

Mid-infrared spectroscopy of refractory inclusions (CAIs) in CV and CO chondrites

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Abstract—We present laboratory mid-infrared absorption spectra (2.5 μm to 16.0 μm) of powdered calcium-aluminum-rich inclusions (CAIs) and matrix separated from the carbonaceous chondrites Allende (CV3.2), Vigarano (CV3.3), and Ornans (CO3.3). Two groups of spectra with different features were found for the CAI: in the first group spectra are dominated by spinel, pyroxene, and sodalite $\pm$ nepheline, where main features occur at 9.3 μm , 10.3 μm , and 11.3 μm . In the second group, characteristic minerals are spinel and melilite with typical band maxima at 11.0 μm and 12.3 μm , and a broad feature between 14.0 μm and 15.0 μm . The position of the broad spinel feature probably depends on its iron content.

Comparison of band positions in spectra from the CAI components to observed circumstellar emission spectra indicates the potential occurrence of CAI-like material. Pyroxene- and spinel-rich features could occur in spectra of dust around the Herbig Ae star HD104237, the T Tauri star Hen3-600 and the post-AGB star R Sge. Melilite- and spinel-rich components possibly appear in the spectrum of HD104237, Hen3-600, 04187_1927, R Sge, and the planetary nebula Hb 12. There is also indication for a spinel component in dust from the Herbig Ae/Be star HD179218. The spectra of the AGB stars R Cas and θ Aps show no features of CAI-type spinel.

INTRODUCTION

Infrared laboratory measurements of minerals are important for the interpretation of the observed emission properties of micron and submicron-sized dust in astronomical environments such as circumstellar dust disks. The laboratory data help to provide a link between astronomical observations and meteorite studies dedicated to the understanding of the formation and evolution of planetary systems. Mid-infrared spectra from synthetic and terrestrial minerals have been used as a reference to identify crystalline and amorphous mineral phases in circumstellar and cometary environments (e.g., Hofmeister et al. 2004). Previous laboratory mid-infrared absorption measurements of chondritic meteorites focussed on bulk meteorites (e.g., Sandford 1984), hydrated components (e.g., Osawa et al. 2005), and dominant minerals, including olivine and pyroxene (Morlok et al. 2006a, 2006b).

Among the components of primitive meteorites, calcium-aluminum-rich inclusions (CAIs) are of special interest because they are the first solids formed from gas and dust in the evolving protoplanetary disk (e.g., Amelin et al. 2002). CAI are most abundant in primitive type 2 and 3 chondrites and occur as irregularly shaped objects with sizes up to several millimeters. They are composed of highly refractory minerals, similar to the phases expected from an equilibrium condensation sequence (e.g., MacPherson et al. 1988; Ebel 2000). As their name implies, their elemental composition is dominated by calcium and aluminum, with significant amounts of titanium and magnesium. Aside from their alteration during formation under nebular conditions (including heating, evaporation and re-condensation) CAIs often suffered aqueous alteration on their parent body (e.g., Russell et al. 1998; Krot et al. 2006). Because CAIs are formed very early in the solar system, they might reasonably be expected to be comparable to the solids in young stellar

objects. Their formation in an equilibrium condensation sequence and CAI-like presolar grains also motivate comparison to dust condensed in the atmospheres of AGB stars (Heras and Hony 2005; Vollmer et al. 2007).

So far, only few infrared spectra have been taken directly from CAIs or their mineral components. Posch et al. (2007) studied two CAIs from CV chondrites, and Cloutis and Gaffey (1993) obtained near-infrared reflectance spectra from terrestrial refractory minerals seen in CAIs from CO chondrites. Recent studies have focussed on synthetic highly refractory minerals for astronomical applications (Hofmeister 2004; Chihara et al. 2007).

As part of our project to compile a database of mid-infrared spectra from minerals of primitive meteorites, we here present mid-infrared absorption data of powdered components separated from CAIs. We compare the obtained spectra with mid-infrared measurements of submicron- and micron-sized dust in circumstellar environments. Due to their size, it is usually not possible to directly identify complete “bulk” CAIs by their mid-infrared spectra in astronomical environments. The results of this study will be only applicable to identify minerals and components of CAIs in observations as long as they are in the micron- and submicron-size range.

ANALYTICAL TECHNIQUES AND SAMPLE SELECTION

Sample Selection

We studied the meteorites Allende (CV3.3) (BM1969,148), Vigarano (CV3.3) (BM1911,174), and Ornans (CO3.3) (BM1985,M149) (BM = catalogue number of the collection of the Natural History Museum in London, UK). All three meteorites are falls and were collected immediately after they fell, which reduces the probability of terrestrial weathering. All samples show only weak shock effects ($S < 2$). Allende belongs to the oxidized subgroup of the CV carbonaceous chondrites and was affected by aqueous alteration on the parent body (e.g., Krot et al. 1998). Vigarano provides a pristine sample of the reduced CV subgroup.

