is considerably in excess of the observed production of sulphur dioxide of 3 wt.% in the 500-800 °C window, demonstrating that sulphides are available in sufficient quantities to produce the observed yields. The only alternative sulphur-bearing phases in Orgueil capable of yielding the required abundance of sulphur dioxide are the sulphates, with gypsum reported at 1.5-3.5 wt.%, Ni-blödite reported at 7.24 wt.% and epsomite reported at 5.1 wt.% (Bullock et al., 2005; Burgess et al., 1991; Fredriksson and Kerridge, 1988; Gounelle and Zolensky, 2001). The thermal stability of sulphate phases suggests that a significant proportion of sulphate could remain in the sample at 1000 °C (Burgess et al., 1991; Greshake et al., 1998). However, as discussed in Section 2.4.2, this is a relatively minor concern and can be addressed by the use of appropriate error bars.

4.3.3. ALH 88045 (CM1)

The water release profile of ALH 88045 (Fig. 4) differs from that of Orgueil, with a less prominent water release peak at low temperatures and a more prominent one at high temperatures. ALH 88045 has experienced an unusual degree of aqueous alteration for a CM chondrite, with anhydrous silicates being apparently absent, hence its designation as a CM1 chondrite (Zolensky et al., 1997). However, the more poorly constrained mineralogy of this chondrite, and its exposure on the Antarctic ice to meltwater and atmospheric oxygen, capable of oxidising sulphides and organic matter and dissolving sulphates and carbonates (Duprat et al., 2007; Kurat et al., 1994; Schultz, 1990; Sephton et al., 2004a; Velbel et al., 1991), makes data more difficult to interpret. The less prominent release of water at low temperatures suggests a chondrite less enriched in phases such as sulphates, ferrihydrite and sorbed water, relative to Orgueil, as supported by mineralogical studies indicating that sulphates are rare in CM1 chondrites and absent in ALH 88045 in particular (Bullock et al.,

2010), potentially resulting from dissolution during exposure to the Antarctic hydrosphere (Kurat et al., 1994). The greater release of water from ALH 88045 at high temperatures, relative to Orgueil, indicates a greater abundance of hydrated phyllosilicates, consistent with reports that anhydrous silicates are absent in ALH 88045 but occur in Orgueil around 14 wt.% (Zolensky et al., 1993; Zolensky et al., 1997). The peak of high-temperature water release occurs at slightly lower temperature in ALH 88045, relative to Orgueil, behaviour that would be consistent with a paucity of thermally resistant saponite, and a greater relative abundance of Mg-serpentine, in ALH 88045.

The carbon dioxide release profile of ALH 88045 is broadly similar to that of Orgueil, showing a gradual rise to a maximum at the 900 °C step. Some of the carbon dioxide released at 900-1000 °C can be attributed to calcite, reported at an abundance of at least 1.9 vol.% (Mahmood, 2013). Assuming that this broadly reflects a 1.9 wt.% calcite abundance enables a maximum yield of carbon dioxide from calcite in ALH 88045 of about 0.8 wt.% to be estimated. The observed carbon dioxide yield of 3.4 wt.% therefore requires a significant contribution from organic matter. The organic content of ALH 88045 is not reported, but assuming an IOM carbon content similar to that of Cold Bokkeveld and Murchison, 0.85 wt.% and 0.83 wt.% respectively (Alexander et al., 2007), implies a carbon dioxide yield up to about 3 wt.%, sufficient to produce the observed carbon dioxide yield. It does, however, as with Orgueil, require an oxidant to react with the organic matter, given the inert helium atmosphere.

Sulphur release from ALH 88045 shows a pattern different to those seen in the other chondrites, lacking both the low-temperature release of sulphur dioxide at 400 °C and the intermediate-temperature peak of release around 500-800 °C seen in Orgueil. Instead, ALH88045 shows a simple, gradual increase in sulphur dioxide yield up to 1000 °C (Fig. 4).

The absence of a low-temperature sulphur dioxide generation event is readily interpreted as a lack of elemental sulphur in ALH 88045 (Bullock et al., 2010), although it is not clear whether this reflects its absence on the pristine meteorite or its destruction by terrestrial alteration. The absence of significant generation at 600-700 °C suggests a paucity of sulphides such as pentlandite and pyrrhotite. This contrasts with a reported combined abundance of 4.5 vol.% (Mahmood, 2013), possibly reflecting a lack of oxidants or a terrestrial alteration of sulphides into more thermally stable sulphates (Duprat et al., 2007; Kurat et al., 1994). Production of sulphur dioxide from ALH 88045 peaks at the highest temperature step, 1000 °C. Production at this temperature is suggestive of sulphates, which are not reported in ALH 88045 (Bullock et al., 2010). However, terrestrial sulphates have been observed in the CM1 chondrite EET 83334 (Zolensky and Barrett, 1988), recovered following prolonged exposure on the Antarctic ice, an experience also shared by ALH 88045. While terrestrial alteration on the Antarctic ice is capable of removing sulphates via dissolution, it would also favour the oxidation of sulphides into additional sulphates (Duprat et al., 2007; Kurat et al., 1994). Hence, we interpret this sulphur dioxide release as evidence of previously unrecognised sulphate in ALH 88045.

4.3.4. Cold Bokkeveld (CM2)

The water release profile of Cold Bokkeveld (CM2) resembles that of Orgueil (CI1). The yield of water at 250 °C from Cold Bokkeveld of 7.9 wt.% suggests, as with Orgueil, a significant contribution from dehydrating sulphates. Although sulphates are much less abundant in CM chondrites, relative to CI chondrites (Bullock et al., 2010), the gypsum content of 0.8 vol.% (Howard et al., 2009, 2011), occurring as fibrous material in veins and fractures (Lee, 1993), is capable of yielding about 0.2 wt.% water upon dehydration. Additional water can come from the 1-2 wt.% tochilinite content (Howard et al., 2009, 2011; Zolensky et al., 1993),

capable of yielding up to 0.3 wt.% water, while the IOM carbon content of 0.85 wt.% and atomic H/C ratio of 0.576 (Alexander et al., 2007) suggests a maximum water yield of about 0.4 wt.%, expected to occur across a wide temperature range. The balance of the low-temperature water budget must therefore come from dehydration of additional sulphates and desorption of atmospheric water. The high-temperature release of water can be assigned to the decomposition of serpentine group minerals, revealed by XRD to be 23.3 vol.% Fe-cronstedtite and 54.1 vol.% Mg-serpentine (Howard et al., 2009, 2011). Assuming an average composition of $\text{Mg}_2\text{FeSi}_2\text{O}_5(\text{OH})_4$ and that the mass abundances of these phases are broadly similar to the quoted volume abundances gives a maximum water yield from these phases of 18 wt.%, similar to the observed yield of 15.9 wt.%.

The production of carbon dioxide increase gradually to a peak in the 800-900 °C step. The temperature of peak production is consistent with the decomposition (Smykatz-Kloss, 1974) of the 1 vol.% calcite content (Howard et al., 2009, 2011), but it does not occur as a discrete peak, suggesting that calcite decomposition continued at 1000 °C. Carbon dioxide production below 900 °C is attributed to organic matter, with the possibility of additional contribution from unrecognised Fe- and Mg-bearing carbonate phases. Stoichiometry of the 1.0 vol.% calcite (Howard et al., 2009, 2011) and 0.85 wt.% IOM carbon (Alexander et al., 2007) phases suggests that together they can produce around 3.5 wt.% carbon dioxide, with organic matter being more important. These phases are insufficient to explain a total yield of carbon dioxide from Cold Bokkeveld measured at 6.4 wt.%. However, a total carbon content in Cold Bokkeveld of 2.16 wt.% has been reported (Pearson et al., 2006), complete conversion of which would yield about 8 wt.% carbon dioxide, suggesting additional carbon-bearing materials capable of evolving carbon dioxide.

The sulphur dioxide production profile of Cold Bokkeveld is very similar to that of Orgueil. Oxidation of the circa 0.5 wt.% elemental sulphur content (Kaplan et al., 1963; Kaplan and Hulston, 1966) is assigned as the source of the 0.6 wt.% yield of sulphur dioxide below 500 °C, while sulphides, occurring as 1-2 wt.% tochilinite, 1.3-2.1 vol.% pentlandite and 0.95-1.6 vol.% pyrrhotite (Howard et al., 2009, 2011; Zolensky et al., 1993) are responsible for the release at intermediate temperatures, 500-800 °C. These three phases, assuming that the reported abundances by volume are similar to the abundances by mass, could contribute up to around 2.5 wt.% sulphur dioxide, close to the 2.6 wt.% sulphur dioxide production from Cold Bokkeveld in the 500-800 °C window. The 900 °C and 1000 °C steps see a yield of sulphur dioxide from Cold Bokkeveld of about 0.8 wt.%. As with Orgueil, this can be attributed to sulphates, with the gypsum content of 0.8 vol.% (Howard et al., 2009, 2011) being capable of contributing about half the observed yield. This shortfall may reflect an underestimate of the abundance of gypsum, or the presence of additional sulphate phases, such as Fe-rich epsomite (Bunch and Chang, 1980). Sulphur in the IOM is not expected to contribute significantly, as combination of the atomic S/C ratio of about 0.030 with the IOM carbon abundance of 0.85 wt.% (Alexander et al., 2007) indicates a maximum yield of sulphur dioxide from the IOM of around 0.1 wt.%.

4.3.5. Murchison (CM2)

The water release profile of Murchison is dissimilar to that of its CM2 counterpart Cold Bokkeveld, instead resembling the CM1 chondrite ALH 88045, with a muted low-temperature release of water and a more intense one at higher temperatures, around 500-700 °C. The reduced prominence of the low-temperature release of water from Murchison suggests a relatively low abundance of hydrated sulphates. However, the reported values of 1.29 wt.% gypsum and 6.07 wt.% epsomite (Burgess et al., 1991) are capable of producing

3.7 wt.% water upon dehydration, while decomposition of the ≤ 4.86 wt.% tochilinite (Burgess et al., 1991; Zolensky et al., 1993) could yield up to 1.0 wt. % water. The sum of these figures is considerably in excess of the observed yield of water at 300 °C and below, of 1.9 wt.%, suggesting that the abundances of these phases may have been overestimated, a conclusion supported by work suggesting abundances of sulphates around an order of magnitude lower (Gao and Thiemens, 1993) than those reported by Burgess et al. (1991). The release of water at high temperatures peaks in the 500-700 °C region, rather cooler than the 700-800 °C peaks of water release in the other chondrites. This behaviour can be attributed to a greater abundance of Fe-cronstedite, possessing a temperature of decomposition lower than that of Mg-serpentine (Mackenzie and Berezowski, 1981; Nozaki et al., 2006). This behaviour supports other analyses indicating that Murchison has endured a lesser degree of aqueous alteration, relative to the other CM chondrites analysed here, producing a chondrite more enriched in tochilinite and Fe-cronstedite (Beck et al., 2010; Browning et al., 1996; Rubin et al., 2007; Zolensky et al., 1997). However, the measured yield of water at 400 °C and above, of 7.4 wt.%, is notably less than the 19 wt.% yield potentially available from the approximately 80 wt.% abundance of serpentine (Bland et al., 2004), and the steady decline of water production after the peak around 600 °C makes it difficult to believe that at least half of the serpentine content survived the final 1000 °C temperature step without decomposing and losing its water. Therefore, the data suggest a lower abundance of hydrated phyllosilicates than expected. Oxidation of the IOM in Murchison is, as with the other chondrites, not expected to be a significant source of water. Combination of the Murchison IOM carbon content of 0.83 wt.% with the atomic H/C ratio of 0.588 (Alexander et al., 2007) suggests a maximum yield of water from the IOM of about 0.4 wt.%.

