

# Identification of iron sulphide grains in protoplanetary disks

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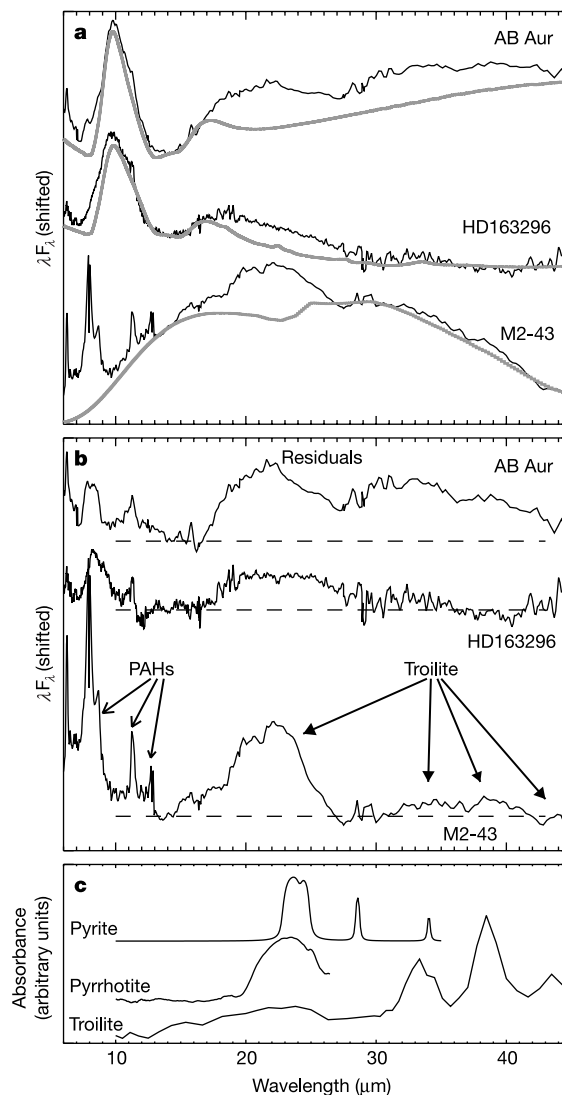
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Sulphur is depleted in cold dense molecular clouds with embedded young stellar objects<sup>1</sup>, indicating that most of it probably resides in solid grains. Iron sulphide grains are the main sulphur species in cometary dust particles<sup>2,3</sup>, but there has been no direct evidence for FeS in astronomical sources<sup>4</sup>, which poses a considerable problem, because sulphur is a cosmically abundant element. Here we report laboratory infrared spectra of FeS grains from primitive meteorites, as well as from pyrrhotite ( $[\text{Fe}, \text{Ni}]_{1-x}\text{S}$ ) grains in interplanetary dust, which show a broad FeS feature centred at  $\sim 23.5$  micrometres. A similar broad feature is seen in the infrared spectra of young stellar objects, implying that FeS grains are an important but previously unrecognized component of circumstellar dust. The feature had previously been attributed to FeO<sup>5-7</sup>. The observed astronomical line strengths are generally consistent with the depletion of sulphur from the gas phase<sup>1</sup>, and with the average Galactic sulphur/silicon abundance ratio<sup>8</sup>. We conclude that the missing sulphur has been found.

