

A photo-chemical method for the production of olivine nanoparticles as cosmic dust analogues

Russell W. Saunders, John M.C. Plane*

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:

Received 16 August 2010

Revised 24 November 2010

Accepted 18 December 2010

Available online 4 January 2011

Keywords:

Meteors

Atmospheres, Chemistry

Earth

Mineralogy

ABSTRACT

This paper describes a new experimental method to synthesise metal silicate particles in the laboratory with compositions and structures which reflect those likely to form in planetary atmospheres and in relatively cool regions of oxygen-rich stellar outflows. Fe–Mg–silicate nanoparticles of olivine composition were produced by the photo-oxidation of a mixture of $\text{Fe}(\text{CO})_5$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ vapours in the presence of O_3 at room temperature and atmospheric pressure. Transmission electron microscope X-ray and electron energy loss analysis of the particles from a number of experiments run with different precursor vapour mixture ratios show that $\text{Mg}_{2x}\text{Fe}_{2-2x}\text{SiO}_4$ particles can be produced ranging from $x = 0$ to 1, where x is linearly proportional to the ratio of $\text{Mg}(\text{OC}_2\text{H}_5)_2/(\text{Fe}(\text{CO})_5 + \text{Mg}(\text{OC}_2\text{H}_5)_2)$. Electronic structure calculations with hybrid density functional/Hartree–Fock theory are then used to explore the pathways involved in producing olivine particles from the FeO_3 , MgO_3 and SiO_2 produced from the photolysis of the organometallic precursors in O_3 . These calculations indicate that highly exothermic reactions lead to the formation of Mg_2SiO_4 , MgFeSiO_4 and Fe_2SiO_4 molecules, which then polymerize. An alternative pathway, also strongly favoured thermodynamically, is the polymerization of MgSiO_3 and FeSiO_3 to form pyroxenes, which then undergo structural rearrangement to olivine and silica phases. The implications for metal silicate formation in planetary atmosphere and stellar outflows are then discussed.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

Speculation on the chemical composition of dust particles found in a variety of extra-terrestrial environments (e.g. interstellar and circumstellar), backed by the large database of optical measurements made over the past half century or so (see Whittet, 2003), invariably identifies metal (primarily iron and magnesium) silicate compounds as a major component (Rietmeijer, 2002; Draine, 2003; Henning, 2010). Indeed, the term ‘astronomical silicate’ has been coined for a general olivine ($\text{Mg}_{2x}\text{Fe}_{2-2x}\text{SiO}_4$; $x \sim 0.5$) structure which provides a best-fit to certain features in the optical data (Draine and Lee, 1984). These dust particles are not only important in that they scatter, absorb and re-radiate light, but also because they act as catalytic substrates for the uptake and reaction of ambient gas-phase species, and hence are thought to be vital for the synthesis of detected molecular species such as H_2 and CO (Williams and Taylor, 1996).

Analysis of peak structure within the diagnostic Si–O bond vibrations at ~ 10 and $18 \mu\text{m}$ suggests a crystalline, Mg-rich ($x > 0.5$) nature for these mineral forms (pyroxene and olivine) of dust in certain high temperature environments i.e. in proximity

to evolving stars (Gail and Sedlmayr, 1999) and also in comets and planetary nebulae (Jäger et al., 1998). However, it has been reported that amorphous Fe-rich ($x < 0.5$) olivine variations are dominant in the interstellar medium or ISM (Draine, 2003; Kemper et al., 2004), with a significant proportion of such grains in the low-density regions of the ISM being less than 3 nm in size (Li and Draine, 2001).

It has long been suggested that nanoparticles of ‘meteoric smoke’ are formed in the upper atmosphere of the Earth, as a result of meteor ablation and subsequent condensation of gas-phase metal oxide and silicate species (Rosinski and Snow, 1961; Hunten et al., 1980). Ablation modelling indicates that the majority of atoms/ions released into the atmosphere from the parent meteoroid are (in approximately equivalent amounts) those of iron, magnesium and silicon (Vondrak et al., 2008). Subsequent oxidation of these species is then likely to initiate condensation of solid-phase siliceous material (smoke particles).

Such particles are predicted to be of the order of only a few nanometres in size and consequently, proof of their existence through optical methods has to date been difficult and largely inconclusive. Recent satellite-bound spectrometer measurements of high altitude particle extinction seem to be the first to identify these tiny smoke particles (Hervig et al., 2009), although compositional fitting of such data is reliant on refractive index data avail-

* Corresponding author. Fax: +44 (0)113 3436565.

E-mail address: j.m.c.plane@leeds.ac.uk (J.M.C. Plane).

able for a limited range of silicate materials prepared in the laboratory.

The interaction of meteoric smoke particles or MSPs with gases such as H_2O and H_2SO_4 in the Earth's atmosphere has long been thought to play a role in such phenomena as high altitude ice particle nucleation, leading to the related phenomena of noctilucent clouds and polar mesosphere summer echoes (Rapp and Thomas, 2006), and the depletion of acidic gases in the upper stratosphere (Turco et al., 1981). Clearly the precise nature of such particle–vapour interactions will be strongly dependent on the particle composition. The formation of meteoric smoke (and subsequent interaction with organic vapours) has recently been postulated to account for the observed 'detached' aerosol layer in Titan's atmosphere (Lavvas et al., 2009). MSPs are also almost certainly the nuclei which form CO_2 -ice clouds in the Mars mesosphere around 80 km (Montmessin et al., 2006). In the ISM, dust particles play a crucial role, for example, in the synthesis of molecules through heterogeneous chemistry (e.g. Williams and Hartquist, 1999).

The critical ingredients for the formation of such smoke and dust particles in the terrestrial and other planetary atmospheres, and in favourable regions of the ISM (see the review of Henning (2010)) such as, for example, the cooling outflows/circumstellar envelopes of oxygen-rich asymptotic giant branch (AGB) stars (e.g. Gail and Sedlmayr, 1999; Gail, 2010), planetary nebulae (e.g. Gorný et al., 2010) or regions chemically enriched by supernovae (e.g. Kotak et al., 2009), are (i) a source of metal and silicon atoms, and (ii) an oxidising species to form the initial gas-phase metal oxide and silicon oxide molecules. These can then react to form molecular silicate species (see Section 3.2). In planetary/satellite atmospheres where the atmospheric pressure is greater than about 1 μbar , meteoric ablation occurs (e.g. McAuliffe and Christou, 2006; Kim et al., 2001; Ip, 1990; English et al., 1996; Molina-Cuberos et al., 2008; Pesnell and Grebowsky, 2000; Whalley and Plane, 2010). The resulting metal and silicon atoms are then oxidized in the presence of O_3 and O_2 , which tend to be present at some level (e.g. Fast et al., 2009; Migliorini et al., 2010; Noll et al., 1997; Hörst et al., 2008). In the ISM, the stellar nucleosynthesis and ejection of metals such as Fe and Mg and of Si accompanied by the presence of oxygen in the form of neutral and ionised forms or in volatile molecules or ices (Jensen et al., 2008) will likewise be conducive to the formation of silicate species.

The production of analogue materials for cosmic dust studies has utilised a number of methods (reviewed by Colangeli et al. (2003)) including room temperature sol–gel preparations (Thompson et al., 1996; Jäger et al., 2003), melt quenching (Dorschner et al., 1995), and vapour condensation methods such as laser ablation–condensation (Brucato et al., 2002) and high temperature evaporation–condensation (Rietmeijer et al., 1999; Nuth et al., 2000). The purpose of such laboratory techniques is not to replicate directly the chemical or physical conditions in which particle formation can occur in the Earth's atmosphere, other planetary atmospheres or the ISM, but to provide a way of forming particles of realistic composition and structure for the subsequent study of their physical and chemical properties under conditions appropriate for a targeted environment.

Sol–gel/melt quenching syntheses can produce amorphous pyroxene and olivine compounds with mixed compositions, but the vapour condensation methods to date have indicated that formation of mixed Mg–Fe silicate materials is not favoured. However, more recent studies using the photo-oxidation of 'binary' mixtures of iron and silicon precursor vapours at room temperature (Saunders and Plane, 2006; Kimura and Nuth, 2007) led to the preferential nucleation and subsequent growth of amorphous particles with end-member olivine composition. To the best of our knowledge, there have, as yet, been no reports of the formation of mixed-composition (Fe–Mg) olivine materials directly from the

gas-phase at low (room) temperature. This has important implications for understanding dust compositions in lower temperature environments such as planetary/satellite atmospheres and the ISM.