SEM/EDS Measurements

We prepared polished blocks of all samples using diamond as the polishing agent. All samples were mapped in backscattered electron (BSE) mode to allow identification of minerals. Chemical compositions of the minerals were determined using energy dispersive X-ray spectroscopy (EDS) analysis on an analytical scanning electron microscope (SEM) (Jeol 5900LV ProbeSEM, probe current 2 nA at 20 keV) for which natural and synthetic standards were used for calibration. Detection limits of the analysis are at about 0.02 wt%. The dominant mineral phases were identified on the basis of stoichiometry.

Preparation and Infrared Measurements

Samples were separated using a steel scalpel mounted on an optical microscope (EZ-Pick). This device allows a spatial accuracy of $\sim 100 \mu\text{m}$. The surface of a sample was scratched with the scalpel and sufficient amounts of material picked with a fine tungsten needle. The material was ground several times to a fine-grained, submicron-sized powder using a diamond compression cell (DAC). Transmission (T) spectra from the material were measured using the diamond window of the compression cell as holder. The background spectrum was measured before and subtracted to determine the spectrum of the material. Spectra were measured in the mid-infrared range at $2.5 \mu\text{m}$ to $16.0 \mu\text{m}$ wavelength with a resolution of 4 cm^{-1} ($0.0025 \mu\text{m} - 0.1018 \mu\text{m}$) using a Perkin Elmer AutoIMAGE FT-IR microscope. Further details can be found in Morlok et al. (2006a, b). Spectra are presented in absorbance A determined by $A = \log_{10}(1/T)$. The spectrum of each sample is an average of 50 scans. In this study we focus on the mineralogical and observational relevant spectral range from $8 \mu\text{m}$ to $16 \mu\text{m}$.

A major obstacle in this study was the fine-grained and heterogeneous nature of the CAIs. This made the characterization of the minerals with SEM/EDS difficult. It was not possible to analyze, e.g., garnet or sodalite without contamination by other minerals. It was also not possible to separate pure minerals for the infrared measurements, so mixtures of several phases were analyzed.

RESULTS

Mineralogy and Petrology

Spinel-Rich CAI Separated from Allende CV3.2 (Fig. 1a)

This elongated CAI is about $1 \text{ mm} \times 0.3 \text{ mm}$ in size and a mixture of very fine-grained material and coarser grains, which are rarely bigger than $10 \mu\text{m}$. The interior is surrounded by a rim-like structure composed of coarse grains of about $10 \mu\text{m}$ in size. The thickness of this rim varies from about $50 \mu\text{m}$ to $100 \mu\text{m}$.

The rim (hereafter Allende RIM) is dominated by a mixture of iron-rich spinel nodules (average 15.4 wt% FeO) rimmed by nepheline and sodalite (with up to 5.02 wt% Cl). Sodalite results diverge from the ideal stoichiometry, which is probably an analytical artefact because of Na-mobilization by the electron beam (Bridges et al. 1997). The CAI interior (hereafter Allende INTERIOR) is a very fine-grained mixture of intergrown hedenbergite, ferroan spinel (average 13.5 wt% FeO), and nepheline. Garnet was probably identified in the interior, but it is possible that the SEM/EDS measurements were affected by surrounding phases.