Spectroscopic analyses of primitive meteorites, cometary dust particles and synthetic analogue materials in the laboratory provide constraints and serve as 'ground truth' for evaluating various hypotheses on the nature of interstellar grains. Comets are primitive bodies that are widely believed to be a large reservoir of preserved interstellar and circumstellar grains along with presolar organic matter. The comparison of laboratory infrared data on cometary dust with astronomical spectra has been facilitated by the high-quality spectra obtained from the Infrared Space Observatory (ISO)<sup>9</sup>. An emission feature is observed<sup>5,10</sup> in ISO spectra at  $\sim 23.5$   $\mu\text{m}$  and is compared here with iron sulphide minerals from meteorites, interplanetary dust particles (IDPs) and terrestrial sources which show infrared features in the same spectral range (Fig. 1). Figure 2 shows infrared spectra from iron oxide and iron sulphide mineral standards. Wüstite ( $\text{FeO}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) show only one strong, narrow feature at  $\sim 17.5$   $\mu\text{m}$ . FeO has been used to model the 23- $\mu\text{m}$  feature in ISO spectra because the position of the FeO feature can be shifted to 23  $\mu\text{m}$  in calculated spectra using experimentally derived optical constants combined with theoretical grain shapes and sizes<sup>7</sup>. Pyrrhotite exhibits a strong, broad, asymmetric absorption maximum centred at  $\sim 23.5$   $\mu\text{m}$ , whereas the feature in troilite is closer to 22  $\mu\text{m}$ . The pyrrhotite spectrum also shows a weak shoulder at  $\sim 17.5$   $\mu\text{m}$  that is consistent with iron oxide. Pyrrhotite is well known to quickly form a thin surface oxide layer when exposed to ambient atmospheric conditions. Figure 3 shows infrared spectra from two pyrrhotite-rich IDPs (L2011\*B6 and

U2012A-2J) together with 23.5- $\mu\text{m}$  features from two Herbig stars (HD163296 and AB Aurigae)<sup>11</sup>. The sulphide mineral standards, as well as the sulphides in the IDPs, provide an excellent match to the 23.5- $\mu\text{m}$  feature in young stellar objects in terms of peak positions, shapes and widths (Figs 1 and 3), although minor differences do exist.

The 23.5- $\mu\text{m}$  band observed in circumstellar disks surrounding young stars matches that of troilite (FeS) in the evolved star M2-43 (Fig. 1). The identification of FeS in M2-43 is based on the good match in peak positions between laboratory and astronomical spectra of not only the 23.5- $\mu\text{m}$  band, but also the longer-wavelength bands at 34-, 38- and 44- $\mu\text{m}$ , and because iron sulphides are a predicted dust component in carbon-rich evolved stars<sup>12</sup>. We observe that the 23.5- $\mu\text{m}$  band is consistently much stronger in the astronomical data than in the laboratory spectrum of FeS derived from optical constants<sup>13</sup>. The 34-, 38- and 44- $\mu\text{m}$  bands

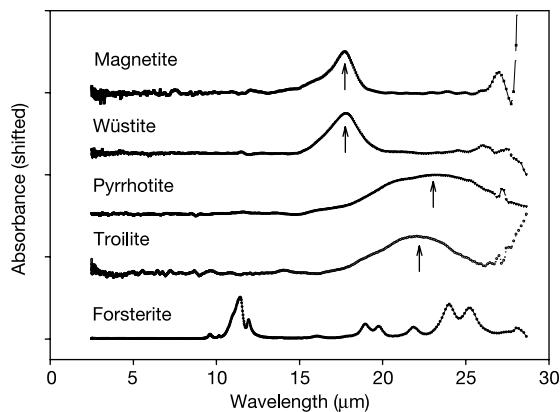


**Figure 1** Infrared spectra of young stars showing a pronounced 23.5- $\mu\text{m}$  feature from iron sulphide grains. **a**, The mid-infrared spectra of the young stars AB Aurigae, HD163296 and the evolved star M2-43. The grey lines in the AB Aur and HD163296 spectrum represent model fits to the full ISO spectra using amorphous silicates, metallic Fe and carbonaceous material<sup>10</sup>. The grey line in the M2-43 spectrum is a fit to the continuum using amorphous carbon and MgS. **b**, Residuals after subtracting the models from the observed ISO spectra. **c**, Infrared spectra of troilite (FeS) and of pyrite ( $\text{FeS}_2$ ) calculated from optical constants, and of pyrrhotite ( $[\text{Fe}, \text{Ni}]_{1-x}\text{S}$ ) from laboratory measurements. We note the major resonances of FeS at 23, 33 and 38  $\mu\text{m}$  in the residual spectrum of M2-43. PAHs, polycyclic aromatic hydrocarbons;  $\lambda F_\lambda$ , flux in units of  $\text{W m}^{-2}$ .