Our earlier study (Saunders and Plane, 2006) was aimed at synthesising and studying the properties of nanomaterials as analogues of meteoric smoke particles or MSPs. This paper extends our investigations to a more realistic 'tertiary' vapour system, whereby a mixture of iron, magnesium and silicon oxide vapours is generated, from which mixed composition olivine nanoparticles are produced. Electron microscope X-ray analysis (TEM-EDX) and electron energy loss spectroscopy (EELS) data from collected material is used to show that (1) the final particle composition is homogeneous and (2), the relative Fe/Mg composition in the particles can be controlled quantitatively from $x = 0$ to 1 by varying the relative flows of the organometallic precursors. To complement the laboratory studies, we use electronic structure theory to identify likely molecular structures and chemical pathways which result in the observed particle compositions.

2. Experimental methods

An aerosol flow reactor system (cylindrical laminar flow glass cell fitted with a series of quartz windows which act as photolysis ports) described in detail previously (Saunders and Plane, 2006) was used for the nucleation and growth of refractory aerosol from the photo-oxidation of mixed vapours of the precursors, iron pentacarbonyl ($\text{Fe}(\text{CO})_5$, 99.999%, Aldrich), magnesium ethoxide ($\text{Mg}(\text{OC}_2\text{H}_5)_2$, 98%, Aldrich) and tetraethyl orthosilicate or TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$, 98%, Aldrich), in N_2 bath gas at 293 K and atmospheric pressure. Photolysis of the precursor vapours was achieved using a broad-band Xe arc lamp ($\lambda > 300 \text{ nm}$), whose beam was directed through the quartz cell windows using a flat mirror, and attenuated using neutral density filters to achieve the desired photolysis rate in the experiments. A total gas flow rate (precursors, O_2 and N_2 bath gas) of 600 cm^3 per minute at STP was used in all experiments. Ozone (10^{13} – 10^{14} cm^{-3}) was generated prior to addition to the aerosol flow reactor by passing the O_2 flow through a small cell with a quartz window adjacent to a Hg pen lamp.

A series of particle production experiments was performed using varying ratios of the three precursor vapours present in the reactor. The ratio was controlled experimentally by varying the relative gas flow fractions of the entrained precursor vapours. Whilst vapour pressure data for the Fe and Si liquid precursors has been reported in the literature (Gilbert and Sulzmann, 1974; Alcott et al., 2004 respectively), no such data appears to exist for the solid Mg precursor. In addition, all experiments were performed at constant lamp irradiance in the flow reactor, corresponding to a calculated photolysis rate (J) of $\sim 2.0 \times 10^{-4} \text{ s}^{-1}$ for $\text{Fe}(\text{CO})_5$ (determined from the wavelength-resolved lamp photon flux and the molecular absorption cross-section – see Saunders and Plane, 2010). No cross-section data is available in the literature for the other precursors. The generated particles were sampled downstream of the flow cell by inertial deposition onto holey-carbon grids (300 mesh Cu, Agar Scientific) suspended in the gas flow, for subsequent TEM (Philips CM200) imaging and quantitative compositional analysis using energy dispersive X-ray (EDX) and electron energy loss techniques.

3. Results and discussion

3.1. Electron microscope and elemental analysis

Fig. 1 is an electron micrograph of a particle aggregate generated by the photo-oxidation of a mixture of the Fe, Mg and Si precursors described previously. Whilst the maximum projected



Fig. 1. Transmission electron micrograph of a typical fractal-like particle aggregate formed from a vapour mixture of Fe, Mg and Si precursors.

length of this structure from the 2D image is in excess of $2\ \mu\text{m}$, it is evident that the fractal-like nature of the aggregate is generated from smaller particle clusters made up of constituent ‘primary’ particles with an observable range of sizes down to $\sim 10\ \text{nm}$. Previous growth modelling analysis of iron oxide and silicate particles generated within the same flow reactor (Saunders and Plane, 2006, 2010) indicate a primary particle size typically between 6–8 nm for such particles under conditions of room temperature and atmospheric pressure.

Fig. 2 shows EDX spectra obtained from particles generated from three different vapour mixtures. The top spectrum was taken from a particle aggregate formed from the photo-oxidation of the iron-silicon system, the middle spectrum from the iron-magnesium-silicon system, and the bottom spectrum from the magnesium-silicon system.

Seven different experiments were performed: one Fe/Si run, one Mg/Si run, and five separate Fe/Mg/Si runs where the Fe and Mg precursor flows were varied. The relative Fe, Mg and Si content in the particles was determined using the integrated EDX peak areas and X-ray scattering cross-sections (Si_K , $\text{Fe}_{K,L}$ and Mg_K) (Goodhew et al., 2001). Analysis was typically performed on five different regions of each sampled particle (using a probe size of 1 nm), and on 5–10 different particles collected in the same experiment. The elemental values obtained in this way were highly consistent, with less than 10% variation for a given particle sample in each experiment. It should be noted that we did not observe any particles of purely iron or magnesium oxide composition from these experiments. The relative abundance data was then used to calculate values of x_{particle} ($=\text{Mg}/(\text{Mg} + \text{Fe})$) for comparison with the olivine and pyroxene stoichiometries – $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$ and

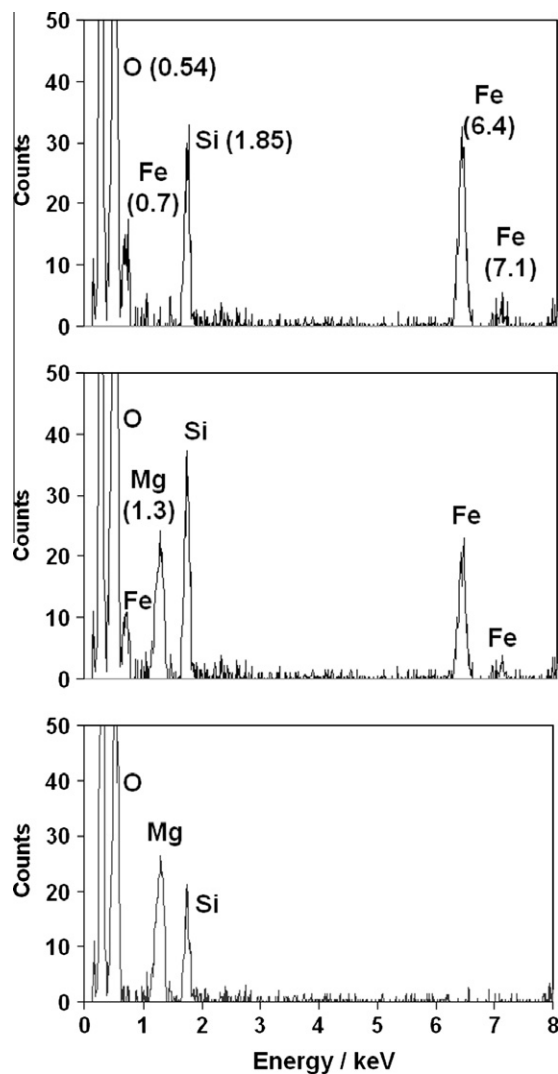


Fig. 2. EDX spectra of particles sampled from three particle production experiments in which no Mg precursor vapour was present (top panel), no Fe precursor vapour was present (bottom panel), and in which all three precursor vapours were present in the flow reactor (middle panel). Characteristic element peaks are indicated at the respective electron energy values.

$\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$, respectively. These are listed in Table 1 along with the flow rates used for the precursor species, oxidant and bath gas (N_2).

Fig. 3 shows particle x values plotted against the ratio of $(\text{Mg} + \text{Fe})/\text{Si}$ for each experiment. Within error, the average particle compositions from all experiments are consistent with olivine and not pyroxene structures.