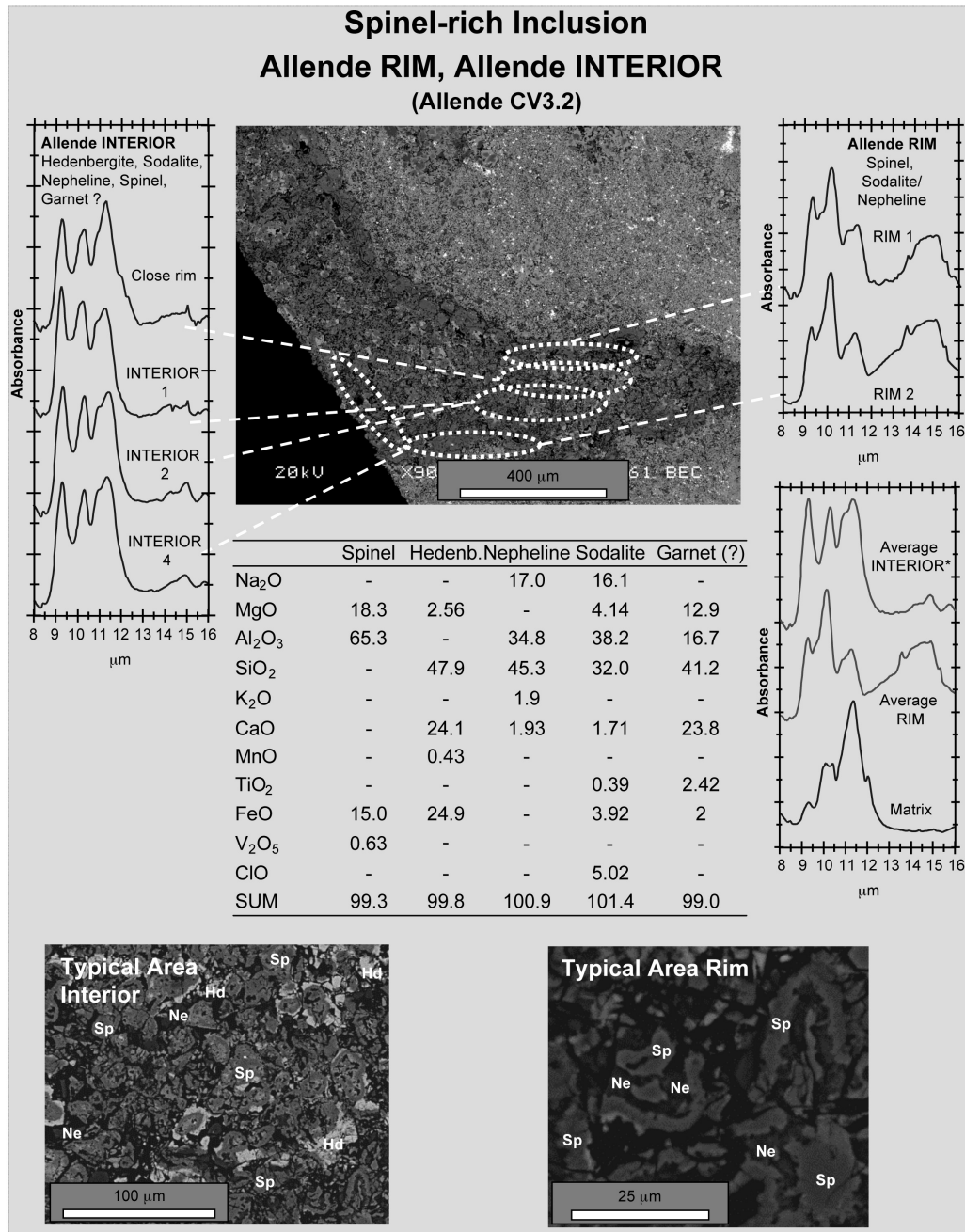


Fig. 1a. Mid-infrared spectra, backscattered electron (BSE) images and SEM/EDS results for the CAI studied in this work. The white dotted ellipsoids are areas from which material for infrared measurements was separated. The white dotted rectangular areas show areas of enlarged images for parts typical of the sample. The table give EDS results and chemical composition of minerals typical for the CAI (in wt%). Infrared spectra are presented as absorbance. An altered, spinel-rich inclusion from Allende (Allende INTERIOR and Allende RIM). Sp = spinel, Hd = hedenbergite, Ne = nepheline, Mel = melilite, Dio = diopside, Pv = perovskite, An = anorthite-like material.

Fine-Grained, Melilite-Rich CAI Separated from Ornans CO3.3 (Fig. 1b)

This fine-grained CAI is about 400 μ m $\times$ 500 μ m in size. It consists of spinel and melilite bands (10 μ m to 20 μ m thick) or nodules (up to about 40 μ m in size). They are surrounded by a layer of diopside ($\pm$ fassaite) with a

thickness of about 10 μ m to 30 μ m. The interior (hereafter Ornans INTERIOR) is composed of gehlenite-rich melilite with an average åkermanite content of 22 mol% (Ak_{22}) and ferroan spinel with 0.81 wt% FeO. The surrounding mantle (hereafter Ornans RIM) mainly consists of diopside and fassaite.