of troilite, although weakly present in the evolved star, are not detected in the young stars; however, we point out that there is spectral structure present in the AB Aurigae spectrum (at low spectral contrast) at approximately the correct wavelength positions for the long-wavelength peaks of FeS (Fig. 1). The lack of a clear signature of FeS in the 30- $\mu\text{m}$  region of the young star can be attributed largely to temperature differences between the FeS in the evolved star and young star. All published spectra of iron sulphides show a characteristic 23.5- $\mu\text{m}$  feature and additional features at longer wavelengths ( $>30\ \mu\text{m}$ )<sup>13–15</sup>. The position and strength of these long-wavelength features vary with mineralogical speciation (Fig. 1) and crystallinity<sup>14</sup>. In addition, grain size and grain shape have significant effects on the sharpness and position of the infrared features. The astronomical spectra almost certainly reflect a mixture of iron sulphide phases (as do most cometary IDPs<sup>3</sup>), which also serves to enhance the 23.5- $\mu\text{m}$  band strength with respect to the longer-wavelength bands.

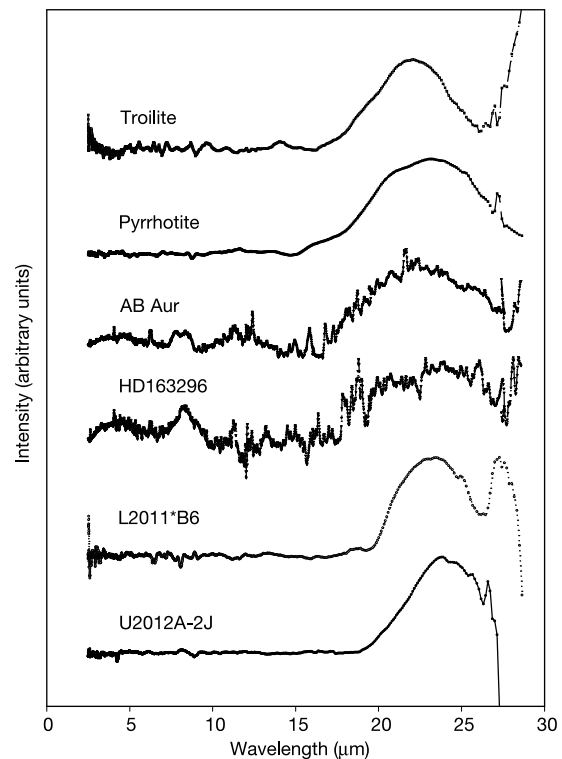
If the ISO feature is indeed due to iron sulphides, then the grains must be small because we were only able to collect useful absorption spectra from specimens  $<200\ \text{nm}$  thick. When the sample thickness exceeds  $\sim 200\ \text{nm}$ , the sulphide standards became infrared opaque, which is consistent with our calculated mass absorption coefficient. There is an extensive literature on similar effects observed for SiC and other dense, strongly infrared-absorbing materials<sup>15,16</sup>. ISO spectra from comet Hale–Bopp show a significantly sharper feature at  $\sim 23.5\ \mu\text{m}$  attributed to forsterite ( $\text{Mg}_2\text{SiO}_4$ )<sup>17,18</sup>. The overlap with forsterite makes it difficult to determine if a broader underlying feature, consistent with iron sulphide, is present in the Hale–Bopp spectrum. As noted above, however, the grain size of the sulphides strongly influences whether or not the feature will be detected.