Table 1

Flows ($\text{cm}^3\ \text{min}^{-1}$ at 293 K and 1 bar) used for the respective precursor vapours (Fe-, Mg- and Si-) present in the particle formation experiments. Calculated atomic ratio ($x_{\text{particle}} = \text{Mg}/(\text{Mg} + \text{Fe})$) from EDX analysis on particles collected from the respective experiments is also shown.

Fe	Mg	Si	O ₂	N ₂	Mg/Fe	x_{particle}
15	0	100	40	445	0	0
11	20	100	40	429	1.82	0.11
9	40	100	40	411	4.44	0.36
6	50	100	40	404	8.33	0.47
3	75	100	40	382	25.0	0.65
3	100	100	40	357	33.33	0.78
0	50	100	40	410	–	1.0

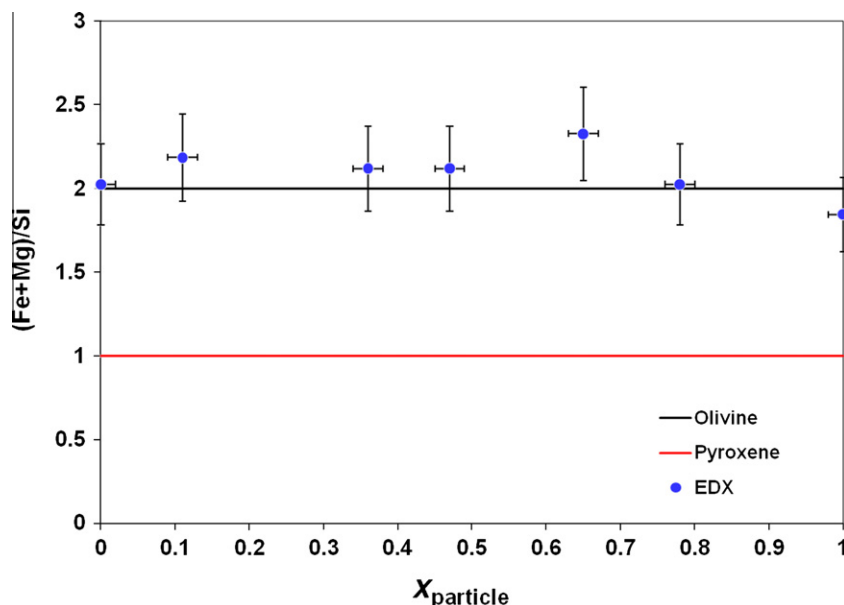


Fig. 3. Plot of the measured elemental ratio (Fe + Mg)/Si in the sampled particles against x , indicating an olivine $[(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4]$ composition in all cases.

For further verification of the particle compositions, electron energy loss spectroscopy (EELS) was also conducted in order to quantify the oxygen content (O_K). These were plotted as a ratio with respect to Fe, Mg and Si atomic content using the integrated peak areas, as discussed in Saunders and Plane (2006), against the x_{particle} values determined above. Fig. 4 indicates that the measured elemental data (coloured points) are in accord with those predicted for olivine structures (solid coloured lines). In addition, as with our earlier study, analysis of the $\text{Fe}_{L_{2,3}}$ line structures (van Aken and Liebscher, 2002) indicated a single (+2) oxidation state. Electron diffraction revealed no diffraction behaviour for any of the particle aggregates analysed at a number of different

points and so confirmed that, for all samples, the particles were entirely amorphous.

The EDX/EELS analysis clearly indicates that particle composition resulting from the photo-oxidation of Fe-, Mg-, and Si-precursor vapours was homogeneous in all cases. From this, it can be concluded that particle nucleation in this system occurs from a homogeneous mix of condensable gas-phase species, the identities of which we will discuss in Section 3.2.

If the Mg and Fe content in the particles are a fraction α of their respective gas-phase precursor concentrations i.e. $\text{Mg} = \alpha_{\text{Mg}}[\text{Mg}(\text{OC}_2\text{H}_5)_2]$ and $\text{Fe} = \alpha_{\text{Fe}}[\text{Fe}(\text{CO})_5]$, then the ratio of Mg/Fe in the particle should be

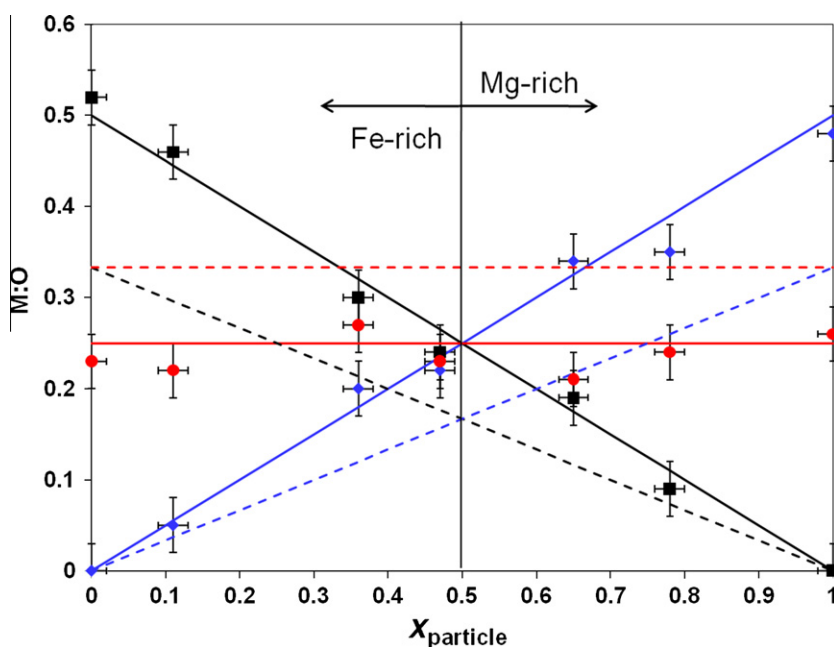


Fig. 4. Calculated element to oxygen ratios M:O (M = Fe (black data points), Mg (blue) and Si (red)) from EELS analysis of particles from the same experiments as in Fig. 3, plotted against x . The solid lines (Fe is black, Mg is blue, Si is red) indicate the relationships that would be expected for a pure olivine composition, and the dashed lines those for pyroxene. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\frac{\text{Mg}}{\text{Fe}} = \frac{\alpha_{\text{Mg}}[\text{Mg}(\text{OC}_2\text{H}_5)_2]}{\alpha_{\text{Fe}}[\text{Fe}(\text{CO})_5]} \quad (\text{I})$$

α combines the precursor photolysis rate and efficiencies with which the resulting metal oxide and silicate condense. Note that in the case of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ there does not appear to be published data on its photolysis cross-section.

Since

$$x = \frac{\text{Mg}}{\text{Mg} + \text{Fe}}$$

then

$$\left(\frac{x}{1-x}\right) = \frac{\alpha_{\text{Mg}}[\text{Mg}(\text{OC}_2\text{H}_5)_2]}{\alpha_{\text{Fe}}[\text{Fe}(\text{CO})_5]} \quad (\text{II})$$

Each vapour is entrained in a flow of N_2 passing through a reservoir cell containing its respective precursor. Under the slow flow conditions used here, the gas-phase precursor concentrations in the photolysis cell are then linearly proportional to the N_2 flows through their respective reservoir cells. Hence, the ratio of the precursor flows, $f(\text{Mg})/f(\text{Fe})$, can be substituted into Eq. (2), yielding

$$\left(\frac{x}{1-x}\right) = \frac{\beta_{\text{Mg}}f(\text{Mg})}{\beta_{\text{Fe}}f(\text{Fe})} \quad (\text{III})$$

where β combines α with the vapour pressure of the respective precursor (data on the vapour pressure of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ does not appear to be available). Fig. 5 is a plot of $x/(1-x)$ against $f(\text{Mg})/f(\text{Fe})$, which is linear with a slope of 0.0956 ($R^2 = 0.938$). Importantly, this demonstrates that the relative abundance of Mg to Fe in the particles has a linear dependence on the relative flows of their precursor vapours, so that particles with a composition anywhere between $x = 0$ and 1 can be made in a simple quantitative way.