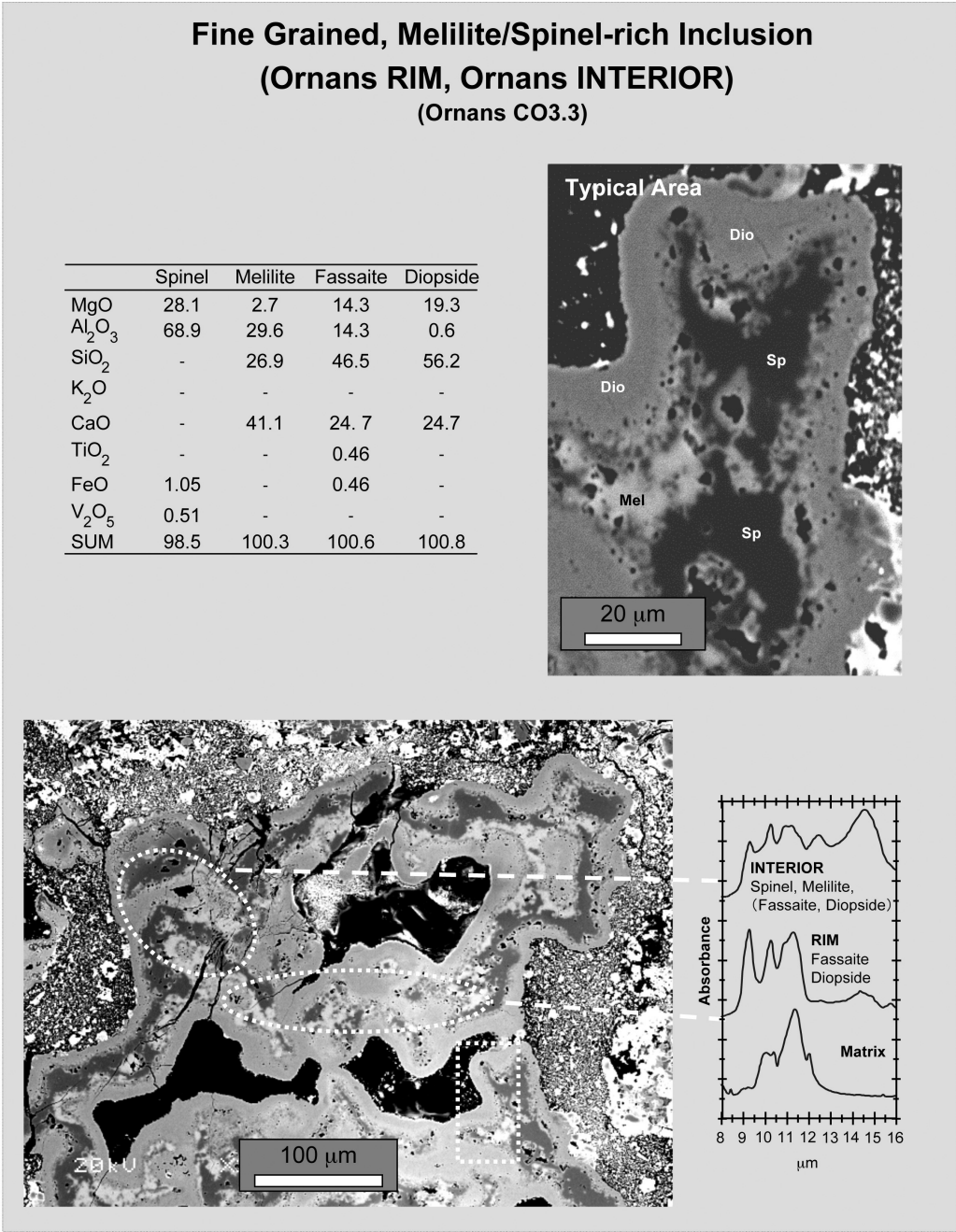


Fig. 1b. Mid-infrared spectra, backscattered electron (BSE) images and SEM/EDS results for the CAI studied in this work. The white dotted ellipsoids are areas from which material for infrared measurements was separated. The white dotted rectangular areas show areas of enlarged images for parts typical of the sample. The table give EDS results and chemical composition of minerals typical for the CAI (in wt%). Infrared spectra are presented as absorbance. A fine-grained, melilite-rich CAI from Ornans (Ornans RIM, Ornans INTERIOR). Sp = spinel, Hd = hedenbergite, Ne = nepheline, Mel = melilite, Dio = diopside Pv = perovskite, An = anorthite-like material.

Coarse-Grained, Melilite-Rich CAI Separated from Vigarano CV3.3 (Fig. 1c)

This irregularly shaped CAI (hereafter Vigarano 1) is 500 μm × 400 μm at its greatest dimensions. It consists of spinel (±perovskite) cores surrounded by a melilite mantle. The interior of the CAI is coarse-grained, with single grain

sizes of up to several tens of μm. This interior is surrounded by a compositionally identical, finer-grained outer part. The mineralogy is mainly dominated by gehlenite-rich melilite (average Ak₆) with smaller contents of spinel and small grains of perovskite. The average iron content of the spinel is 1.81 wt% FeO.