The profile of carbon dioxide release from Murchison is similar to that of the other chondrites, with a steady increase in yield up to a peak at 900 °C. As with the other

chondrites, this reflects progressive production of carbon dioxide from organic matter, accompanied by production from carbonates at high temperatures. The IOM carbon content of 0.83 wt.% (Alexander et al., 2007) suggests a potential carbon dioxide yield of 3.0 wt.%; alternatively, complete oxidation of the total carbon content of 2.7 wt.% of Pearson et al. (2006) would yield around 10 wt.% carbon dioxide. Part of the difference between these two estimates reflects the soluble organic species not included in the IOM carbon contents of Alexander et al. (2007). Decomposition of the reported 1.1 wt.% calcite content (Bland et al., 2004) would yield about 0.5 wt.% carbon dioxide, requiring a significant additional contribution from organic matter to account for the observed release of carbon dioxide of 3.9 wt.%.

The sulphur dioxide release profile of Murchison is rather different to that of its more aqueously altered counterparts. Murchison shows no low-temperature release of sulphur dioxide at 400 °C, and production at 600 °C is also reduced. The absence of sulphur dioxide at 400 °C suggests that Murchison is relatively depleted in elemental sulphur, a conclusion supported by reports of <0.15 wt.% elemental sulphur in Murchison (Bullock et al., 2010). Murchison contains a great number of simple organic sulphur species such as sulphonic acids, but they occur at low abundances, typically a few tens of ppm (Cooper et al., 1995; Sephton, 2002), and are therefore not expected to contribute significantly to the sulphur dioxide production. Sulphur in the IOM occurs with an atomic S/C ratio of about 0.018; combining this figure with the IOM carbon abundance of 0.83 wt.% (Alexander et al., 2007) suggests a potential yield of sulphur dioxide from the IOM of just 0.1 wt.%.

Significant production of sulphur dioxide from Murchison begins at 500 °C and continues to 1000 °C, peaking in the 700-800 °C temperature step. Sulphides are assigned as the source of sulphur dioxide at lower end of this region, while the contribution from sulphates becomes

more important at higher temperatures, following the behaviour seen in the other chondrites. Sulphides are fairly abundant in Murchison, with 2.9 wt.% pyrrhotite and 0.9 wt.% pentlandite being reported (Bland et al., 2004), along with ≤ 4.86 wt.% tochilinite (Burgess et al., 1991; Zolensky et al., 1993). Complete conversion of the sulphur in pyrrhotite and pentlandite to sulphur dioxide could yield about 2.6 wt.% sulphur dioxide, while the tochilinite could contribute up to about 2.9 wt.% in addition, figures readily compatible with the observed yield of sulphur dioxide from Murchison in the 500-800 °C range of 1.3 wt.%. At 900 °C and 1000 °C, an additional 0.8 wt.% sulphur dioxide was released, attributed to sulphides reacting with oxygen and decomposing sulphates.

4.3.6. *Mokoia (CV3)*

Mokoia is a sample of regolith breccia containing both oxidised and phyllosilicate-containing phases, interpreted as representing material altered in a wet parent body environment and later transported into a dry region (Tomeoka and Ohnishi, 2011). Very little water was produced by Mokoia, with a yield measured at just 0.2 wt.%, concentrated in the initial 250 °C temperature step. This represents the evolution of sorbed atmospheric water, given that sulphates are not reported from this chondrite. A small further release of water occurs at 400 °C, likely resulting from the dehydration of saponite in the 3.7 vol.% phyllosilicate content (Howard et al., 2010; Krot et al., 1998; Tomeoka and Buseck, 1990; Tomeoka and Ohnishi, 2010, 2011). This should be accompanied by further water release at higher temperatures as saponite and other water-bearing phyllosilicates decompose, but an instrument error resulted in the loss of data at the 900 °C step of this sample. Complete decomposition of a 3.7 wt.% abundance of saponite would generate a water yield of about 0.8 wt.%; the observed yield, significantly below this value, suggests that decomposition of saponite was incomplete, that our sample contained less than the reported 3.7 vol.%

(Howard et al., 2010) or that additional water was released at 900 °C but not recorded because of the instrumental error. IOM carbon occurs in Mokoia at 0.54 wt.% with an atomic H/C ratio of 0.204 (Alexander et al., 2007), implying a maximum yield of water of just 0.1 wt.%, an insignificant figure given its expected dispersion across a wide temperature range.

Carbonates are not reported from Mokoia (Howard et al., 2010; Krot et al., 1998; Zolensky et al., 1997). Mokoia has an IOM carbon content around 0.54 wt.%, with the IOM containing about 68.9% carbon (Alexander et al., 2007), for a bulk meteorite IOM content of about 0.8 wt.%. This material is capable of yielding up to 2.0 wt.% carbon dioxide. The observed yield of carbon dioxide of 0.7 wt.% is therefore compatible with a reasonable degree of degradation of this material, as is the release profile, showing a general increase in production to the peak at 1000 °C, similar to those of the other chondrites.

The sulphur dioxide release pattern of Mokoia resembles that of Murchison. No low-temperature peak in sulphur dioxide production is apparent, indicating an absence of elemental sulphur. Significant production of sulphur dioxide begins only at 600 °C, thereafter remaining at similar levels to 800 °C. Production in this region is interpreted as originating from sulphides, reported in Mokoia around 8.1 vol.% (Howard et al., 2010). Data for the 900 °C step was lost because of an instrument error, but the very minor yield of sulphur dioxide at 1000 °C may reflect a contribution from rare sulphates, estimated at 0.1 wt.% (Kaplan and Hulston, 1966), as well as from sulphides.

4.4. Low-temperature water yields and the problem of terrestrial contamination

It was noted in Section 2.6 that certain hygroscopic phases, particularly sulphates, have the ability to release sorbed terrestrial water at low temperatures, reducing the reliability of the

calculated yields of water. The abundances of water released at low temperatures, together with the analyses of the volatile source phases performed above, indicates that this concern was well-founded. Hence, we will report two separate values of water yields: one excluding the yields at 250 °C and described as the “indigenous” water yield, and the other including the water evolved at 250 °C, described as the “total” water yield. Hence, the yields of indigenous water can be described as 7.6 wt.% from Orgueil, 9.5 wt.% from ALH 88045, 7.9 wt.% from Cold Bokkeveld, 7.6 wt.% from Murchison and 0.1 wt.% from Mokoia. The total water yields are 13.3 wt.% from Orgueil, 11.7 wt.% from ALH 88045, 15.9 wt.% from Cold Bokkeveld, 9.3 wt.% from Murchison and 0.2 wt.% from Mokoia. The yields of carbon dioxide and sulphur dioxide are not subject to this consideration, because of the low yields of carbon dioxide and sulphur dioxide at the 250 °C steps and the paucity of these species in the terrestrial atmosphere.

4.5. Consideration of errors

As discussed in Section 4.2, the Antarctic meteorite ALH 88045 has been excluded from the consideration of mean yields of volatiles, on the basis that mineralogical alteration on the Antarctic ice has resulted in yields of volatiles unrepresentative of a pristine meteorite. Therefore, averaging the measured yields of volatiles from Orgueil, Cold Bokkeveld and Murchison results in yields of 7.7-12.8 wt.% water, 5.8 wt.% carbon dioxide and 3.5 wt.% sulphur dioxide, with the range of water yields reflecting the uncertainty over the origin of water released at 250 C. However, these figures are subject to errors. Firstly, the process of quantification of the volatile yields has an uncertainty of about $\pm 5\%$, reflecting errors in the processes of measuring the masses of samples and standards, as discussed in Section 2.3. Secondly, the potential for incomplete degradation of volatile-producing phases, particularly sulphates, needs to be considered, as well as the possibility that the repeated heating cycles

1025 has resulted in excessive decomposition. As discussed in Section 2.4.2, an uncertainty of
1026 $\pm 15\%$ is appropriate here. Addition in quadrature of these independent errors, taking the
1027 square root of the sums of the squares of the fractional errors, results in an error of 16%.
1028 This results in volatile yields of 7.7 (± 1.2) wt.% indigenous water, 12.8 (± 2.0) wt.% total
1029 water, 5.8 (± 0.9) wt.% carbon dioxide and 3.5 (± 0.6) wt.% sulphur dioxide.

1030

5. MICROMETEOROIDAL INFALL: FROM THE PRESENT DAY TO THE LHB

5.1. Rate of micrometeoroidal infall at the present day

Our previous work investigating the production of volatiles from micrometeoroidal infall (Court and Sephton, 2011) used the estimate of the present-day infall rate of around $4 (\pm 2) \times 10^{10} \text{ g yr}^{-1}$ produced by the LDEF experiment (Love and Brownlee, 1993). However, recent reinterpretation of these data has suggested much lower rates, of $4.2 (\pm 0.5) \times 10^9 \text{ g yr}^{-1}$ of 29.0 km s^{-1} cometary material or $7.4 (\pm 1) \times 10^9 \text{ g}$ of 18.6 km s^{-1} asteroidal material (Cremonese et al., 2012), a figure broadly supported by radar observations using the Arecibo dish that indicate a micrometeoroid flux of about $1.8 \times 10^9 \text{ g yr}^{-1}$ with a high average speed of about 50 km s^{-1} (Mathews et al., 2001). This disparity in infall rates and velocities represents a serious obstacle to attempts to determine the rate of production of volatile gases from the present-day micrometeoroid flux, and greatly hinders attempts to extrapolate these data to other environments.