3.2. Chemical pathways to final particle compositions

Photolysis of the precursor vapours produces Fe, Mg and Si atoms, and the reaction kinetics of these atoms and their oxides with O_2 and O_3 have been studied previously in our group (Gómez-Martín et al., 2009a,b; Helmer and Plane, 1994a; Rollason and Plane, 2000, 2001). Inspection of the rate coefficients listed in

Table 2 shows that in the large excess of O_2 and O_3 employed in the present experiments, Fe and Mg would have been rapidly oxidized to FeO_3 and MgO_3 , and Si to SiO_2 .

In order to investigate the subsequent steps to particle formation, we now employ electronic structure calculations using the Gaussian 09 suite of programs (Frisch et al., 2009). The hybrid density functional/Hartree–Fock B3LYP method was employed together with the 6–311 + G(2d,p) triple zeta basis set, which is a reasonably large, flexible basis set with both polarization and diffuse functions added to the atoms. The expected uncertainty in the calculated reaction enthalpies is $\pm 20 \text{ kJ mol}^{-1}$ at this level of theory. For each molecule the geometry was first optimised, and then vibrational frequencies calculated to determine the zero point energy correction. For the Fe-containing species, all possible spin multiplicities were investigated. The most stable isomers (invariably spin high), are reported here.

The present experiments were performed with a small excess of SiO_2 over the metal oxides (as in our previous study on Fe_2SiO_4 formation, Saunders and Plane, 2006). Therefore, starting from the feedstock of MgO_3 , FeO_3 and SiO_2 it is likely that the metal silicate molecules MgSiO_3 and FeSiO_3 first form via the following highly exothermic reactions:



Table 2

List of the reactions and rate coefficients involved in the oxidation of Fe, to FeO_3 , Mg to MgO_3 , and Si to SiO_2 .

Reaction	k (293 K) ^a	Reference
$\text{Fe} + \text{O}_3 \rightarrow \text{FeO} + \text{O}_2$	2.1×10^{-10}	Helmer and Plane (1994a)
$\text{Fe} + \text{O}_2 (+\text{N}_2) \rightarrow \text{FeO}_2$	1.0×10^{-13}	Helmer and Plane (1994b)
$\text{FeO} + \text{O}_3 \rightarrow \text{FeO}_2 + \text{O}_2$	1.6×10^{-10}	Rollason and Plane (2000)
$\text{FeO} + \text{O}_2 (+\text{N}_2) \rightarrow \text{FeO}_3$	9.5×10^{-11}	Rollason and Plane (2000)
$\text{FeO}_2 + \text{O}_3 \rightarrow \text{FeO}_3 + \text{O}_2$	2.5×10^{-10}	Self and Plane (2003)
$\text{Mg} + \text{O}_3 \rightarrow \text{MgO} + \text{O}_2$	1.4×10^{-10}	Plane and Helmer (1995)
$\text{MgO} + \text{O}_3 \rightarrow \text{MgO}_2 + \text{O}_2$	3.4×10^{-11}	Plane and Helmer (1995)
$\text{MgO}_2 + \text{O}_3 \rightarrow \text{MgO}_3 + \text{O}_2$	Not measured	See Plane and Helmer (1995)
$\text{Si} + \text{O}_2 \rightarrow \text{SiO} + \text{O}$	1.1×10^{-10}	Gómez-Martín et al., (2009a)
$\text{Si} + \text{O}_3 \rightarrow \text{SiO} + \text{O}_2$	4.0×10^{-10}	Gómez-Martín et al., (2009a)
$\text{SiO} + \text{O}_3 \rightarrow \text{SiO}_2 + \text{O}_2$	4.4×10^{-13}	Gómez-Martín et al. (2009b)

^a Rate coefficient at 293 K, units: $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

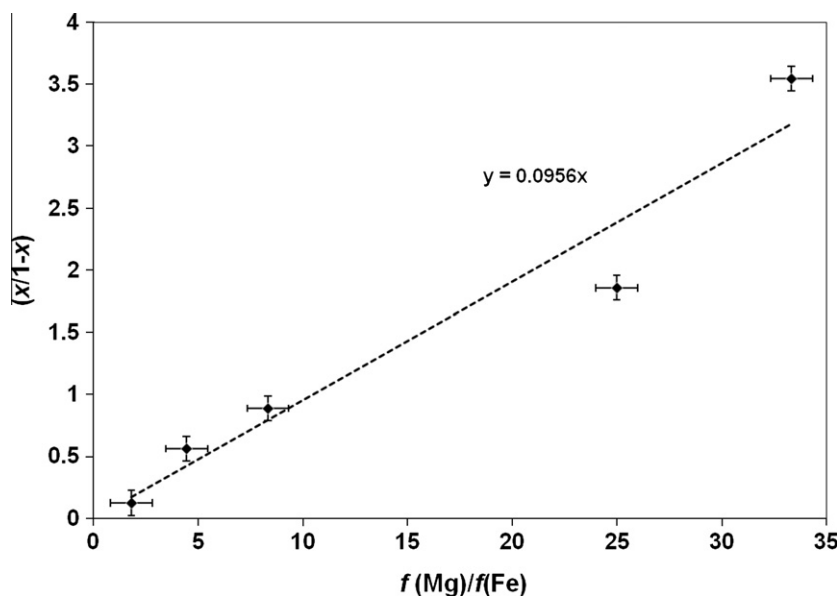


Fig. 5. Correlation plot of the ratio (f) of magnesium to iron precursor vapour flows (Table 1) employed in the respective experiments against calculated atomic ratio ($x = \text{Mg}/(\text{Mg} + \text{Fe})$) in generated mixed silicate particles.

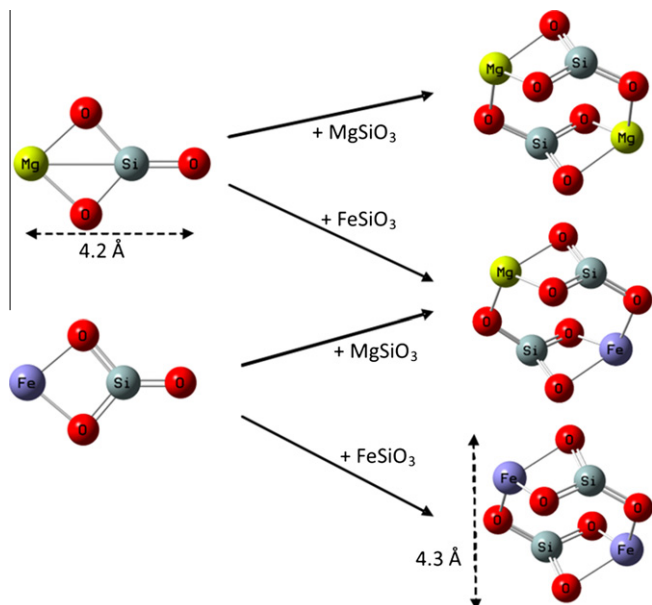
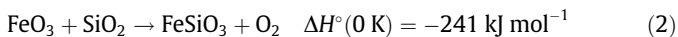
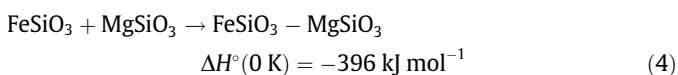
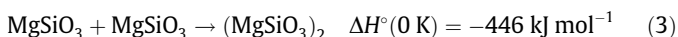


Fig. 6. Electronic structure calculations at the B3LYP/6-311+g(2d,p) level of theory of the optimised geometries of MgSiO_3 , FeSiO_3 and their dimers and mixed polymer.



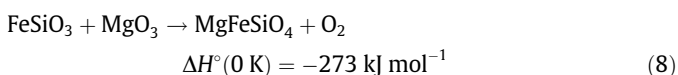
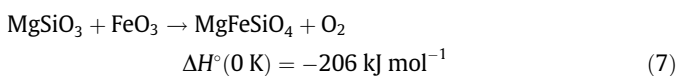
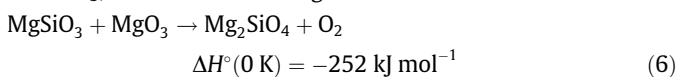
As shown in Fig. 6, these silicate molecules have planar kite-shaped geometries (the most stable electronic state of FeSiO_3 has quintet spin multiplicity i.e. four parallel unpaired electrons; MgSiO_3 is a singlet with no unpaired spins). A distinctive feature of the silicates is that they possess very large electric dipole moments: $\mu(\text{MgSiO}_3) = 12.2$ Debye and $\mu(\text{FeSiO}_3) = 9.5$ Debye. This will favour polymerization of the silicates, which should occur rapidly because of the long-range attractive forces generated between the polar molecules.