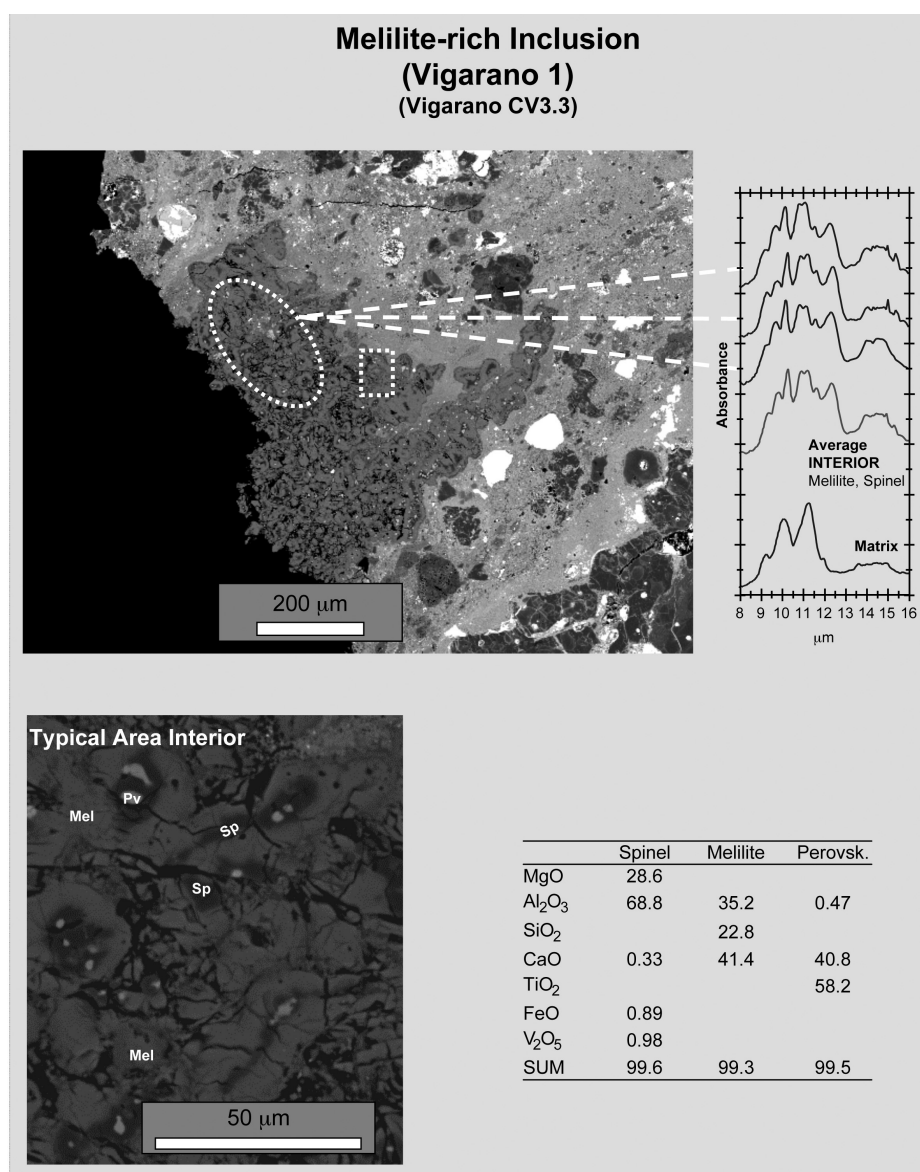


Fig. 1c. Mid-infrared spectra, backscattered electron (BSE) images and SEM/EDS results for the CAI studied in this work. The white dotted ellipsoids are areas from which material for infrared measurements was separated. The white dotted rectangular areas show areas of enlarged images for parts typical of the sample. The table give EDS results and chemical composition of minerals typical for the CAI (in wt%). Infrared spectra are presented as absorbance. Melilite-rich inclusion from Vigarano (Vigarano 1). Sp = spinel, Hd = hedenbergite, Ne = nepheline, Mel = melilite, Dio = diopside Pv = perovskite, An = anorthite-like material.

Coarse-Grained, Melilite- and Spinel-Rich CAI Separated from Vigarano CV3.3 (Fig. 1d)

Sample material was taken from one part of a fragmented CAI (different from Vigarano 1). The segment is about 200 μm × 200 μm in size. The interior is surrounded by a Wark-Lovering rim structure (Brearley and Jones 1998) with a thickness of ~50 μm attached on one side (hereafter Vigarano 2 RIM). The sequence of the Wark-Lovering rim from inside to outside is spinel (~30 μm), diopside (~15 μm), and forsterite (~5 μm). The other side of the interior is covered with an about 10 μm to 40 μm thick layer of anorthite-like material. The interior of this CAI (hereafter

Vigarano 2 INTERIOR) consists mainly of gehlenite-rich melilite (average Ak₂₉) enclosing grains of spinel.