One fundamental question regarding these results is whether



**Figure 2** Infrared transmission spectra from iron oxides are compared with iron sulphide standards. The iron oxides display a narrow diagnostic feature between 17 and 18  $\mu\text{m}$  whereas the iron sulphides have a broad feature showing its intensity maximum between 22 and 24  $\mu\text{m}$ . Also shown for comparison is the spectrum from meteoritic forsterite ( $\text{Mg}_2\text{SiO}_4$ ) which displays several Si–O bending modes between 15 and 25  $\mu\text{m}$ . Spectra were obtained using a SpectraTech  $\text{Irr}_{\mu\text{s}}$  Fourier transform infrared microspectrometer on the intense infrared beamline (U10B) at the National Synchrotron Light Source at Brookhaven National Laboratory. The infrared instrument is sensitive over the 2.5–28.5  $\mu\text{m}$  ( $4,000\text{--}350\ \text{cm}^{-1}$ ) wavelength range, although the spectra become very noisy above  $\sim 26\ \mu\text{m}$  owing to absorption of the signal in the KBr beamsplitter. Infrared spectra were collected from ultramicrotome thin sections of terrestrial pyrrhotite, troilite, synthetic wüstite and magnetite that were sectioned in epoxy and supported on carbon-film transmission electron microscope (TEM) grids. We used an aperture of  $32 \times 32\ \mu\text{m}$  for the measurements because smaller apertures resulted in spectral artefacts from diffraction effects at long wavelengths. Final baseline corrected (and smoothed) spectra were obtained by subtracting the background spectrum from the thin carbon film substrates from the sample spectrum. Between 256 and 1,000 scans (interferograms) were collected from each specimen with  $4\ \text{cm}^{-1}$  resolution.

the amount of iron sulphide required to produce the infrared feature is consistent with abundance constraints imposed by gas-phase depletions in dense molecular clouds. For this analysis, we compared the intrinsic strength of the 18- $\mu\text{m}$  silicate feature to the 23.5- $\mu\text{m}$  sulphide feature, because it minimizes the effects of temperature gradients on the band-strength analysis (the 10- $\mu\text{m}$  silicate band is very sensitive to the presence of hot silicate grains). The relative band strength can be related quantitatively to composition provided we know  $\mu^{\text{sil}}$  and  $\mu^{\text{FeS}}$  (the molecular weights of astronomical silicate and FeS),  $\kappa_{\text{sil}}^{18\ \mu\text{m}}$  and  $\kappa_{\text{FeS}}^{23.5\ \mu\text{m}}$  (the mass absorption coefficients for the silicate and FeS respectively), and  $I_{18\ \mu\text{m}}$  and  $I_{23.5\ \mu\text{m}}$  (the intensities of the 18- and 23.5- $\mu\text{m}$  features observed in the ISO spectra). There are however, several assumptions that enter into this calculation. We assume that the grain temperature differences are negligible, and we know that the full-widths at half-maximum for both features are approximately the same, so these terms drop out of the calculation. The mass absorption coefficient of the 18- $\mu\text{m}$  silicate feature depends on the composition of the silicate<sup>19</sup>. We adopt a  $\kappa_{\text{sil}}^{18\ \mu\text{m}}$  of  $\sim 1,000\ \text{cm}^2\ \text{g}^{-1}$ , which is somewhat lower than the widely used value<sup>20</sup> of  $1,200\ \text{cm}^2\ \text{g}^{-1}$ , because we do not factor in the underlying continuum. We have calculated a  $\kappa_{\text{FeS}}^{23.5\ \mu\text{m}}$  of  $\sim 1,340\ \text{cm}^2\ \text{g}^{-1}$  from our laboratory spectra of pyrrhotite, which is similar to other reported values<sup>14</sup>, but is significantly larger than that obtained using reflectance methods<sup>13</sup>. This large difference in cross-sections requires further investigation. Using the band



**Figure 3** Infrared spectra of sulphide standards and sulphide-rich IDPs compared to ‘23.5- $\mu\text{m}$ ’ features in two Herbig stars showing similar peak positions, shapes, and bandwidths. The ‘23.5- $\mu\text{m}$ ’ features of AB Aur and HD 163296 were obtained by subtracting our best-fit radiative transfer model<sup>10</sup> without the contribution of ‘FeO’ (see ref. 11). The dust components used in our best-fit model include glassy silicates, forsterite, carbonaceous material, metallic iron and water ice. The IDP infrared spectra were collected from ultramicrotome thin sections ( $\sim 70\ \text{nm}$  thick) of IDPs that had been sectioned in sulphur and supported on carbon-film TEM grids under the same conditions as given in Fig. 2. L2011\*B6 is a fragment of a deuterium-rich cluster IDP, indicating that it contains some presolar molecular cloud material. The mineralogy of L2011\*B6 is dominated by pyrrhotite grains, as well as minor GEMS (glass with embedded metal and sulphides), enstatite and carbonaceous material. U2012A-2J is also dominated by low-Ni Fe-sulphides.