Fig. 6 illustrates the geometries of the polymers formed between these silicates. The binding energies are extremely large:



Since the enthalpies for the addition of further silicate molecules to an embryonic particle are likely to be similarly large, there is unlikely to be a free energy barrier to spontaneous nucleation and growth.

However, the analysis of the particles formed in our experiments shows that they are composed of olivines rather than pyroxenes. There are two likely ways in which this happens. First, olivine molecules may actually form in the gas phase. This is because the MgSiO_3 and FeSiO_3 molecules are produced in an excess of MgO_3 and FeO_3 , so that the following reactions can occur:



Once again, all these reactions are very favourable thermodynamically. The olivine molecules, which are illustrated in Fig. 7, should also polymerize spontaneously through highly exothermic reactions. For example, for the two dimers shown in Fig. 7:

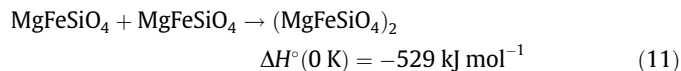
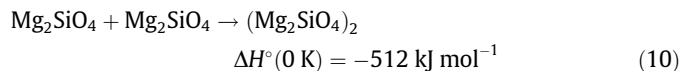
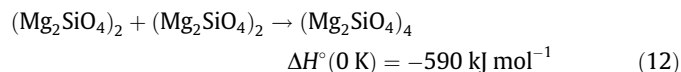
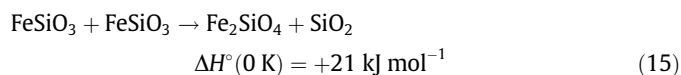
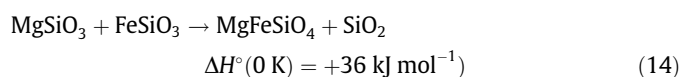
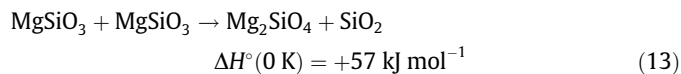


Fig. 7 also shows the Mg_2SiO_4 tetramer, formed from the polymerization of two Mg_2SiO_4 dimers:

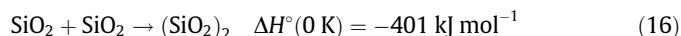


This process is also extremely exothermic (calculated at the B3LYP/3-21+g level of theory), underlining the strong thermodynamic force behind polymerization of these molecules. Thus there is a plausible route involving reactions (1) and (2) to form the silicate molecules, followed by reaction (6)–(9) to form the olivine molecules, which would generate particles with the observed olivine structure where x would be equal to the relative rates of photochemical production of Mg to Fe atoms.

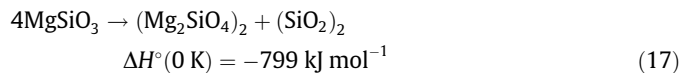
Note, however, that this reaction sequence requires reactions (6)–(9) to be faster than reactions (3)–(5) (where the silicates polymerize directly together). If in fact silicate polymerization is competitive, then the resulting amorphous pyroxene particles must rearrange internally to form olivines. This is the second way in which the observed olivine particles could form. To get a sense of the thermodynamic requirements for structural rearrangement, consider the enthalpies for the following reactions which convert pyroxene to olivine molecules:



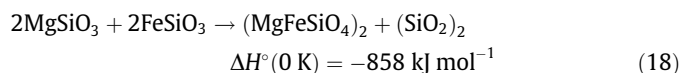
The dimerization of SiO_2 is strongly exothermic:



Hence, combining reactions $2 \times (13) + (10) + (16)$ gives:



and combining reactions $2 \times (14) + (11) + (16)$ gives:



Reactions (17) and (18) are therefore highly exothermic. This indicates that pyroxene might rearrange into olivine in small particles by forming a separate SiO_2 phase. Of course, the “separate phases” considered here only consist of dimers of olivine and silica molecules, and further theoretical investigation in this direction would be extremely computer-intensive. We therefore conclude

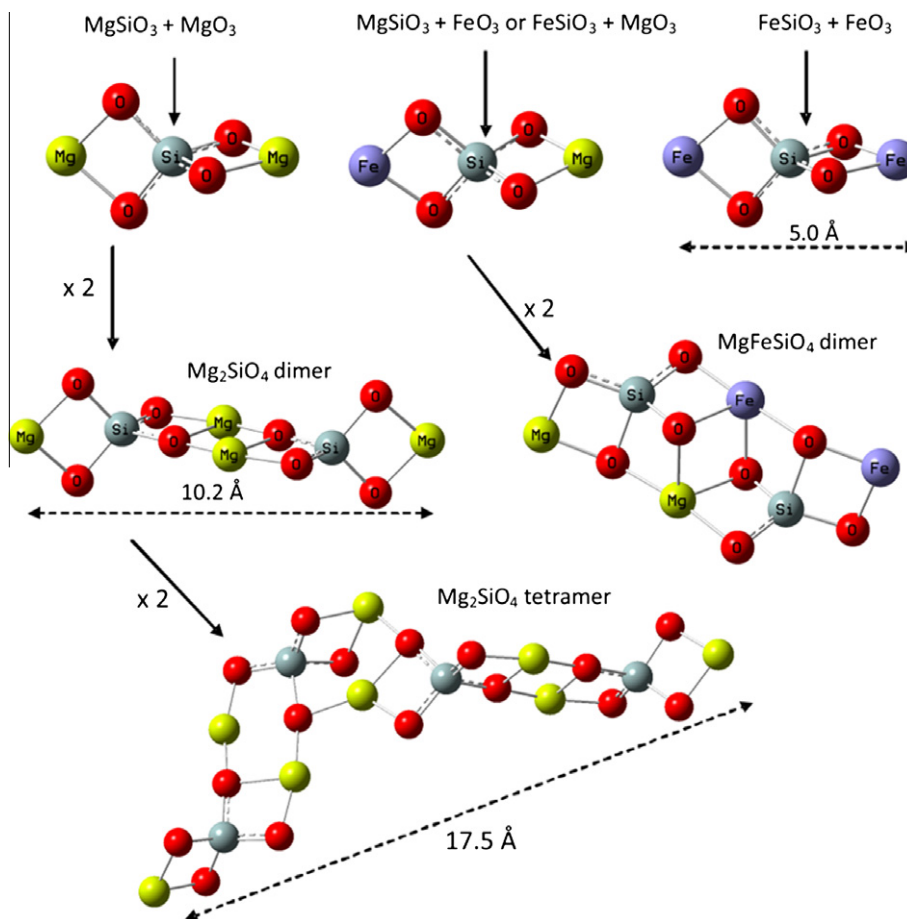


Fig. 7. Electronic structure calculations of the optimised geometries of Mg_2SiO_4 , MgFeSiO_4 and Fe_2SiO_4 ; the dimers of Mg_2SiO_4 and MgFeSiO_4 ; and the Mg_2SiO_4 tetramer.

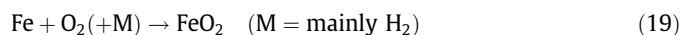
that both direct formation of gas-phase olivine molecules, and possibly some structural rearrangement of condensed silicates, play a role under our experimental conditions.