However, other estimates of micrometeoroidal infall rates are available. Assuming that the intensity of the micrometeoroidal infall flux is fairly constant over the geological timescales in question, within a factor of two of the present-day value (Hartmann et al., 2000; Peucker-Ehrenbrink, 1996), the iridium and osmium in ocean sediments can act as proxies of micrometeoroidal infall, suggesting infall rates around $(3-7) \times 10^{10} \text{ g yr}^{-1}$, compatible with the LDEF data of Love and Brownlee (1993). While these data are apparently contradicted by helium isotope data from similar deep-sea sediments, which suggest much lower infall rates of less than $5 \times 10^8 \text{ g yr}^{-1}$ (Karner et al., 2003; McGee and Mukhopadhyay, 2013), this disparity is likely to be the result of the extensive degassing of noble gases during ablation (Farley et al., 1997; Füri et al., 2013; McGee and Mukhopadhyay, 2013). The helium isotope data

would therefore represent a significant underestimate of the real infall rate, with the osmium and iridium data being closer approximations. Furthermore, the high micrometeoroid velocities assumed by the reinterpretation of Cremonese et al. (2012) have themselves been questioned, with modelling suggesting that Poynting-Robertson drag would circularise the orbits of micrometeoroids, whether asteroidal or cometary in origin, reducing the entry speed of both classes at Earth to below 15 km s^{-1} (Nesvorný et al., 2010), resulting in infall rates more compatible with the original estimate of Love and Brownlee (1993). Overall, therefore, we consider that the data support the LDEF estimate of the present-day micrometeoroid flux of around $4(\pm 2) \times 10^{10} \text{ g yr}^{-1}$ (Love and Brownlee, 1993) and will use this estimate in our calculations.

5.2. Micrometeoroidal infall during the LHB

Previous estimates of the production of volatiles from infalling micrometeoroids during the LHB relied on assumptions about the intensity of micrometeoroidal infall. However, recent novel ideas about the nature of the LHB require a reassessment of micrometeoroidal infall rates and their potential of micrometeoroidal infall to alter atmospheric chemistry and climate.

5.2.1. Nature of an E-belt LHB

The LHB is the term given to a prolonged period of greatly enhanced infall rates around 4.2-3.7 Ga, understood to have been caused by the migration of the gas giants (e.g., Gomes et al., 2005). While the original model of Gomes et al. (2005) proposed an intense and relatively brief bombardment, more recent work has suggested that a less intense but prolonged event is more plausible.

1083

1084 Before the LHB, the asteroid belt is proposed to have had an inner component, the E-belt,
1085 closer to Mars around 1.7-2.1 AU. Inclusion of the E-belt, survivors of which now comprise
1086 the high-inclination Hungaria asteroids, in models of the LHB indicates a longer-lasting event
1087 during which an asteroid flux dominated by high-velocity enstatite chondrites impacted the
1088 Earth (Bottke et al., 2012; Morbidelli et al., 2012). The mass of the E-belt, prior to the LHB,
1089 has been estimated to be 16-18% of the mass of the primordial main belt (Bottke et al.,
1090 2012; Morbidelli et al., 2012). The probability of an E-belt asteroid hitting the Earth or Moon
1091 during the LHB is modelled to have been about ten times greater than that of a main belt
1092 asteroid, with the E-belt supplying about three times more impactors than the main belt
1093 (Bottke et al., 2012). An initiation of the LHB around 4.1 Ga has been often cited (Bottke et
1094 al., 2012; Morbidelli et al., 2012) and we have followed this assumption in this work. It
1095 should be noted, however, that recent analyses of lunar melt rocks suggest a basin-forming
1096 impact event around 4.2 Ga, implying that the LHB began rather earlier than previously
1097 thought (Norman and Nemchin, 2014), further supporting the concept of a prolonged,
1098 relatively low-intensity LHB.

1099

1100 An impactor flux dominated by asteroids is supported not only by considerations of the size-
1101 frequency distributions of contemporaneous craters in the inner solar system, which
1102 resemble the size-frequency distributions of asteroids rather than comets (Bottke et al.,
1103 2012; Broz et al., 2013; Strom et al., 2005), but also by studies of highly siderophilic elements
1104 in lunar impact melts dated to around the time of the LHB, which show an affinity for
1105 ordinary or enstatite chondrites, rather than CI or CM chondrites (Galenas et al., 2011; Joy et
1106 al., 2012; Kring and Cohen, 2002; Norman et al., 2002). The paucity of evidence for cometary
1107 impactors in the inner solar system is suspected to reflect the tendency of comets to
1108 disintegrate when approaching the Sun (Levison et al., 2002; Wiegert and Tremaine, 1999).

Extension of this concept to comets of the LHB would allow a significant cometary contribution to micrometeoroidal dust while retaining the paucity of cometary impact craters on the Moon and the absence of a cometary signature in impact breccias.

5.2.2. Sources of micrometeoroids

The E-belt model of the LHB posits three general sources of micrometeoroids: the main belt, the E-belt and comets. The relative contribution of these sources to the micrometeoroid flux at Earth is controlled by the size of the source, the ease of production of micrometeoroidal dust and the efficiency of its subsequent transport to Earth. If we assume that micrometeoroids were delivered to Earth in the same proportions as the impactor flux, then around three-quarters of the micrometeoroid flux would reflect the composition of the E-belt, with comets and the main belt being minor sources. The position of the E-belt sunwards of the main belt implies that it was probably a repository of material left over from the formation of the terrestrial planets, suggesting abundant material resembling enstatite chondrites, ordinary chondrites and CV carbonaceous chondrites, possibly with a few more primitive objects. This is supported by observations of the current Hungaria family, understood to represent survivors of the E-belt, revealing E/X and S-type asteroids, in contrast to observations of the main belt, where, of bodies larger than 13 km diameter, 56% are C-type and 20% are S-type (Mothé-Diniz et al., 2003).

Enstatite and ordinary chondrites contain little water and carbon, and hence their inclusion in the micrometeoroid flux during the LHB could significantly reduce the amount of water and carbon dioxide delivered to the terrestrial planets. Enstatite chondrites are dominated by anhydrous silicates such as enstatite and other pyroxenes, olivine, plagioclase and spinel, with a water content around 0.01 wt.% (Hutson and Ruzicka, 2000). Abundant sulphur is

present, typically as troilite, but the ability of this phase to produce sulphur dioxide upon infall is hindered by the paucity of oxygen in these highly reduced chondrites (e.g., Keil, 1968; Weisberg et al., 2006). Carbon occurs below 0.6 wt.%, averaging 0.28 wt.%, as species such as graphite and cohenite (Keil, 1968; Moore and Lewis, 1966), capable of generating at most around 2 wt.% carbon dioxide in the event of complete oxidation. Ordinary chondrites also contain little water, with abundances typically around 0.1 wt.% (Robert, 2003, and references therein). Carbon occurs up to about 0.6 wt.% (Moore and Lewis, 1967) and sulphur occurs around 2 wt.% (Cripe and Moore, 1975).

However, three lines of evidence suggest that the micrometeoroid flux at Earth was different in composition to the asteroid flux. These are a) the different dynamics of micrometeoroids and asteroids; b) the varying efficiency of production of dust from asteroids of different compositions and c) the nature of the micrometeoroid flux at Earth. Firstly, the dynamics of micrometeoroids in interplanetary space are dominated by non-gravitational forces such as Poynting-Robertson drag, with micrometeoroids typically taking around 100-1000 kyr to reach Earth from the asteroid belt (Burns et al., 1979; Meier et al., 2014; Nishiizumi et al., 1991). In contrast, larger meteoroids are controlled by interactions with resonances and gravitational focusing (Vokrouhlicky and Farinella, 2000). This has particular implications for the balance of material delivered to Earth because, in the E-belt scenario, asteroids in the E-belt are much more prone to resonant destabilisation than their counterparts in the main belt (Bottke et al., 2012), while micrometeoroids produced by collisions in both E-belt and main belt have similar tendencies to migrate under Poynting-Robertson drag into the inner solar system. This rationale indicates that asteroidal dust in an E-belt scenario should reflect the composition of the asteroid belt as a whole, abundant in C-type asteroids, and hence be much more enriched in carbonaceous material and hydrated mineral phases than the impactor flux at Earth.

1161

1162 Secondly, experimental evidence shows that hydrous meteorites such as Murchison produce
1163 approximately an order of magnitude more small, <400 μm diameter fragments upon
1164 experimental hypervelocity disruption, relative to anhydrous ordinary chondrites (Flynn and
1165 Durda, 2004; Flynn et al., 2009; Tomeoka et al., 2003), a result that fits well with the
1166 conclusion that most micrometeoroid mass arriving at Earth occurs as particles with a
1167 diameter of 220 μm (Love and Brownlee, 1993). A similar effect was also observed in
1168 comparison of hydrated greenstones and anhydrous basalts (Flynn et al., 2005).
1169 Furthermore, discussions of asteroidal dust neglect the role of comets. At the present day,
1170 Jupiter-family comets (JFCs) are regarded as an important and possibly dominant source of
1171 micrometeoroids at Earth (Nesvorný et al., 2010). The original Nice model of the LHB (Gomes
1172 et al., 2005) described a flux of trans-Neptunian comets that was approximately similar in
1173 mass to the asteroidal flux (Gomes et al., 2005). However, the evidence for such a flux was
1174 noted as becoming sparser closer to the Sun (Broz et al., 2013, and references therein), with
1175 lunar craters possessing a size-frequency distribution that resembles that of asteroids, and
1176 lunar impact glasses that geochemically resemble asteroidal impactors (Galenas et al., 2011;
1177 Joy et al., 2012; Kring and Cohen, 2002; Marchi et al., 2012; Marchi et al., 2009; Strom et al.,
1178 2005){Norman, 2002 #12165}. One solution to this paradox is to invoke the disintegration of
1179 cometary nuclei as they penetrate into the inner solar system (Bottke et al., 2012; Levison et
1180 al., 2002; Nesvorný et al., 2010). At the present day, the chance of a splitting event per orbit
1181 of a JFC is estimated to be around 1%, although this figure is uncertain because many events
1182 are not observed (Chen and Jewitt, 1994; Fernández, 2005), leading to the suggestion that
1183 over a typical lifetime of 10 kyr (Levison and Duncan, 1997), a JFC might undergo 100
1184 splitting events, caused by thermal stress, the build-up of internal pressure from subliming
1185 ices and disintegration of a spinning nucleus as its mass and gravity diminishes via
1186 sublimation of ices (e. g., Boehnhardt, 2004). Interpretation of the absence of abundant

cometary impact events in the inner solar system during the LHB in terms of the widespread disintegration of cometary nuclei suggests an additional highly fertile source of carbonaceous dust.