Infrared Measurements

Spectra from each sample are shown in Figs. 1a–d: the dominant band positions observed in the spectra are compared to each other in Fig. 2. The respective peak positions derived from the data are summarized in Table 1. The minerals attributed to bands in the CAI spectra are compared with reported mineral spectra. Based on spectral characteristics, we distinguish two groups of CAI:

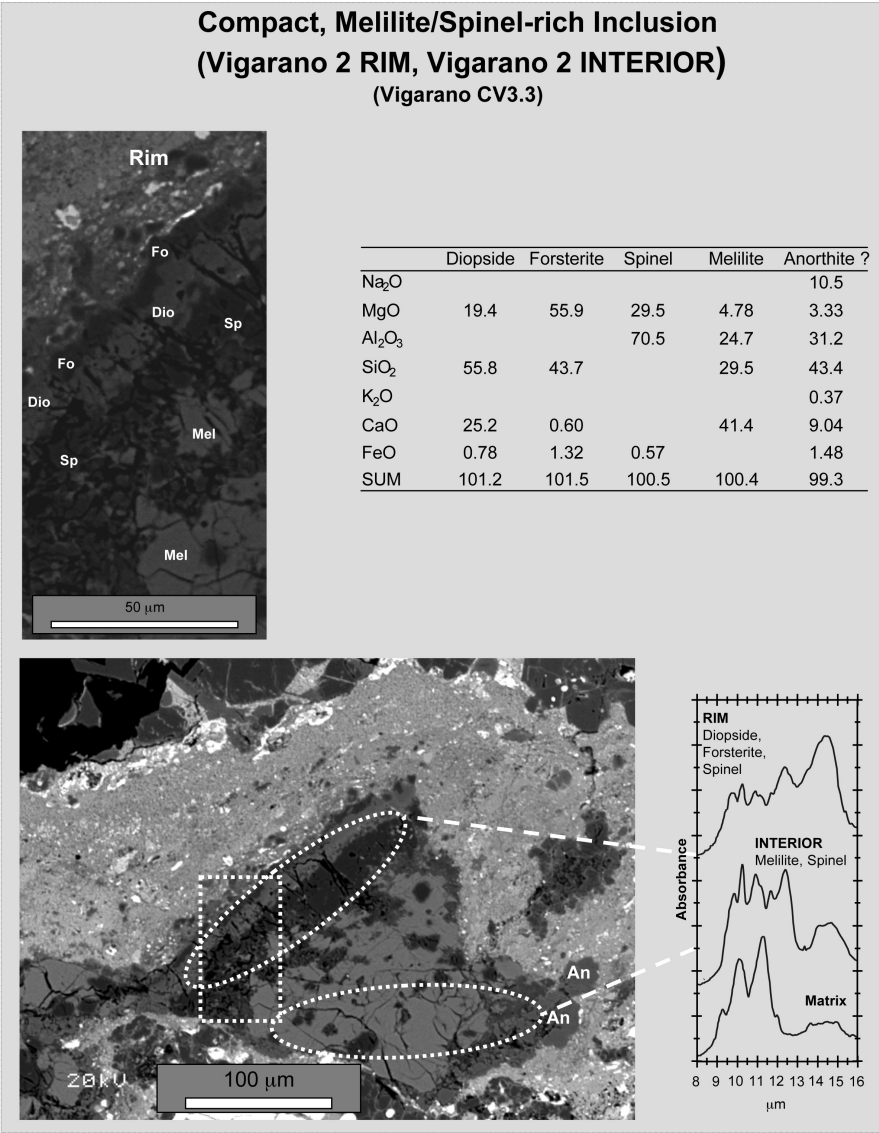


Fig. 1d. Mid-infrared spectra, backscattered electron (BSE) images and SEM/EDS results for the CAI studied in this work. The white dotted ellipsoids are areas from which material for infrared measurements was separated. The white dotted rectangular areas show areas of enlarged images for parts typical of the sample. The table give EDS results and chemical composition of minerals typical for the CAI (in wt%). Infrared spectra are presented as absorbance. A second CAI from Vigarano, part of several pieces from a fragmented CAI (Vigarano 2 RIM, Vigarano 2 INTERIOR). Sp = spinel, Hd = hedenbergite, Ne = nepheline, Mel = melilite, Dio = diopside Pv = perovskite, An = anorthite-like material.

Group 1: Pyroxene and Spinel (Fig. 2)

The first group comprises spectra from Allende RIM and INTERIOR and Ornans RIM. Ca-rich pyroxenes are identified by characteristic features at 9.3 µm, 10.3 µm, 10.9 µm, ~11.3 µm, and ~15.7 µm (Salisbury et al. 1992; Jäger et al. 1998; Koike et al. 2000) in all measured spectra. EDS results for Allende INTERIOR show hedenbergite where a band might be expected at 11.6 µm. The spectrum of Allende INTERIOR shows a strong band at 11.3 µm which is shifted by 0.3 µm compared to the expected hedenbergite (Salisbury et al. 1992). Due to the analytical problems with fine-grained phases, we cannot rule out undetected Ca-rich

pyroxenes which would provide better fits (e.g., diopside or augite, Koike et al. 2000).