3.3. Comparison with other laboratory studies of Mg–Fe-silicate formation

While the present study appears to be the first attempt to investigate the formation of tertiary Mg–Fe-silicate meteoric smoke particles relevant to planetary atmospheres, there have been a number of studies to investigate the formation of metal silicates under the conditions of stellar outflow regions and the ISM. Replicating the conditions – temperatures, pressures and timescales – of these environments in the laboratory is challenging (Nuth et al., 2000). There have been essentially two types of experimental approach. In the first, a sample of olivine, for example, is vaporized by flash heating (Nagahara et al., 1988) or laser ablation (Brucato et al., 2002); the condensation products of the resulting vapours are then collected and analysed. In the second type of experiment, vapours of Fe, Mg and Si are produced in the presence of an oxidant by decomposition of appropriate precursors, either photochemically (the present study) or in a high temperature (500–1500 K) thermal reactor (Rietmeijer et al., 1999; Nuth et al., 2000). This second type of experiment is designed to control the molecular “building blocks” of the silicate particles, and here we will compare the results of the photo-chemical and thermal systems. The experiments of Nuth and co-workers employed the thermal decomposition of $\text{Fe}(\text{CO})_5$ and SiH_4 in the presence of O_2 at a total pressure of around 90 Torr (mostly made up of H_2). Magnesium atoms were

added by vaporizing Mg metal in a crucible within the thermal reactor. There are therefore two important differences between the photo-chemical reactor used in the present study and the thermal reactor: the use of O_3 versus O_2 as the oxidant; and a temperature of 293 K versus temperatures typically above 1000 K, respectively. A further possibly significant difference is that in the present experiment the three photolytic precursors are well-mixed before entering the photolysis cell, whereas in the thermal reactor there must be some spatial separation between the region where the Fe and Si precursors start to decompose upon entering the hot region of the reactor, and the Mg vapour is produced from the crucible.

The gas-phase chemistry in the two systems is somewhat different. In our photo-chemical reactor, the building blocks of the metal silicates are FeO_3 , MgO_3 and SiO_2 , produced under well-defined kinetic conditions (Section 3.2). In contrast, the chemistry in the thermal reactor is quite complex. The metal dioxides FeO_2 and MgO_2 will form at the relatively high pressure in the reactor:



Both these reactions have small barriers in their entrance channels so that, unusually for recombination reactions, their rate coefficients increase with temperature (Helmer and Plane, 1994b; Nien et al., 1993). The reactions forming the metal monoxides

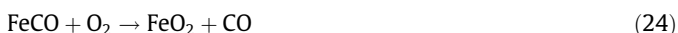


are not competitive. The rate of reaction (21) (Akhmadov et al., 1988) only becomes equal to that of reaction (19) above 1500 K (at the pressure of the thermal reactor experiment). Although a rate expression for reaction (22) has been published (Kashireninov et al., 1982), this is clearly incorrect because the activation energy of 48 kJ mol^{-1} is much lower than the endothermicity of the reaction, $\Delta H_0 = 246 \text{ kJ mol}^{-1}$ (Rollason and Plane, 2001). The upper limit to k_{22} must therefore be extremely small: e.g. $<4 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1200 K. SiO will be produced by the decomposition of SiH₄ in O₂ (Gómez-Martin et al., 2009a), but SiO₂ may then form via the reaction



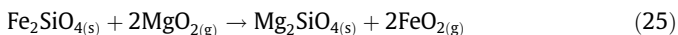
Since reaction (23) is only modestly endothermic ($\Delta H_0 = 63 \text{ kJ mol}^{-1}$ (Gómez-Martin et al., 2009b)), it may proceed at a rate similar to reactions (19) and (20) in the thermal reactor. Thus the main building blocks in the thermal reactor are FeO₂, MgO₂ and SiO and/or SiO₂.

A further complication in the thermal reactor is the decomposition of Fe(CO)₅ which occurs through sequential loss of CO. A reaction such as



may be very fast, because the reaction is highly exothermic: $\Delta H_0 = -236 \text{ kJ mol}^{-1}$, calculated here at the B3LYP/6–311 + g(2d,p) level of theory. Thus formation of Fe silicate particles could occur at temperatures well below 1000 K once Fe(CO)₅ starts to decompose, whereas the Mg silicates cannot form until reaction (22) becomes fast enough within the hot region of the reactor.

It is important to note that in spite of these differences in the molecular building blocks of the two systems, olivine-type particles are produced in both cases. We have shown in Section 3.2 that in the case of the photo-chemical reactor at low temperatures, the production of olivine particles can be explained by the quenching from the gas phase of molecules of olivine (or pyroxene). So this should be a kinetically controlled system, where the ratio of Fe to Mg in the particles is controlled by the relative uptake rates of their respective metal silicate molecules from the gas phase. In the thermal reactor experiments, Nuth et al. (2000) observed the formation of pure magnesium silicate and pure iron silicate amorphous grains above 1000 K. Strikingly, they did not observe any mixed Fe–Mg particles with olivine composition. They attributed this surprising result to the lack of eutectic compositions in the FeO–MgO phase diagram (Nuth et al., 2002). In fact, thermodynamic considerations show that the condensation of particles from a Fe–Mg–Si–O mixture under equilibrium conditions above 1000 K should produce mainly pure forsterite (Mg₂SiO₄) and some enstatite (MgSiO₃) (Gail and Sedlmayr, 1999). Although the initial polymerization may well be kinetically controlled, reactions such as



where the Fe²⁺ ions are displaced by Mg atoms, are very exothermic ($\Delta H = -670 \text{ kJ mol}^{-1}$, calculated using $\Delta H = -157 \text{ kJ mol}^{-1}$ for the reaction $\text{Fe}_2\text{SiO}_{4(s)} + 2 \text{Mg}_{(g)} \rightarrow \text{Mg}_2\text{SiO}_{4(s)} + 2\text{Fe}_{(g)}$ (Gail and Sedlmayr, 1999), and $\Delta H = -256 \text{ kJ mol}^{-1}$ for the gas-phase reaction $\text{MgO}_2 + \text{Fe} \rightarrow \text{FeO}_2 + \text{Mg}$, calculated at the B3LYP/6–311 + g(2d,p) level of theory). Thus the thermal reactor results can be explained by the kinetic formation of mixed silicate particles, subsequent displacement of Fe to form pure Mg silicates, and finally the formation of Fe silicates once all the magnesium has been removed from the gas phase. In contrast, in the low-temperature photochemistry system the composition of the particles is frozen at the composition determined by the quenching kinetics, so that a single solid phase is produced.

4. Implications

This new synthetic method for producing amorphous olivine nanoparticles is not supposed to replicate the ambient conditions of either planetary atmospheres or oxygen-rich stellar outflows. Nevertheless, some important conclusions can be drawn regarding the formation of these particles in both types of environment. The rapidity with which the particles form and grow in the laboratory, combined with the results of the electronic structure calculations, suggests that particle formation is a spontaneous process i.e., there are no free energy barriers to nucleation. Indeed, the long-range magnetic dipole forces in Fe-containing particles which drive this rapid growth were explored by us in a previous study (Saunders and Plane, 2006), where we showed that the rates of magnetic dipole-controlled reactions actually get slightly faster at lower temperatures. Hence, particle formation can be expected even at the very low temperatures of the ISM.

The pathway to particle formation in the photo-chemical reactor – formation of FeO₃, MgO₃ and SiO₂ in the presence of O₃ and O₂ – is quite probably the route to forming MSPs in the atmospheres of the terrestrial planets. The composition of MSPs in the Earth's atmosphere has been a subject of speculation because their small dimensions both precluded optical detection and also created major difficulties for direct rocket-borne sampling and uncontaminated return from the mesosphere. However, there has been a recent report of detectable particle extinction at two near-IR wavelengths at altitudes above 50 km made from the AIM satellite (Hervig et al., 2009). Although this extinction is consistent with refractive index data for the pyroxene structure Mg_{0.4}Fe_{0.6}SiO₃, new work using additional wavelengths in the near-UV and near-IR indicates that the particles have an olivine structure Mg_{2x}Fe_{2–2x}SiO₄, where $x \sim 0.5$ (unpublished data from M. Hervig, presented at the 38th COSPAR General Assembly, Bremen, 2010). This is consistent both with the results of the present study, and with the model prediction that meteoric ablation produces roughly equal quantities of Fe, Mg and Si (Vondrak et al., 2008). However, it should be borne in mind that since the formation of olivine particles requires the condensation of Fe- and Mg-containing species with SiO₂, and all three are trace species in the upper mesosphere (mixing ratios <10 ppb), it is also likely that meteoric vapours produce particles containing oxides such as Fe₂O₃ (Saunders and Plane, 2010), and hydroxides and carbonates.