A cometary source of micrometeoroids at the present day has long been proposed (e. g., Engrand and Maurette, 1998; Flynn, 1989a, b; Nesvorný et al., 2010; Reach et al., 2003). While such a source implies a high velocity of atmospheric entry, over 25 km s^{-1} , resulting in the vaporisation of most particles (Love and Brownlee, 1991), modelling indicates that Poynting-Roberston drag can circularise the orbits of cometary dust particles, slowing them to asteroidal velocities around 14 km s^{-1} (Nesvorný et al., 2010), while orbital resonances with Jupiter could also result in dust being driven into low-eccentricity orbits (Kortenkamp et al., 2001). Cometary micrometeoroids would therefore arrive at Earth along asteroidal trajectories, leading to the suggestion that 85% of the present-day micrometeoroid flux derives from JFCs (Nesvorný et al., 2010), which are also proposed to be the source of some proportion of the meteorite flux, such as the CM chondrite Maribo (Haack et al., 2010) and Orgueil itself (Gounelle et al., 2006). Hence, the nature of the present-day micrometeoroid flux offers clues to the nature of comets and the cometary dust produced during the LHB.

Unmelted fine-grained micrometeorites, which comprise around 10-30% of the micrometeorites recovered from polar ice (Engrand and Maurette, 1998; Genge et al., 1997; Taylor et al., 2012), are dominated by a fine-grained porous groundmass of micron-sized grains, whose major and minor element compositions resemble the matrix material found in CI1, CM2 and CR2 carbonaceous chondrites, rich in hydrated minerals and carbonaceous matter (Genge et al., 1997; Kurat et al., 1994). An alternative line of evidence comes from samples collected directly from comets. Analysis of carbonaceous material collected from Comet 81P/Wild 2 indicates that it resembles that found in IDPs and carbonaceous

meteorites, being particularly enriched in aliphatic hydrocarbons (Wirick et al., 2009). Although no phyllosilicates were found (Zolensky et al., 2008), they may have existed in debris ejected from Tempel 1 by the Deep Impact spacecraft (Lisse et al., 2006). These data suggest that, although the balance between cometary and asteroidal sources of the micrometeoroidal flux at Earth during the LHB is still unclear, the flux was dominated by carbonaceous material and was likely broadly similar in composition to the modern flux.

The third line of evidence relates to the ancient micrometeoroid flux. Examination of xenoliths, fossil micrometeorites, in meteorites suggests that the current domination of the micrometeoroid flux by carbonaceous material is not anomalous, with the most common microxenoliths being mineralogically and petrographically similar to carbonaceous chondrites (Bischoff et al., 2006; Briani et al., 2012; Briani et al., 2011; Lipschutz et al., 1989; Meibom and Clark, 1999; Wilkening, 1977). Also, pitting of crystals recovered from 3 m depth in the lunar regolith indicate that the intensity of the micrometeoroid flux at 3 Ga was similar to the present-day value, suggesting that the present-day micrometeoroid flux is not anomalously high or low (Hartmann et al., 2000; Morrison and Zinner, 1976; Peucker-Ehrenbrink, 1996; Popeau et al., 1977). Overall, assuming an LHB micrometeoroid flux similar in composition to that experienced at the present day implies a flux with about an 80(±5)% carbonaceous component (Brownlee et al., 1997; Genge, 2006b, 2008a; Levison et al., 2009; Taylor et al., 2012).

5.2.3. Micrometeoroidal infall rates during an E-belt LHB

A mass of LHB impactors at Earth in the vicinity of 3×10^{23} g has been cited (Gomes et al., 2005; Kring and Cohen, 2002), a mass regarded as consistent with the lunar impactor mass of 6×10^{21} g inferred from the number and size distribution of lunar craters (Hartmann et al.,

2000; Levison et al., 2001). However, the mass of micrometeoroids associated with this flux is not clear. Insight comes from consideration of the present-day flux. Examination of the near-Earth asteroid size-frequency distribution and frequency intervals suggests that the average annual mass delivered by micrometeoroids and small meteoroids is approximately 25% of the average long-term total infall rate, although the sensitivity of this figure to rare large impactors should be noted (Stokes et al., 2003). Since the mechanisms of the production and destruction of dust operating today, such as collisions and disintegration of cometary nuclei, would appear to be comparable to those operating during the LHB, it seems reasonable to assume a ratio of impactors to dust during the LHB that was broadly similar to that of the present day, of 3:1 (Stokes et al., 2003).

The E-belt model of the LHB (Bottke et al., 2012; Morbidelli et al., 2012) implies an LHB less intense than that described by Gomes et al. (2005), occurring from 4.1 Ga to 3.7 Ga, with many asteroids lingering in the Hungaria region, in which asteroids are relatively protected from dynamic disturbances. A mass of lunar impactors after 4.1 Ga of 2×10^{21} g is estimated, with 15-25% being main-belt bodies and 75-85% originating from the E-belt, about 90% of which, 1.8×10^{21} g, arrived in the period of 3.7-4.1 Ga (Morbidelli et al., 2012). These data can be used to estimate a figure for the Earth of about 3.1×10^{22} g of impactors of similar chemistries across the 4.1-3.7 Ga period, using an Earth:Moon asteroid mass ratio of about 17:1 (Bottke et al., 2012), considerably lower than the approximately 3×10^{23} g previously estimated (Gomes et al., 2005; Kring and Cohen, 2002).

This impactor mass flux can be combined with the 3:1 mass ratio of impactors to micrometeoroids (Stokes et al., 2003) to estimate the mass of micrometeoroidal dust arriving at Earth during the LHB. However, this assumes that the ratio of micrometeoroidal infall at Earth relative to the Moon is the same as the ratio of asteroidal infall, and it is well

known that the gravitational cross-section of a planetary body is influenced by the velocities of the infalling particles. For the case of the LHB micrometeoroid flux, produced by JFCs or in the asteroid belt and subjected to circularisation via Poynting-Robertson drag, velocities similar to those of the present-day micrometeoroid flux are implied, around 14 km s^{-1} (Nesvorný et al., 2010). This is considerably lower than the velocities of asteroidal impactors during the LHB, estimated around $20\text{-}21 \text{ km s}^{-1}$ (Bottke et al., 2012). Hence, a more appropriate ratio is given by the present day ratio of micrometeoroidal infall between Earth and the Moon.

The micrometeoroidal infall rate at the Moon is around $1.8 \times 10^9 \text{ g yr}^{-1}$ of dust, 0.045 of Earth's $4 \times 10^{10} \text{ g yr}^{-1}$ (Vanzani et al., 1997). An alternative estimate is $5 \times 10^9 \text{ g yr}^{-1}$ (Cremonese et al., 2013), but this relies on a rather low estimate of the terrestrial micrometeoroidal infall rate of $7.4 \times 10^9 \text{ g yr}^{-1}$ (Cremonese et al., 2012), at odds with measurements of iridium and osmium in ocean sediments (Karner et al., 2003) and employing particle velocities considerably higher than those proposed elsewhere (e.g., Nesvorný et al., 2010). Using the figure of Vanzani et al. (1997) of $1.8 \times 10^9 \text{ g yr}^{-1}$ yields a mass ratio of micrometeoroids from Earth to the Moon of about 22:1, rather than the 17:1 asteroidal mass ratio (Bottke et al., 2012). Incorporation of this ratio into the micrometeoroid mass flux calculation yields a mass of micrometeoroids arriving at Earth in the 4.1-3.7 Ga window of $1.3 \times 10^{22} \text{ g}$, and an average dust infall rate of about $3.3 \times 10^{13} \text{ g yr}^{-1}$, approximately 1000 times the modern flux.

However, the E-belt model of Morbidelli et al. (2012) describes infall rates that peak near the start of the LHB, gradually diminishing thereafter over hundreds of Myr as reservoirs were depleted (Bottke et al., 2012; Morbidelli et al., 2012). Given the genetic link between asteroids, comets and micrometeoroids, and the relatively rapid transport to Earth under Poynting-Robertson drag, it is reasonable to assume that micrometeoroidal infall rates

would follow a similar pattern. Fig. 5 shows the rate of infall of micrometeoroids at Earth as projected from the model of Morbidelli et al. (2012), assuming that the Earth received 22 times more micrometeoroidal mass than the Moon and that the micrometeoroid flux was about a third as massive as the impactor flux (Stokes et al., 2003). In Table 5, these data have been used to estimate masses and rates of delivery of micrometeoroids for 50-Myr intervals across the LHB. The data indicate that average infall rates of micrometeoroids at Earth of around $8.4 \times 10^{13} \text{ g yr}^{-1}$ were sustained for the peak 50 Myr of the LHB.

5.3. Consideration of errors

The estimates of $8.4 \times 10^{13} \text{ g yr}^{-1}$ of micrometeoroidal infall at Earth during the peak 50 Myr of the LHB, and a total mass of $1.3 \times 10^{22} \text{ g}$ in the 4.1-3.7 Ga period, come with considerable uncertainties. Three main sources can be identified. Firstly, the mass of asteroids accreted by the Moon in the period of 4.1-3.7 Ga, of $1.8 \times 10^{21} \text{ g}$, can be ascribed an uncertainty of 25% in recognition of the single significant figure present in the estimate of $2 \times 10^{21} \text{ g}$ of the post-4.1 Ga flux from which it is derived. This is generally similar to the error bars present in the estimates of cratering density (Bottke et al., 2012; Morbidelli et al., 2012; Neukum and Ivanov, 1994). Secondly, and most significantly, the ratio of the mass delivered by micrometeoroids and asteroids during the LHB was estimated to be uncertain by about 50%, reflecting the ability of a few large impactors to distort the mass ratios (Stokes et al., 2003). Thirdly, the mass ratio of micrometeoroids delivered to the Earth and the Moon of 22:1 (Vanzani et al., 1997) can be considered to be uncertain by approximately 10%, by comparison to the modelled mass ratio of faster asteroids of 17:1 (Bottke et al., 2012). We will assume that a similar margin of uncertainty also applies when extrapolating to Mars.

Addition in quadrature of these independent fractional errors yields an overall margin of uncertainty of 57%. Application of this margin to the estimates of the total LHB micrometeoroid flux at Earth yields figures of $1.3(\pm 0.8) \times 10^{22}$ g at a peak 50-Myr rate of $8.4(\pm 4.7) \times 10^{13}$ g yr⁻¹. As discussed in Section 2.2, we assume that about 80(±5)% of this flux was composed of carbonaceous micrometeoroids similar in composition to carbonaceous chondrites, yielding an additional independent 6.25% error. This additional error does not significantly alter the previously calculated uncertainty of 57%, modifying the mass of carbonaceous micrometeoroids arriving at Earth in the 4.1-3.7 Ga period to $1.1(\pm 0.6) \times 10^{22}$ g, with a peak 50-Myr rate of $6.7(\pm 3.8) \times 10^{13}$ g yr⁻¹.