strengths extracted from the ISO spectra of HD163296, we obtain a  $[S/Si]_{\text{calc}} \cong 0.63$ . This ratio is consistent with the cosmochemical (solar) abundance<sup>8</sup> of Si and S (atom ratio 0.52). We conclude from this analysis that the sulphur abundance constraints are broadly consistent with the infrared spectra, although the error bars are large. The implication of this analysis is that most if not all of the sulphur resides in solid grains of FeS.

In the diffuse interstellar medium, sulphur is usually not strongly depleted from the gas phase<sup>21</sup>, indicating that little sulphur is incorporated into solid grains in this environment. Either iron sulphides are not produced in significant quantities in stellar outflows, or their lifetime in the interstellar medium is very short owing to rapid destruction. One probable mechanism for their destruction is the reduction of iron sulphide through irradiation, a process that produces Fe metal as a by-product and returns sulphur to the gas phase. A similar mechanism is known to occur in lunar Fe-oxides exposed to the solar wind<sup>22</sup> as well as in GEMS (proposed presolar silicate grains) in cometary IDPs<sup>23</sup>. The situation is very different in cold, dense molecular clouds, where sulphur is highly depleted from the gas phase<sup>1</sup>. In these environments, only trace amounts of sulphur in molecular form or in ice mantles are detected<sup>4</sup>. Therefore, we believe the bulk of the depletion must be accommodated through incorporation of sulphur into solid grains of iron sulphide. The bulk of the iron sulphide is formed either in the collapse phase of the molecular cloud, or in the disk surrounding the young star. Support for this hypothesis comes from observations of iron sulphide grains in IDPs which are intimately associated with carbonaceous material showing H and N isotopic signatures of molecular cloud environments<sup>24,25</sup>.

From ISO data, crystalline magnesium-rich silicates (forsterite and enstatite) have been recently discovered in a number of sources. It is probable that iron sulphides are manifest in many ISO spectra as well. Iron sulphides, magnesium-rich crystalline silicates and amorphous silicates are the main components of primitive cometary IDPs. These results thus provide new links between primitive IDPs, comets and presolar materials, and resolves a long-standing dilemma. Iron sulphides have long been recognized as a major component of primitive meteoritic materials, but until now they had escaped detection in astronomical observations of objects similar to the early solar nebula. Isotopic measurements for both iron and sulphur in primitive IDPs may uniquely identify presolar iron sulphide grains. A major implication of this work is that early Earth and other Solar System bodies accreted most of their sulphur in the form of crystalline iron sulphide grains. □

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## Competing interests statement

The authors declare that they have no competing financial interests.

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# Formation and propagation of matter-wave soliton trains

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Attraction between the atoms of a Bose–Einstein condensate renders it unstable to collapse, although a condensate with a limited number of atoms<sup>1</sup> can be stabilized<sup>2</sup> by confinement in an atom trap. However, beyond this number the condensate collapses<sup>3–5</sup>. Condensates constrained to one-dimensional motion with attractive interactions are predicted to form stable solitons, in which the attractive forces exactly compensate for wave-packet dispersion<sup>1</sup>. Here we report the formation of bright solitons of <sup>7</sup>Li atoms in a quasi-one-dimensional optical trap, by magnetically tuning the interactions in a stable Bose–Einstein condensate from repulsive to attractive. The solitons are set in motion by offsetting the optical potential, and are observed to propagate in the potential for many oscillatory cycles without spreading. We observe a soliton train, containing many solitons; repulsive interactions between neighbouring solitons are inferred from their motion.

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