Regarding silicate grain formation in the ISM, the relevant precursor species in oxygen-rich circumstellar outflows are thought to be MgO, FeO and SiO/SiO₂ (Gail, 2010; Gail and Sedlmayr, 1999; Nuth et al., 2000), which at first glance are different from the species in the photo-chemical reactor. However, FeO₃ and MgO₃ have the structures OFe–O₂ and OMg–O₂ (Rollason and Plane, 2000, 2001), where the weakly-bound O₂ acts as a chaperone to the metal oxide. Thus the chemistry in our system may not be very different from that in the ISM. In any case, the fact that olivine-type particles are produced in the photo-chemical and the thermal reactors (Section 3.3) implies that the precise nature of the metal oxide is secondary.

Thermal reactor experiments (Nuth et al., 2000; Rietmeijer et al., 1999) demonstrate that magnesium silicate (forsterite and enstatite) particles are the major product at high temperatures (>1000 K). This is in accord with observations of a high forsterite abundance in the circumstellar dust shells of stars with high mass loss rates, where nucleation and growth of silicate particles will be faster and thus occur at higher temperatures (de Vries et al., 2010; Nuth et al., 2002). The results of the present study should therefore be applicable to low mass loss rate stars, where condensation will be slow enough that it mostly occurs in cooler regions. Indeed, there is experimental evidence that Fe-rich olivines form at temperatures around 800 K (Nagahara et al., 1988), which is consistent

with the thermodynamic prediction that fayalite and ferrosilite should condense below 900 K (Gail, 2010). Our experiments were carried out at 293 K and, as explained above, there is no reason that the condensation of these species will not occur even at very low temperatures. The formation of Fe-rich olivine particles in low mass loss rate environments will have two important consequences. First, because condensation is slower and the concentration of gas-phase species is continuously diluted in the outflow, much smaller particles are likely to result. Second, the particles will almost certainly be amorphous, as observed in the present study at 293 K. Annealing of Mg–Fe-silicates to form crystalline olivines requires temperatures in excess of 1000 K (Nuth et al., 2002).

5. Conclusions

This paper describes a photo-chemical technique for generating amorphous olivine nanoparticles over a controlled composition range. Quantitative compositional analysis of the particles formed by the photo-oxidation of a mixture of Mg-, Fe- and Si-organometallic vapours in O₃ at room temperature is consistent with a range of olivine (Mg_{2x}Fe_{2–2x}SiO₄; 0 ≤ x ≤ 1) structures. Starting from the known gas-phase chemistry of Mg, Fe and Si atoms in the presence of O₃ and O₂, which produces MgO₃, FeO₃ and SiO₂, we have used electronic structure calculations to elucidate the likely pathways to the formation of olivine particles: direct condensation of olivine molecules, and/or the condensation of metal silicates followed by solid-phase structural rearrangement into separate olivine and silica phases.

The observed preferential nucleation and growth of amorphous mixed-metal silicate particles from a suitable metal and silicon oxide gas-phase environment, indicates the likely *spontaneous* formation of such materials in any environment where iron and magnesium oxide molecules are present together with SiO₂ i.e. in planetary atmospheres where meteoric ablation occurs, and in cooler regions of the ISM, for example the gas outflows of low mass loss rate oxygen-rich stars.

Our photo-oxidation experiments, although not performed under realistic conditions (temperature and pressure) with respect to planetary atmospheres or the ISM, point to an efficient method for the production of nanoparticles of the composition and structure found in these environments.

Acknowledgment

This work was supported by funding from the UK Natural Environment Research Council (Grant NE/E005659/1).

References

- Akhmadov, U.S. et al., 1988. Mechanism and kinetics of interaction of Fe, Cr, Mo, and Mn atoms with molecular oxygen. *Kinet. Catal.* 29 (2), 251–257.
- Alcott, G.R., van de Sanden, R.M.C.M., Kondic, S., Linden, J.L., 2004. Vapor pressures of precursors for the CVD of silicon-based films. *Chem. Vap. Deposition* 10, 20–22.
- Brucato, J.R., Mennella, V., Colangeli, L., Rotundi, A., Palumbo, P., 2002. Production and processing of silicates in laboratory and in space. *Planet. Space Sci.* 50, 829–837.
- Colangeli, L. et al., 2003. The role of laboratory experiments in the characterisation of silicon-based cosmic material. *Astron. Astrophys. Rev.* 11, 97–152.
- de Vries, B.L., Min, M., Waters, L.B.F.M., Blommaert, J.A.D.L., Kemper, F., 2010. Determining the forsterite abundance of the dust around asymptotic giant branch stars. *Astron. Astrophys.* 516, A86. doi:10.1051/0004-6361/200913588.
- Dorschner, J., Begemann, B., Henning, Th., Jäger, C., Mutschke, H., 1995. Steps towards interstellar silicate mineralogy. II. Study of Mg–Fe silicate glasses of variable composition. *Astron. Astrophys.* 300, 503–520.
- Draine, B.T., 2003. Interstellar dust grains. *Annu. Rev. Astron. Astrophys.* 41, 241–289.
- Draine, B.T., Lee, H.M., 1984. Optical properties of interstellar graphite and silicate grains. *Astrophys. J.* 285, 89–108.
- English, M.A., Lara, L.M., Lorenz, R.D., Ratcliff, P.R., Rodrigo, R., 1996. Ablation and chemistry of meteoric materials in the atmosphere of Titan. *Adv. Space Res.* 17, 157–160.
- Fast, K.E. et al., 2009. Comparison of HIPWAC and Mars Express SPICAM observations of ozone on Mars 2006–2008 and variation from 1993 IRHS observations. *Icarus* 203, 20–27.
- Frisch, M.J. et al., 2009. Gaussian 09, Revision A.1. Gaussian Inc., Wallingford, CT.
- Gail, H.-P., 2010. Formation and evolution of minerals in accretion discs and stellar outflows. *Lect. Notes Phys.* 815, 61–141.
- Gail, H.-P., Sedlmayr, E., 1999. Mineral formation in stellar winds. I. Condensation sequence of silicate and iron grains in stationary oxygen rich outflows. *Astron. Astrophys.* 347, 594–616.
- Gilbert, A.G., Sulzmann, K.G., 1974. Vapor pressure of iron pentacarbonyl. *J. Electrochem. Soc.* 121, 832–834.
- Gómez-Martín, J.C., Blitz, M.A., Plane, J.M.C., 2009a. Kinetic studies of atmospherically relevant silicon chemistry. Part I: Silicon atom reactions. *Phys. Chem. Chem. Phys.* 11, 671–678.
- Gómez-Martín, J.C., Blitz, M.A., Plane, J.M.C., 2009b. Kinetic studies of atmospherically relevant silicon chemistry. Part II: Silicon monoxide reactions. *Phys. Chem. Chem. Phys.* 11, 10945–10954.
- Goodhew, P.J., Humphreys, F.J., Beanland, R., 2001. *Electron Microscopy and Analysis*, third ed. Taylor & Francis, London. 243pp.
- Gorny, S.K., Perea-Calderón, J.V., García-Hernández, D.A., García-Lario, P., Szczerba, R., 2010. New groups of planetary nebulae with peculiar dust chemistry towards the Galactic bulge. *Astron. Astrophys.* 516, A39. doi:10.1051/0004-6361/200913010.
- Helmer, M., Plane, J.M.C., 1994a. Kinetic study of the reaction between Fe and O₃ under mesospheric conditions. *J. Chem. Soc. Faraday Trans.* 90, 31–37.
- Helmer, M., Plane, J.M.C., 1994b. Experimental and theoretical study of the reaction Fe + O₂ + N₂ → FeO₂ + N₂. *J. Chem. Soc. Faraday Trans.* 90, 395–401.
- Henning, T., 2010. Cosmic silicates. *Annu. Rev. Astron. Astrophys.* 48, 21–46.
- Hervig, M.E., Gordley, L.L., Deaver, L.E., Siskind, D.E., Stevens, M.H., Russell III, J.M., Bailey, S.M., Megner, L., Bardeen, C.G., 2009. First satellite observations of meteoric smoke in the middle atmosphere. *Geophys. Res. Lett.* 36, L18805. doi:10.1029/2009GL039737.
- Hörst, S.M., Vuitton, V., Yelle, R.V., 2008. Origin of oxygen species in Titan's atmosphere. *J. Geophys. Res.* 113, E10006. doi:10.1029/2008JE003135.
- Hunten, D.M., Turco, R.P., Toon, O.B., 1980. Smoke and dust particles of meteoric origin in the mesosphere and stratosphere. *J. Atmos. Sci.* 37, 1342–1357.
- Ip, W.H., 1990. Meteoroid ablation processes in Titan's atmosphere. *Nature* 345, 511–512.
- Jäger, C., Molster, F.J., Dorschner, J., Henning, Th., Mutschke, H., Waters, L.B.F.M., 1998. Steps towards interstellar silicate mineralogy. IV. The crystalline revolution. *Astron. Astrophys.* 339, 904–916.
- Jäger, C., Dorschner, J., Mutschke, H., Posch, Th., Henning, Th., 2003. Steps towards interstellar silicate mineralogy. VII. Spectral properties and crystallisation behaviour of magnesium silicates produced by the sol–gel method. *Astron. Astrophys.* 408, 193–204.
- Jensen, A.G., Markwick-Kemper, F., Snow, T.P., 2008. Oxygen in the interstellar medium. *Rev. Mineral. Geochem.* 68, 55–72.
- Kashirenin, O.E. et al., 1982. Improvement of oxidation kinetic constants of alkali-metal vapors. *Z. Fiz. Khimii* 56 (4), 1030–1031.
- Kemper, F., Vriend, W.J., Tielens, A.G.G.M., 2004. The absence of crystalline silicates in the diffuse interstellar medium. *Astrophys. J.* 609, 826–837.
- Kim, Y.H., Pesnell, W.D., Grebowsky, J.M., Fox, J.L., 2001. Meteoric ions in the ionosphere of Jupiter. *Icarus* 150, 261–278.
- Kimura, Y., Nuth III, J.A., 2007. What is the driving force to form refractory oxide grains? Silicate spectra depend on their formation environment. *Astrophys. J.* 664, 1253–1263.
- Kotak, R. et al., 2009. Dust and the type II-plateau supernova 2004ET. *Astrophys. J.* 704, 306. doi:10.1088/0004-637X/704/1/306.
- Lavvas, P., Yelle, R.V., Vuitton, V., 2009. The detached haze layer in Titan's mesosphere. *Icarus* 201, 626–633.
- Li, A., Draine, B.T., 2001. On ultrasmall silicate grains in the diffuse interstellar medium. *Astrophys. J.* 550, L213–L217.
- McAuliffe, J.P., Christou, A.A., 2006. Modelling meteor ablation in the venusian atmosphere. *Icarus* 180, 8–22.
- Migliorini, A., Piccioni, G., Cardesin Moinelo, A., Drossart, P., 2010. Hydroxyl airglow on Venus in comparison with Earth. *Planet. Space Sci.*, in press.
- Molina-Cuberos, J.G., López-Moreno, J.J., Arnold, F., 2008. Meteoric layers in planetary atmospheres. *Space Sci. Rev.* 137, 175–191.
- Montmessin, F. et al., 2006. Subvisible CO₂ ice clouds detected in the mesosphere of Mars. *Icarus* 183, 403–410.
- Nagahara, H., Kushiro, I., Mysen, B.O., Mori, H., 1988. Experimental vaporization and condensation of olivine solid solution. *Nature* 331, 516–518.
- Nien, C.F., Rajasekhar, B., Plane, J.M.C., 1993. Unusual kinetic behaviour of the reactions Mg + O₂ + M and Ca + O₂ + M (M = N₂, He) over extended temperature ranges. *J. Phys. Chem.* 97, 6449–6456.
- Noll, K.S., Roush, T.L., Cruikshank, D.P., Johnson, R.E., Pendleton, Y.J., 1997. Detection of ozone on Saturn's satellites Rhea and Dione. *Nature* 388, 45–47.
- Nuth III, J.A., Hallenbeck, S.L., Rietmeijer, F.J.M., 2000. Laboratory studies of silicate smokes: Analog studies of circumstellar materials. *J. Geophys. Res.* 105 (A5), 10387–10396.
- Nuth III, J.A., Rietmeijer, F.J.M., Hill, H.G.M., 2002. Condensation processes in astrophysical environments: The composition and structure of cometary grains. *Meteorit. Planet. Sci.* 37, 1579–1590.