6. NEW ESTIMATES OF VOLATILE PRODUCTION FROM MICROMETEOROIDAL INFALL

6.1. Production of volatiles at Earth and Mars

6.1.1. Present-day Earth

In Section 4.5, the measured yields of volatiles from the samples of carbonaceous chondrite were modified to account for the margins of uncertainty resulting from incomplete decomposition and the quantification process itself. This results in volatile yields of 7.7 (± 1.2) wt.% indigenous water, 12.8 (± 2.0) wt.% total water, 5.8 (± 0.9) wt.% carbon dioxide and 3.5 (± 0.6) wt.% sulphur dioxide. These yields can be applied to the present-day LDEF micrometeoroid flux of 4×10^{10} g yr⁻¹. However, two additional errors need to be incorporated. Firstly, it was assumed that 80(± 5)% of the 4×10^{10} g yr⁻¹ infall occurred as carbonaceous material, yielding a 6.25% error. Secondly, the LDEF figure of 4×10^{10} g yr⁻¹ is uncertain by 50% (Love and Brownlee, 1993). Incorporation in quadrature of these two independent errors, in addition to the ones related to measurement of the yields of volatiles from the samples of carbonaceous chondrite, results in a final error of 53%. This gives rates of around $2.5 (\pm 1.3) \times 10^9$ g yr⁻¹ of indigenous water, $4.1 (\pm 2.2) \times 10^9$ g yr⁻¹ of total water, $1.9 (\pm 1.0) \times 10^9$ g yr⁻¹ of carbon dioxide and about $1.1 (\pm 0.6) \times 10^9$ g yr⁻¹ of sulphur dioxide. It should be noted that the dominant source of error in this calculation is the $\pm 50\%$ uncertainty in the LDEF data, rather than errors relating to the experimental process applied here.

6.1.2. Earth during the LHB

Table 5 lists the average infall rate of micrometeoroids during 50-Myr periods of the LHB at Earth and Mars, along with the expected yields of volatiles, assuming an 80% carbonaceous

component of the micrometeoroid flux (Genge, 2006b; Taylor et al., 2012) and using the means of volatile yields from Orgueil (CI1), Cold Bokkeveld (CM2) and Murchison (CM2). This gives production rates of $5.1 \times 10^{12} \text{ g yr}^{-1}$ of indigenous water, $8.6 \times 10^{12} \text{ g yr}^{-1}$ of total water, $3.9 \times 10^{12} \text{ g yr}^{-1}$ of carbon dioxide and $2.3 \times 10^{12} \text{ g yr}^{-1}$ of sulphur dioxide. Total production of volatiles in the 4.1-3.7 Ga period are $8.3 \times 10^{20} \text{ g}$ of indigenous water, $1.4 \times 10^{21} \text{ g}$ of total water, $6.3 \times 10^{20} \text{ g}$ of carbon dioxide and $3.8 \times 10^{20} \text{ g}$ of sulphur dioxide.

These figures are subject to the six margins of uncertainty discussed above, being $\pm 25\%$ from the mass of asteroids arriving at the Moon during the LHB, $\pm 50\%$ from the ratio of asteroid mass to micrometeoroid mass, $\pm 10\%$ from the ratio of the mass of micrometeoroids at Earth and the Moon, $\pm 6.25\%$ from the uncertainty regarding the carbonaceous component of the micrometeoroid flux, $\pm 5\%$ from the error of quantification of volatiles during the py-FTIR experiments and $\pm 15\%$ from the uncertainty regarding whether complete decomposition of volatiles occurred during experimental pyrolysis. Addition in quadrature of these independent fractional errors gives a total error of 59%. Application of these to the yields of volatiles listed above modifies them to $8.3 (\pm 4.9) \times 10^{20} \text{ g}$ indigenous water, $1.4 (\pm 0.8) \times 10^{21} \text{ g}$ total water, $6.3 (\pm 3.7) \times 10^{20} \text{ g}$ carbon dioxide and $3.8 (\pm 2.2) \times 10^{20} \text{ g}$ sulphur dioxide in the 4.1-3.7 Ga period, with peak 50-Myr rates of $5.1 (\pm 3.1) \times 10^{12} \text{ g yr}^{-1}$ indigenous water, $8.6 (\pm 5.1) \times 10^{12} \text{ g yr}^{-1}$ total water, $3.9 (\pm 2.3) \times 10^{12} \text{ g yr}^{-1}$ carbon dioxide and $2.3 (\pm 1.4) \times 10^{12} \text{ g yr}^{-1}$ sulphur dioxide.

The dominant source of error in this calculation is the $\pm 50\%$ uncertainty in the mass ratio of micrometeoroids and asteroids data, rather than errors relating to the analytical process applied here, meaning that reduction in the analytical uncertainties would not significantly reduce the calculated errors. This emphasises the need for an improved understanding of micrometeoroids throughout solar system history. This dominant source of error can only be

addressed by an estimate of the mass of infalling micrometeoroidal dust that is not derived from the asteroid flux, and hence lunar crater counting. It is possible that modelling of the evolution of the asteroid belt and JFCs during the LHB may be able to directly estimate the production of dust and its transport into the inner solar system, improving on the indirect method used here.

For water and carbon dioxide, these figures are substantially greater than our previous estimates (Court and Sephton, 2009b); however, the production rate of sulphur dioxide is about one order of magnitude lower than previously estimated, reflecting the changes in our understanding of the nature of the LHB and the yield of sulphur dioxide from chondritic meteorites (Court and Sephton, 2011). The calculated masses of water, around 10^{21} g, are about 0.1% of the mass of the modern hydrosphere, around 1.4×10^{24} g. The mass of carbon dioxide of around $6.3 (\pm 3.7) \times 10^{20}$ g is around 200 times the mass of carbon dioxide in the modern atmosphere of Earth, and about 10% of the mass of the modern atmosphere in total. These figures suggest that the flux of micrometeoroids during the LHB did not significantly alter the volume of the terrestrial hydrosphere, which appears to have been well established prior to the LHB (Valley et al., 2002; Wilde et al., 2001). Abundant carbon dioxide is often invoked as a mechanism capable of producing the greenhouse needed to maintain liquid water on the early Earth, given the fainter young Sun. However, these figures are typically in the range of several bars of carbon dioxide, significantly greater than the contribution of 0.1 bars estimated here. The bulk volatile content of Earth can be understood in terms of a 2 (± 1) % contribution of carbonaceous chondritic material, around 2×10^{26} g, to a drier, enstatite chondrite-like precursor (e.g., Marty, 2012), a figure approximately four orders of magnitude greater than the LHB carbonaceous micrometeoroid contribution of $1.1 (\pm 0.6) \times 10^{22}$ g reported here.

6.1.3. *Present-day Mars*

At the present day, Mars is estimated to have a micrometeoroidal infall rate of about 0.17 of that of Earth (Flynn and McKay, 1990), a rate of about $6.8 \times 10^9 \text{ g}^{-1}$, relative to the LDEF estimate of $4(\pm 2) \times 10^{10} \text{ g yr}^{-1}$ (Love and Brownlee, 1993). Production of volatiles from ablating micrometeoroids at Mars can be estimated using the yields outlined in Section 2.5, accounting for the less intense heating experienced by particles entering the thinner atmosphere of this less massive planet, of 6.7 wt.% indigenous water, 11.8 wt.% total water, 4.4 wt.% carbon dioxide and 2.8 wt.% sulphur dioxide (Table 4), in conjunction with the assumption that 80(± 5)% of the flux is carbonaceous. This gives rates of $3.6 \times 10^8 \text{ g yr}^{-1}$ of indigenous water, $6.4 \times 10^8 \text{ g yr}^{-1}$ of all water, $2.4 \times 10^8 \text{ g yr}^{-1}$ of carbon dioxide and $1.5 \times 10^8 \text{ g yr}^{-1}$ of sulphur dioxide. As with Earth, the errors of these figures can be estimated, using the same figures as outlined in Section 6.1.1, yielding an error of 53%. An additional source of error could be attributed to the factor of 0.17 used to scale the micrometeoroid flux at Earth to the one at Mars (Flynn and McKay, 1990), but its magnitude is unclear and we will assume that it is small relative to the LDEF error. Application of these errors to the infall rates results in modern production rates at Mars of $3.6 (\pm 1.9) \times 10^8 \text{ g yr}^{-1}$ of indigenous water, $6.4 (\pm 3.4) \times 10^8 \text{ g yr}^{-1}$ of all water, $2.4 (\pm 1.3) \times 10^8 \text{ g yr}^{-1}$ of carbon dioxide and $1.5 (\pm 0.8) \times 10^8 \text{ g yr}^{-1}$ of sulphur dioxide.

This rate of production of carbon dioxide production is insignificant relative to the carbon dioxide-rich atmosphere of Mars. Similarly, the production of water vapour is vastly smaller than the atmospheric abundance of water vapour, measured to be around 9.6 precipitable micrometres, equivalent to about $1.4 \times 10^{15} \text{ g}$, although it should be noted that the location of injection of meteoroidal water, around 100 km altitude, may contribute to the generation of mesospheric clouds (e.g., Sefton-Nash et al., 2013). The case of sulphur dioxide is more

interesting, as sulphur dioxide has not been detected in the modern atmosphere of Mars. Instrument detection limits indicate a maximum sulphur dioxide abundance of 0.3 ppb, representing a maximum atmospheric mass of no more than 1.1×10^{10} g and a maximum rate of production of about 5×10^9 g yr⁻¹ (Encrenaz et al., 2011; Krasnopolsky, 2005; Krasnopolsky, 2012).

Exogenous sources of sulphur dioxide have been previously considered, with the flux of meteoroids and micrometeoroids being considered to be able to yield about 3.5×10^8 g yr⁻¹ (Court and Sephton, 2011; Krasnopolsky, 2005). Our new data suggest that this is very much an upper limit, and that about $1.5 (\pm 0.8) \times 10^8$ g yr⁻¹ is a more plausible production rate. These data confirm that ablating micrometeoroids are only a minor source of martian sulphur dioxide and, via scaling of the reported sulphur dioxide maxima of 0.3 ppb atmospheric abundance and 5×10^9 g yr⁻¹ production (Encrenaz et al., 2011; Krasnopolsky, 2005; Krasnopolsky, 2012), suggest that the micrometeoroid flux may be capable of supporting a mass of atmospheric sulphur dioxide of around 3.3×10^8 g and an abundance of about 9 (± 5) ppt.