The 11.3 µm and 9.3 µm bands in the Allende RIM spectrum are much weaker compared to the Allende INTERIOR spectrum. Since stoichiometric analyses of Allende rim material show no pyroxene, the characteristic pyroxene features occurring at 11.3 µm and 9.3 µm in the spectrum could be due to mixing with material from the interior. This is not implausible, since the border between rim and interior is not always clear. Pyroxene could be present as a further component in the RIM too small for analysis with SEM/EDS.

Spinel is a further significant mineral of this group. It is

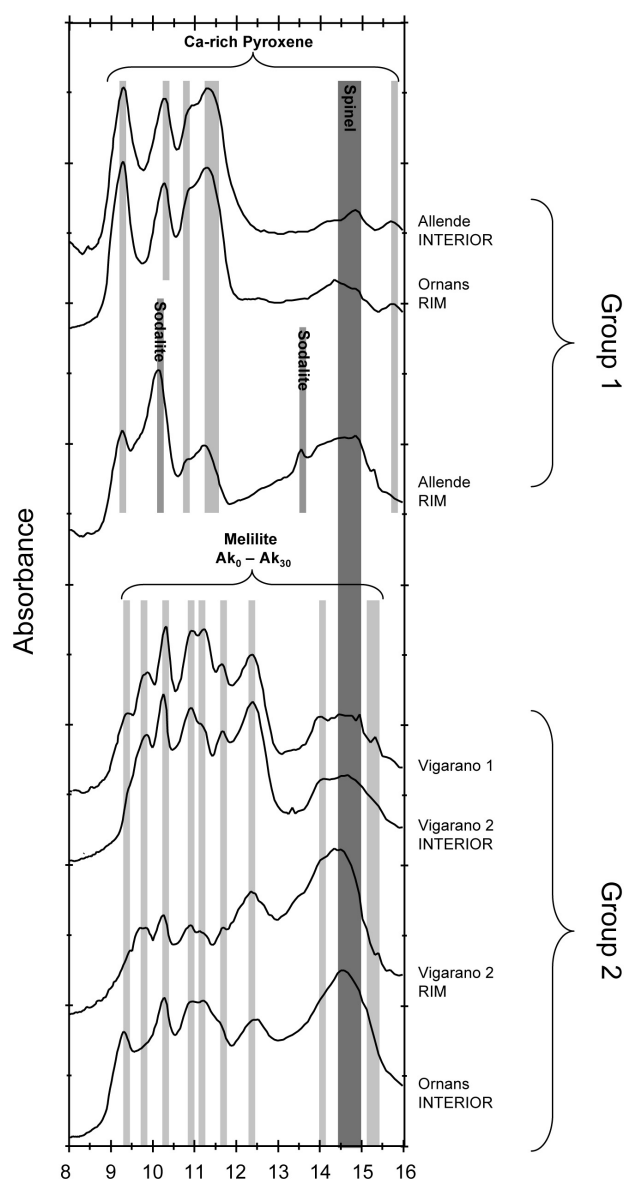


Fig. 2. Typical spectra for components in CAI, sorted into two groups. Group 1 is dominated by Ca-rich pyroxene and spinel, group 2 by melilite and spinel. Grey vertical bands mark characteristic features from literature data: melilite: Chihara et al. (2007); spinel: Gadsen (1975), Karr (1975), Ferraro (1982), Chihara et al. (2000), Fabian et al. (2001); Ca-rich pyroxene (diopside, augite, hedenbergite): Salisbury et al. (1992); Koike et al. (2000); forsterite ($\text{Fo}_{50}\text{--}\text{Fo}_{100}$): Morlok et al. (2006); sodalite: Farmer (1976), Salisbury et al. (1992).

indicated by a broad band between $\sim 13.5\ \mu\text{m}$ and $15.0\ \mu\text{m}$ with a maximum between $14.0\ \mu\text{m}$ and $14.9\ \mu\text{m}$ (Gadsen 1975; Karr 1975; Ferraro 1982; Chihara et al. 2000). In the spectra of Allende RIM and INTERIOR as well as Ornans RIM this broad band is unambiguously measured.

Sodalite is identified in Allende RIM by a sharp peak at $13.6\ \mu\text{m}$ and a weak band at $14.9\ \mu\text{m}$. A strong sodalite band overlaps with a pyroxene feature at $10.2\ \mu\text{m}$. (Farmer 1976; Salisbury et al. 1992).

There is no indication of the tentative identified minor garnet in Allende INTERIOR. An altered CAI from Allende studied by Posch et al. (2007) shows features similar to the Allende RIM.

Group 2: Melilite and Spinel (Fig. 2)

The second group consists of Ornans INTERIOR, Vigarano 2 RIM/INTERIOR and Vigarano 1.