- Pesnell, W.D., Grebowky, J., 2000. Meteoric magnesium ions in the martian atmosphere. *J. Geophys. Res.* 105 (E1), 1695–1707.
- Plane, J.M.C., Helmer, M., 1995. Laboratory study of the reactions $Mg + O_3$ and $MgO + O_3$: Implications for the chemistry of magnesium in the upper atmosphere. *Faraday Discuss.* 100, 411–430.
- Rapp, M., Thomas, G.E., 2006. Modeling the microphysics of mesospheric ice particles: Assessment of current capabilities and basic sensitivities. *J. Atmos. Sol. Terr. Phys.* 68, 715–744.
- Rietmeijer, F.J.M., 2002. The earliest chemical dust evolution in the solar nebula. *Chem. Erde* 62, 1–45.
- Rietmeijer, F.J.M., Nuth III, J.A., Karner, J.M., 1999. Metastable eutectic condensation in a $Mg-Fe-SiO-H_2-O_2$ vapor: Analogs to circumstellar dust. *Astrophys. J.* 527, 395–404.
- Rollason, R.J., Plane, J.M.C., 2000. The reactions of FeO with O_3 , H_2 , H_2O , O_2 and CO_2 . *Phys. Chem. Chem. Phys.* 2, 2335–2343.
- Rollason, R.J., Plane, J.M.C., 2001. A kinetic study of the reactions of MgO with H_2O , CO_2 and O_2 : Implications for magnesium chemistry in the mesosphere. *Phys. Chem. Chem. Phys.* 3, 4733–4740.
- Rosinski, J., Snow, R.H., 1961. Secondary particulate matter from meteor vapors. *J. Meteorol.* 18, 736–745.
- Saunders, R.W., Plane, J.M.C., 2006. A laboratory study of meteor smoke analogues: Composition, optical properties and growth kinetics. *J. Atmos. Sol. Terr. Phys.* 68, 2182–2202.
- Saunders, R.W., Plane, J.M.C., 2010. The formation and growth of Fe_2O_3 nanoparticles from the photo-oxidation of iron pentacarbonyl. *J. Aeros. Sci.* 41, 475–489.
- Self, D.E., Plane, J.M.C., 2003. A kinetic study of the reactions of iron oxides and hydroxides relevant to the chemistry of iron in the upper mesosphere. *Phys. Chem. Chem. Phys.* 5, 1407–1418.
- Thompson, S.P., Evans, A., Jones, A.P., 1996. Structural evolution in thermally processed silicates. *Astron. Astrophys.* 308, 309–320.
- Turco, R.P., Toon, O.B., Hamill, P., Whitten, R.C., 1981. Effects of meteoric debris on stratospheric aerosols and gases. *J. Geophys. Res.* 86 (C2), 1113–1128.
- van Aken, P.A., Liebscher, B., 2002. Quantification of ferrous/ferric ratios in minerals: New evaluation schemes of Fe L_{23} electron energy-loss near-edge spectra. *Phys. Chem. Miner.* 29, 188–200.
- Vondrak, T., Plane, J.M.C., Broadley, S., Janches, J., 2008. A chemical model of meteoric ablation. *Atmos. Chem. Phys.* 8, 7015–7031.
- Whalley, C.L., Plane, J.M.C., 2010. Meteoric ion layers in the martian atmosphere. *Faraday Discuss.* 147, 349–368.
- Whittet, D.C.B., 2003. *Dust in the Galactic Environment*, second ed. IOP Publishing, Bristol. 378pp.
- Williams, D.A., Hartquist, T.W., 1999. The chemistry of star-forming regions. *Acc. Chem. Res.* 32, 334–341.
- Williams, D.A., Taylor, S.D., 1996. The chemical role of cosmic dust. *Q. J. R. Astron. Soc.* 37, 565–592.