6.1.4. Mars during the LHB

The atmosphere of Mars around 4 Ga was thicker and warmer than the modern one (e.g., Fassett and Head, 2011), meaning that the yields of volatiles described for modern Mars in Section 6.1.3 may not be appropriate. Instead, we have taken the means of the yields of volatiles for modern Mars and modern Earth, and used the data range between these two points as an additional source of error. Hence, the yields of volatiles assumed for micrometeoroids ablating in the atmosphere of Mars during the LHB are 7.2 wt.% of

indigenous water, 12.3 wt.% of total water, 5.1 wt.% of carbon dioxide and 3.2 wt.% of sulphur dioxide.

Table 5 lists the average infall rate of carbonaceous micrometeoroids during 50-Myr periods of the LHB at Mars. These figures were determined by adjusting the infall rate at Earth by a factor of 0.17 (Flynn and McKay, 1990). Although this factor was determined for the present-day infall, it should be reasonably similar to the one at the time of the LHB, given the similar mechanisms of dust production, from collision and disintegrating comets, and the method of transport into the inner solar system under Poynting-Robertson drag. The yields of volatiles from ablating micrometeoroids are also listed, using the yields listed above. Table 5 shows that the most intense 50-Myr period of the LHB at Mars was accompanied by infall rates of micrometeoroids around $1.4 \times 10^{13} \text{ g yr}^{-1}$, of which about $1.1 \times 10^{13} \text{ g yr}^{-1}$, was carbonaceous in composition, assuming an 80% carbonaceous proportion. These rates resulted in production of about $8.2 \times 10^{11} \text{ g yr}^{-1}$ of indigenous water, $1.4 \times 10^{12} \text{ g yr}^{-1}$ of total water, $5.8 \times 10^{11} \text{ g yr}^{-1}$ of carbon dioxide and $3.6 \times 10^{11} \text{ g yr}^{-1}$ of sulphur dioxide, figures lower than previously estimated (Court and Sephton, 2011), reflecting the more sophisticated models of the LHB and ablation. Over the entire 400 Myr of the LHB, the total masses of volatiles delivered are around $1.3 \times 10^{20} \text{ g}$ of indigenous water, $2.2 \times 10^{20} \text{ g}$ of total water, $9.3 \times 10^{19} \text{ g}$ of carbon dioxide and around $5.8 \times 10^{19} \text{ g}$ of sulphur dioxide.

These figures are subject to the six sources of error listed for Earth during the LHB. As noted, the yields of volatiles during ablation were assumed to be intermediate between the yields for modern Mars and modern Earth, because of the uncertainty regarding the thickness of the ancient martian atmosphere. This results in an uncertainty of about $\pm 10\%$, but it is more appropriate to merge this error with the more general one of $\pm 15\%$ reflecting the uncertainty whether complete decomposition occurred during experimental pyrolysis.

Hence, the margin of uncertainty is the same as that used for Earth during the LHB, $\pm 59\%$. As with Earth, the dominant influence on these errors is the uncertainty regarding the mass ratio of micrometeoroids to asteroids. Application of these errors to the masses and rates of production of volatiles at Mars results in $1.3 (\pm 0.8) \times 10^{20}$ g of indigenous water, $2.2 (\pm 1.3) \times 10^{20}$ g of total water, $9.3 (\pm 5.5) \times 10^{19}$ g of carbon dioxide and around $5.8 (\pm 3.4) \times 10^{19}$ g of sulphur dioxide across the entire 400-Myr LHB, with peak 50-Myr rates of $8.2 (\pm 4.8) \times 10^{11}$ g yr^{-1} of indigenous water, $1.4 (\pm 0.8) \times 10^{12}$ g yr^{-1} of total water, $5.8 (\pm 3.5) \times 10^{11}$ g yr^{-1} of carbon dioxide and $3.6 (\pm 2.1) \times 10^{11}$ g yr^{-1} of sulphur dioxide.

Emplacement of the $3 \times 10^8 \text{ km}^3$ of the Tharsis volcanic province on Mars has been proposed to have contributed to the maintenance of clement conditions on early Mars, via the release of volcanic greenhouse gases such as water and carbon dioxide (e.g., Phillips et al., 2001). Given that the LHB was roughly contemporaneous with the emplacement of Tharsis, it is interesting to compare estimates of the masses of volatiles produced by each system. However, the volatile content of Tharsis magmas is not very well constrained, with a water content of 0.05-0.8 wt.% being proposed (Gaillard et al., 2013; Gaillard and Scaillet, 2009), resulting in the injection of $(4.7-74) \times 10^{20}$ g of water. In contrast, our estimates suggest that micrometeoroidal dust delivered around $(0.5-3.5) \times 10^{20}$ g of water. As can be seen, Tharsis easily remains the dominant source of water, but the contribution of water from the carbonaceous micrometeoroid flux is not negligible.

The carbon dioxide content of the Tharsis magma is similarly uncertain, with figures of 80-900 ppm proposed (Gaillard and Scaillet, 2009; Hirschmann and Withers, 2008), yielding a total mass of around $(8-90) \times 10^{19}$ g. The lower end of this range is similar to our estimate of carbon dioxide production from infalling micrometeoroids of around $9.3 (\pm 5.5) \times 10^{19}$ g. The abundance of sulphur dioxide released by Tharsis magmas has been estimated at 500-3500

ppm, resulting in the injection of $(5-35) \times 10^{20}$ g of sulphur dioxide. The $5.8 (\pm 3.4) \times 10^{19}$ g of micrometeoroidal sulphur dioxide reported here represents roughly a tenth of this figure at most. In each case, therefore, the micrometeoroid flux during the LHB appears to have delivered a small, but not negligibly so, mass of volatiles into the atmosphere of Mars, with subsequent implications for atmospheric chemistry and surface climate.

It should be noted that these estimates have all referred to production from the carbonaceous micrometeoroid flux during the LHB. This is clearly not the whole story – most of the mass delivered to Mars at this time came as asteroids, capable of delivering additional volatiles despite the modelled preference for ordinary and enstatite chondritic impactors, and also capable of depleting the volatile budget of the martian atmosphere via impact erosion. Furthermore, the comparison between Tharsis and micrometeoroids is hindered by the considerable uncertainties in the masses and volatile yields, and also by the uncertainty regarding the duration and hence rate of emplacement of Tharsis.

6.2. Effects of volatile production from micrometeoroids on radiative balance

The three gases measured here, sulphur dioxide, carbon dioxide and water, are all capable of influencing the radiative balance of a terrestrial planet and hence its climate. Water, carbon dioxide and sulphur dioxide all have a positive radiative forcing effect, warming the planetary surface beneath. For sulphur dioxide, however, the effect is transient because subsequent contact with water leads to the formation of sulphate aerosols that can cool the surface by scattering sunlight. At the present day, the rate of micrometeoroidal infall is sufficiently low to make the climatic effects negligible for each of these extraterrestrially-sourced gases.

During the LHB, however, the data presented here indicates rates of production of these volatiles at rates of around $(1-10) \times 10^{12} \text{ g yr}^{-1}$ on Earth and around $(1-10) \times 10^{11} \text{ g yr}^{-1}$ on Mars. While the temperature effects of these rates of production of water and carbon dioxide seem likely to have been fairly small, the production rates of sulphur dioxide may have had more notable consequences. Sulphur dioxide is a greenhouse gas, but when the atmosphere is able to oxidise sulphur dioxide, within a matter of months the warming effects of sulphur dioxide are followed by the cooling effects of sulphate aerosols (Tian et al., 2010; Ward, 2009). The cooling from sulphate aerosols is the most influential consequence of sulphur dioxide production and the effects persist for years (Bluth et al., 1993). Furthermore, sulphur dioxide can be rapidly removed from an atmosphere by rain, further reducing its attractiveness as a method of maintaining clement surface conditions on early Mars (McGouldrick et al., 2011; Tian et al., 2010).

Modelling suggests the need for the addition of about $4 \times 10^{11} \text{ moles yr}^{-1}$ of sulphur, equivalent to $1.3 \times 10^{12} \text{ g yr}^{-1}$ of sulphur dioxide, to maintain the martian atmospheric concentration of 10 ppmv needed to raise surface temperatures above freezing point before considering aerosol effects (Tian et al., 2010). Our data, indicating an annual rate of production of $3.6 (\pm 2.1) \times 10^{11} \text{ g yr}^{-1}$ of sulphur dioxide on Mars during the peak 50 Myr of the LHB, suggests that micrometeoroidal infall during the LHB was unable to produce the requisite amounts of sulphur dioxide alone. However, certain differences between volcanic and micrometeoroidal sulphur dioxide should be highlighted. While volcanic sulphur dioxide is injected into the lower regions of the atmosphere from where it can be readily rained out, micrometeoroidal sulphur dioxide is produced at very high altitudes, mostly above 50 km, where the low atmospheric pressure would not only inhibit the rainout of sulphur dioxide, but also would hinder the formation of sulphate aerosols. Hence, it is possible that micrometeoroidal sulphur dioxide would accumulate in the upper atmosphere, producing a

greenhouse effect in excess to that expected from the same mass of sulphur dioxide at lower altitudes. It is therefore desirable that future investigations into the effects of sulphur dioxide on the climate of early Mars would take into account these different mechanism and location of introduction of sulphur dioxide. For Earth, the injection of 2×10^{13} g of sulphur dioxide into the atmosphere by the 1991 eruption of Mt Pinatubo (Bluth et al., 1993), led to sulphate aerosol production and a radiative forcing effect of -2.97 W m^{-2} (Ammann et al., 2003; Wigley et al., 2005) and a corresponding 1992 global tropospheric temperature anomaly of $-0.4 \text{ }^{\circ}\text{C}$ (McCormick et al., 1995). Historical data for Earth reveal that incremental introduction of sulphur dioxide and the consequent aerosols can lead to cooling that drives the climate into major ice ages (Ward, 2009). The rate of production of micrometeoroidal sulphur dioxide estimated here for the LHB at Earth, $2.5 (\pm 1.5) \times 10^{12} \text{ g yr}^{-1}$ during the peak 50 Myr of the LHB, could have augmented other forcings of long term climate.

It should be noted that the LHB was a particularly violent time in solar system history. Climatic effects relating to micrometeoroidal infall would have competed alongside other influences, particularly the rapid injections of volatiles resulting from the delivery of asteroid-scale impactors and large-scale volcanism. Discerning the climatic effects of the background flux of micrometeoroids would be a challenging task, but also one necessary to determine not only climate during quiescent periods, but also the effects of large impact events.

7. CONCLUSIONS

1. We have used stepped py-FTIR to determine the yields of volatiles from a range of carbonaceous chondrites, simulating conditions experienced by micrometeoroids during atmospheric entry. Water, carbon dioxide and sulphur dioxide were detected and quantified using calibration curves. There is a general trend of increasing volatile yields with increasing exposure to aqueous alteration on the meteorite parent body.

2. The patterns of volatile release during stepped pyrolysis can be used to infer the source phases of the volatiles. Low-temperature release of water can be assigned to hydrated mineral phases such as sulphates, tochilinite and ferrihydrite, while high-temperature water results from the decomposition of hydrated phyllosilicates. Carbon dioxide is released by organic matter and carbonates, with the temperature of production depending on carbonate chemistry. Low-temperature production of sulphur dioxide is ascribed to elemental sulphur, while sulphur dioxide released at higher temperature is assigned to sulphides and sulphates.

3. The patterns of volatile production with temperature of pyrolysis can be used to infer the volatiles produced from micrometeoroids heated to specific temperatures upon atmospheric entry. In general, heating at low temperatures, up to 600 °C, produces volatiles dominated by water, but it is not clear whether water released at the initial temperature step of 250 °C is indigenous to the chondrite or represents terrestrial alteration. Further heating to 1000 °C sees the production of carbon dioxide and sulphur dioxide increase in relative importance. Hence, micrometeoroids that experience gentler heating, such as small particles slowly entering the thin atmosphere of a light planet such as Mars at high obliquities would produce volatile yields enriched in water. In contrast, larger heavier

micrometeoroids entering the thicker atmosphere of Earth would experience more intense heating, with volatile yields possessing greater proportions of sulphur dioxide and carbon dioxide, relative to water.

4. At the present day, the $4 (\pm 2) \times 10^{10} \text{ g yr}^{-1}$ of micrometeoroids infalling at Earth are estimated to yield $2.5 (\pm 1.3) \times 10^9 \text{ g yr}^{-1}$ of indigenous water (excluding water produced by pyrolysis at 250°C), $4.1 (\pm 2.2) \times 10^9 \text{ g yr}^{-1}$ of total water, $1.9 (\pm 1.0) \times 10^9 \text{ g yr}^{-1}$ of carbon dioxide and $1.1 (\pm 0.6) \times 10^9 \text{ g yr}^{-1}$ of sulphur dioxide. At Mars, the infall of $6.8 (\pm 3.4) \times 10^9 \text{ g yr}^{-1}$, 80% of which is assumed to be carbonaceous, is estimated to yield $3.6 (\pm 1.9) \times 10^8 \text{ g yr}^{-1}$ of indigenous water, $6.4 (\pm 3.4) \times 10^8 \text{ g yr}^{-1}$ of total water, $2.4 (\pm 1.3) \times 10^8 \text{ g yr}^{-1}$ of carbon dioxide and $1.5 (\pm 0.8) \times 10^8 \text{ g yr}^{-1}$ of sulphur dioxide.

5. We have used the recently-developed E-belt model of the LHB to estimate the production of indigenous water, total water, carbon dioxide and sulphur dioxide from the accompanying carbonaceous micrometeoroid flux, at Earth and Mars. During the peak 50 Myr of the LHB, the average infall rate of carbonaceous micrometeoroids at Earth of $6.7 (\pm 3.8) \times 10^{13} \text{ g yr}^{-1}$ at Earth is estimated to yield $5.1 (\pm 3.1) \times 10^{12} \text{ g yr}^{-1}$ of indigenous water, $8.6 (\pm 5.1) \times 10^{12} \text{ g yr}^{-1}$ of total water, $3.9 (\pm 2.3) \times 10^{12} \text{ g yr}^{-1}$ of carbon dioxide and $2.3 (\pm 1.4) \times 10^{12} \text{ g yr}^{-1}$ of sulphur dioxide, resulting in total production in the 4.1-3.7 Ga period of $8.3 (\pm 4.9) \times 10^{20} \text{ g}$ of indigenous water, $1.4 (\pm 0.8) \times 10^{21} \text{ g}$ of total water, $6.3 (\pm 3.7) \times 10^{20} \text{ g}$ of carbon dioxide and $3.8 (\pm 2.2) \times 10^{20} \text{ g}$ of sulphur dioxide. For Mars, the $1.1 (\pm 0.6) \times 10^{13} \text{ g yr}^{-1}$ of carbonaceous micrometeoroids at Mars during the peak 50 Myr of the LHB is estimated to have yielded $8.2 (\pm 4.8) \times 10^{11} \text{ g yr}^{-1}$ of indigenous water, $1.4 (\pm 0.8) \times 10^{12} \text{ g yr}^{-1}$ of total water, $5.8 (\pm 3.5) \times 10^{11} \text{ g yr}^{-1}$ of carbon dioxide and $3.6 (\pm 2.1) \times 10^{11} \text{ g yr}^{-1}$ of sulphur dioxide, with total 4.1-3.7 Ga production of $1.3 (\pm 0.8) \times 10^{20} \text{ g}$ of indigenous water, $2.2 (\pm 1.3) \times 10^{20} \text{ g}$ of total water, $9.3 (\pm 5.5) \times 10^{19} \text{ g}$ of carbon dioxide and $5.8 (\pm 3.4) \times 10^{19} \text{ g}$ of sulphur dioxide. The dominant

source of error in the present-day data is the 50% uncertainty in the LDEF figure of $4 (\pm 2) \times 10^{10} \text{ g yr}^{-1}$ of micrometeoroids, while the uncertainty in the LHB data is dominated by the comparable $\pm 50\%$ uncertainty in the mass ratio of micrometeoroids to asteroids. These large uncertainties demonstrate the need for an improved understanding of micrometeoroid production, transport and infall rates.

6. The total mass of water, carbon dioxide and sulphur dioxide produced by micrometeoroidal infall during the LHB at Mars is estimated to be generally 1-10% of the mass of the corresponding volatile released by emplacement of the Tharsis magmatic province, although the large margins of uncertainty in the estimates of both volatile contents of the magmas and the volatile yields from micrometeoroids should be noted. The estimate of the rate of production of sulphur dioxide from micrometeoroidal infall on Mars during a single year of the peak 50 Myr of the LHB, of $3.6 (\pm 2.1) \times 10^{11} \text{ g yr}^{-1}$, represents about 1% of the $4 \times 10^{11} \text{ moles yr}^{-1}$ of sulphur, as indicated by modelling, required to raise the surface temperature above the freezing point of water, ignoring the cooling effects of sulphate aerosols. However, the high altitude of injection of micrometeoroidal sulphur dioxide, relative to gas injected by effusive volcanism, may have resulted in a greater lifetime and hence accumulation of sulphur dioxide at high altitudes, with the higher-altitude gas being less vulnerable to removal by rain or by reaction to sulphate aerosols. Future investigations into the climate of early Mars should therefore investigate whether the relationship between the altitude of injection and the warming potential of sulphur dioxide.

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Table captions

Table 1. Yields of carbon dioxide, water and sulphur dioxide produced upon pyrolysis of the samples, as measured in ppm per degree Celsius. ¹Org. = Orgueil, CB = Cold Bokkeveld and Murch. = Murchison; ALH 88045 and Mokoia are excluded from this mean because of their terrestrial alteration and thermal metamorphism, respectively. ²Data not available because of instrumental error. These data have a margin of uncertainty about $\pm 5\%$, relating to errors in sample measurement and purity.

Table 2. Temperatures of decomposition of volatile-generating phases in carbonaceous chondrites.

¹Dehydration refers to the loss of molecular water of hydration; decomposition refers to the loss of bound OH⁻, CO₃²⁻ or SO₃²⁻ groups and the formation of an anhydrous product; oxidation refers to reaction with externally-derived oxygen. ²Fe-rich serpentine decomposes at the lower end of this range. ³Decomposition can occur at 900 °C under oxygen (Burgess et al., 1991); also note other reactions of calcium sulphate as discussed in Section 4.3.1 (Strydom et al., 1997; van der Merwe et al., 1999). ⁴Enrichment in iron results in a decomposition temperature closer to 400 °C. References are: [1] Sandford and Bradley (1989), [2] Bullock et al. (2005), [3] Subrt et al. (1992), [4] Mitov et al. (2002), [5] Akai (1992), [6] Brindley and Zussman (1957), [7] Nozaki et al. (2006), [8] Greshake et al. (1998), [9] Brindley and Hayami (1965), [10] Mackenzie and Berezowski (1981), [11] Burgess et al. (1991), [12] Paulik et al. (1981), [13] Bish and Scanlan (2006), [14] Fuchs et al. (1973), [15] Browning and Bourcier (1997), [16] Smykatz-Kloss (1974), [17] Sephton (2002).

Table 3. Summary of the fractions of the micrometeoroidal infall at Mars at the present day that experience certain temperatures, and the subsequent production of volatiles. The carbonaceous infall is assumed to comprise 80(± 5)% of the total infall. The infall in each size range is taken from Flynn (1996) and Hughes (1978), but has been scaled here by a factor of 0.57, reflecting a total

micrometeoroid infall rate at Mars of $6.8 \times 10^9 \text{ g yr}^{-1}$ rather than the original rate of Flynn (1996), produced using pre-LDEF data of Hughes (1978), of $1.2 \times 10^{10} \text{ g yr}^{-1}$. The rate of $6.8 \times 10^9 \text{ g yr}^{-1}$ was produced by scaling the $4 \times 10^{10} \text{ g yr}^{-1}$ flux at Earth (Love and Brownlee, 1993) to Mars by a factor of 0.17 (Flynn and McKay, 1990). See Section 2.5 for further details.

Table 4. Heating experienced by carbonaceous micrometeoroids at Mars at the present day. Infall rates at Mars have been scaled from the original figures of Flynn (1996), based on Hughes (1978), using the LDEF infall rate of Love and Brownlee (1993), itself scaled to Mars by a factor of 0.17 (Flynn and McKay, 1990). See Section 2.5 for explanation of assignment of peak temperatures and scaling operations. See Section 6.1.3 for derivation of the 53% error.

Table 5. The masses of micrometeoroids arriving at Earth and Mars during the LHB, as calculated using the E-belt LHB model of Morbidelli et al. (2012), and the subsequent rates of production of volatiles from the 80% carbonaceous mass fraction. The uncertainties listed for each volatile are discussed in Section 6.1. The ranges of data for production rates of water reflect the uncertainty whether water released by pyrolysis at 250 °C is indigenous. See Section 6.1.2 for derivation of the 59% uncertainty.

Figure captions

Figure 1. Spectra of the pyrolysis products of Orgueil at each temperature step. Bands are: 1 – water; 2 – carbon dioxide; 3 – sulphur dioxide.

Figure 2. Calibration curves of water, carbon dioxide and sulphur dioxide, produced by the decomposition of sodium hydrogencarbonate and the injection of sulphur dioxide. The equations describe the curves formed by the data, along with the correlation coefficient r^2 , while the root mean square error (RMSE) describes the difference between the measured data points and those predicted by the equations. When a single equation could not be found to satisfactorily describe the data, multiple equations are shown, each describing different areas of the data. See Section 2.3 and Court and Sephton (2009b, c, 2011) for further details. These data have a margin of uncertainty about 5%, relating to errors in sample measurement and purity.

Figure 3. Comparison between the yields of volatiles produced here by stepped py-FTIR ($\uparrow, \diamond$), and by previous py-FTIR experiments involving a single pyrolysis step at 1000 °C ($\blacksquare$) (Court and Sephton, 2009b, 2011). Water yields as calculated here are marked in Fig. 3A by the data ranges, with the lower bound representing indigenous water, excluding water produced at 250 °C, and the upper bound representing all water production, including the water produced at 250 °C, as described in Section 4.4. Agreement between the data presented here and the data of Court and Sephton (2009b, 2011) is good for carbon dioxide, less good for water and rather poor for sulphur dioxide, with the stepped analyses reported here indicating considerably higher yields of sulphur dioxide than previously reported (Court and Sephton, 2011). These data have a margin of uncertainty about $\pm 5\%$, relating to errors in sample measurement and purity.

Figure 4. Production of volatiles upon stepped pyrolysis, as measured as ppm °C⁻¹, relative to the original sample mass. These data have a margin of uncertainty about ±5%, relating to errors in sample measurement and purity.

Figure 5. Micrometeoroidal dust arriving at the top of the atmosphere of Earth during the LHB. Panel A shows the rate of arrival; Panel B shows the accumulating mass. Data is produced using the timeline of lunar bombardment for a LHB beginning at 4.1 Ga as described by Morbidelli et al. (2012), assuming that the Earth received 22 times more mass of micrometeoroids than the Moon (Bottke et al., 2012; Vanzani et al., 1997) and assuming a 3:1 ratio of the mass of asteroids to the mass of micrometeoroids arriving at Earth (Stokes et al., 2003). The data have a ±57% margin of uncertainty (Section 5.3), as denoted by the dashed lines.

Table 1

		Yield (ppm °C ⁻¹)																	
Temp. (°C)		Orgueil CI1			ALH 88045 CM1			Cold Bokkeveld CM2			Murchison CM2			Mokoia CV3			Mean of Org., CB and Murch. ¹		
		H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂
250		230.5	0.2	0.0	87.4	1.9	0.0	317.7	2.9	0.0	67.3	2.1	0.0	7.6	0.2	0.0	205.2	1.7	0.0
300		147.3	7.9	14.2	38.7	4.5	0.0	203.9	12.1	9.8	45.8	4.5	0.0	0.0	2.1	0.0	132.3	8.2	8.0
400		151.1	26.5	76.0	53.2	8.4	0.0	156.5	30.7	40.5	74.7	14.3	0.0	4.9	6.6	0.0	127.5	23.9	38.8
500		90.4	53.6	26.5	95.1	23.0	0.0	103.4	51.2	11.7	116.6	31.9	0.6	0.7	10.3	1.7	103.5	45.6	12.9
600		83.4	83.5	98.6	173.9	33.1	1.4	95.3	79.5	92.2	160.2	46.2	12.1	0.0	7.8	29.6	113.0	69.7	67.7
700		95.6	113.8	114.1	226.5	45.0	9.3	92.4	97.9	96.3	158.8	63.7	56.0	0.0	8.4	39.6	115.6	91.8	88.8
800		138.0	124.6	60.8	252.3	57.5	14.7	132.0	122.1	58.8	126.9	64.0	63.1	0.0	14.6	38.5	132.3	103.6	60.9
900		106.4	205.9	32.4	112.4	87.0	17.6	85.4	134.4	42.9	73.5	81.8	44.0	n/a	n/a	n/a ²	88.4	140.7	39.8
1000		16.8	113.6	37.1	14.9	79.5	28.6	24.9	113.2	41.2	27.9	76.9	34.5	0.0	20.8	3.9	23.2	101.2	37.6
Yield (wt.%)	250 °C	5.8	0.0	0.0	2.2	0.0	0.0	7.9	0.1	0.0	1.7	0.1	0.0	0.2	0.0	0.0	5.1	0.0	0.0
	≥300 °C	7.6	7.3	4.5	9.5	3.4	0.7	7.9	6.4	3.9	7.6	3.8	2.1	0.1	0.7	1.1	7.7	5.8	3.5
	Total	13.3	7.3	4.5	11.7	3.4	0.7	15.9	6.4	3.9	9.3	3.9	2.1	0.2	0.7	1.1	12.8	5.8	3.5

Table 2

Phase	Approximate composition	Reaction ¹	Volatile evolved	Temperature of evolution (°C)	References
Sorbed water	H ₂ O	Desorption	H ₂ O	<300	[1]
Ferrihydrite	Fe ₅ O ₇ OH·H ₂ O	Dehydration Decomposition	H ₂ O H ₂ O	100-200 500-600	[2-4]
Serpentine	(Mg ₂ Fe)Si ₂ O ₅ (OH) ₄	Decomposition	H ₂ O	400-600 ²	[5-10]
Saponite	Mg ₂ FeSi ₃ AlO ₁₀ (OH) ₂ ·4(H ₂ O)	Dehydration Decomposition	H ₂ O H ₂ O	400-600 700-800	[5,7-9]
Gypsum	CaSO ₄ ·2H ₂ O	Dehydration Decomposition	H ₂ O SO ₂	<200 1200 ³	[11]
Epsomite	MgSO ₄ ·7H ₂ O	Dehydration Decomposition	H ₂ O SO ₂	310 1100	[11,12]
Ni-blödite	(Na,Mg,Ni)(SO ₄) ₂ ·2H ₂ O	Dehydration Decomposition	H ₂ O SO ₂	260 ?	[11,13]
Tochilinite	Mg,Fe(OH) ₂ ·FeS	Dehydration Oxidation	H ₂ O SO ₂	<400 400-600	[7,11,14,15]
Breunnerite	(Mg(Fe,Mn)(CO ₃) ₂)	Decomposition	CO ₂	400-650 ⁴	[7,8,16]
Dolomite	MgCa(CO ₃) ₂	Decomposition	CO ₂	700	[7]
Calcite/aragonite	CaCO ₃	Decomposition	CO ₂	890	[16]
Sulphur	S	Oxidation	SO ₂	<200	[11]
Sulphides	S ²⁻	Oxidation	SO ₂	400-600	[11]
IOM	C ₁₀₀ H ₄₈ N _{1.8} O ₁₂ S ₂	Oxidation	H ₂ O, SO ₂ , CO ₂	-	[17]

Table 3

Mass range (μg)	Infall scaled to LDEF (10^6 g yr^{-1})	Fraction exceeding:		Carbonaceous infall (10^6 g yr^{-1})		
		627 °C	1327 °C	Not heated to 627 °C	Exceeding 1327 °C	Experiencing 627-1327 °C
10^{-6} - 10^{-5}	1	0.00	0.00	1	0	0
10^{-5} - 10^{-4}	3	0.00	0.00	3	0	0
10^{-4} - 10^{-3}	40	0.05	0.00	31	0	2
10^{-3} - 10^{-2}	115	0.12	0.00	81	0	11
10^{-2} - 10^{-1}	346	0.25	0.00	207	0	69
10^{-1} - 10^0	864	0.54	0.02	318	14	360
10^0 - 10^1	1729	0.76	0.10	332	138	913
10^1 - 10^2	1729	0.93	0.30	97	415	871
10^2 - 10^3	1153	0.99	0.50	9	461	452
10^3 - 10^4	576	1.00	0.80	0	369	92
10^4 - 10^5	173	1.00	0.95	0	131	7
10^5 - 10^6	58	1.00	0.99	0	46	0
10^6 - 10^7	12	1.00	1.00	0	9	0
Sum	6800	-	-	1080	1583	2777
% of total	100	-	-	20	29	51

Table 4

Temp. (°C)	Carbonaceous infall		Yield upon infall (wt.%)			Production (10 ⁶ g yr ⁻¹ , ±53%)		
	10 ⁶ g yr ⁻¹	%	H ₂ O	CO ₂	SO ₂	H ₂ O	CO ₂	SO ₂
≤600	1080	20	4.1-9.2	1.5	1.2	44-100	16	13
700	463	8.5	5.3-10.4	2.4	2.1	24-48	11	10
800	463	8.5	6.6-11.7	3.4	2.7	30-54	16	13
900	463	8.5	7.5-12.6	4.8	3.1	35-58	22	14
>1000	2972	55	7.7-12.8	5.8	3.5	229-381	174	104
Sum	5440	100	-	-	-	362-641	239	154
Overall yields (wt.%)						6.7-11.8	4.4	2.8

Table 5

	Period (Ga)	Mass of micro- meteoroids (10^{19} g)	Average infall rate (10^{12} g yr $^{-1}$)	Production rate of volatiles (10^{11} g yr $^{-1}$, $\pm 59\%$)		
				H ₂ O	CO ₂	SO ₂
Earth	3.70-3.75	37	7.5	4.6-7.7	3.5	2.1
	3.75-3.80	53	11	6.5-11	4.9	3.0
	3.80-3.85	74	15	9.2-15	7.0	4.2
	3.85-3.90	100	21	13-22	9.8	5.9
	3.90-3.95	150	30	18-30	14	8.3
	3.95-4.00	210	42	26-43	20	12
	4.00-4.05	300	59	36-61	28	17
	4.05-4.10	420	84	51-86	39	23
Mars	3.70-3.75	6.4	1.3	0.73-1.3	0.52	0.32
	3.75-3.80	9.0	1.8	1.0-1.8	0.73	0.45
	3.80-3.85	13	2.5	1.5-2.5	1.0	0.64
	3.85-3.90	18	3.6	2.0-3.5	1.5	0.91
	3.90-3.95	25	5.0	2.9-5.0	2.1	1.3
	3.95-4.00	36	7.1	4.1-7.0	2.9	1.8
	4.00-4.05	50	10	5.8-9.9	4.1	2.6
	4.05-4.10	71	14	8.2-14	5.8	3.6

Figure 1

Figure 1

Figure 2

Figure 2

Figure 3

Figure 3

Figure 4

Figure 4

Figure 5

Figure 5