Strong melilite bands at $\sim 10.3\ \mu\text{m}$ and two close “twin peaks” at $10.9\ \mu\text{m}$ – $11.2\ \mu\text{m}$ and at $12.3\ \mu\text{m}$ – $12.5\ \mu\text{m}$ are characteristic for spectra of this group (e.g., Chihara et al. 2007).

Weaker melilite bands at $9.4\ \mu\text{m}$, about $11.6\ \mu\text{m}$, $14.0\ \mu\text{m}$ and $15.3\ \mu\text{m}$ only occur in some spectra of this group (e.g., Chihara et al. 2007). A feature at about $9.8\ \mu\text{m}$ occurring in Vigarano 1 and 2 could be either a melilite or spinel band (Gadsen 1975; Chihara et al. 2007). Since the melilite features in the Vigarano 2 RIM spectrum show low relative intensities, the amount of melilite could arise from contamination with INTERIOR material. Occasional sharp features at $15.0\ \mu\text{m}$ are possibly CO_2 bands.

A broad spinel feature arises in the $13.0\ \mu\text{m}$ to $16.0\ \mu\text{m}$ region and peaks between $14.0\ \mu\text{m}$ and $14.9\ \mu\text{m}$. The exact position of the band maximum varies with the iron content of spinel (Gadsen 1975; Karr Jr., 1975; Ferraro 1982; Chihara et al. 2000).

The spectrum of a melilite- and spinel-rich CAI from Leoville (CV3) reported in Posch et al. (2007) is similar to the spectra of this group. However, the characteristic $11.2\ \mu\text{m}$ feature and bands at $9.3\ \mu\text{m}$ and $14.5\ \mu\text{m}$ are lacking.

Matrix Material (Fig. 2)

To estimate potential contamination with matrix material during the separation of the CAI material, infrared spectra of several random matrix samples from each meteorite were measured. The matrix of Ornans, Vigarano and Allende consist of olivine which show mid-infrared features between $10\ \mu\text{m}$ and $12\ \mu\text{m}$ (see Figs. 1a–d) (e.g., Koike et al. 1993). Compared to the measured CAI spectra in this study, olivine cannot unambiguously be identified, since the strong olivine bands overlap with pyroxene (CAIs of group 1) and melilite features (CAIs of group 2).

DISCUSSION

Spectral Characteristics of Minerals in CAIs

In this study, spectra are obtained from mixtures of CAI minerals where features of different materials overlap. Because individual phases and mass absorption coefficients cannot be obtained, band positions are compared to spectra of terrestrial materials and to astronomical spectra to determine the material composition of cosmic dust.

Literature data for the Ca-rich pyroxenes diopside, hedenbergite and augite are discussed together because they have similar mid-infrared features. For the Ca-rich pyroxene

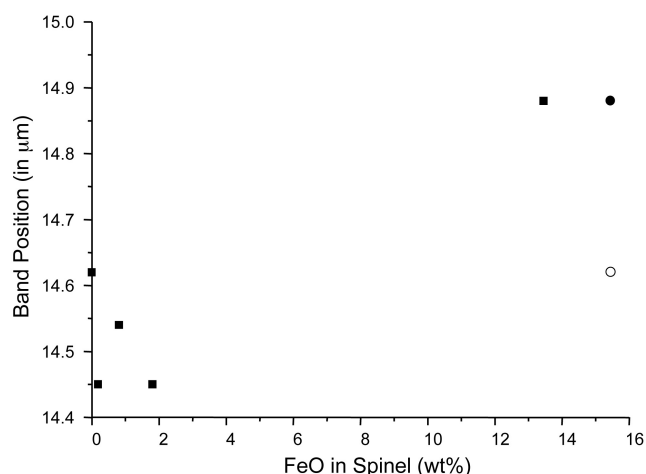


Fig. 3. Relationship between iron content in spinel and the band position of the strong spinel feature between 14.4 μm to 14.9 μm . Band position are in μm , iron content in wt% FeO. The open circle is the position at 14.62 μm , the filled circle the band at 14.88 μm for the spinel feature in Allende RIM.

fassaite, which was detected by EDS measurements, no literature data were available. The strong characteristic bands of Ca-rich pyroxenes and melilite (Fig. 2, Table 1) in our study agree well with literature data or show deviations smaller than 0.1 μm (Sahama and Lehtinen 1967; Gadsen et al. 1975; Salisbury et al. 1992; Koike et al. 2000; Chihara et al. 2007). The deviations could occur due to small compositional differences or technical differences between the spectrometers. The sodalite bands in the measured spectra agree well with reference data (Farmer 1976; Salisbury et al. 1992). Although abundant nepheline was found in the EDS data (Fig. 1a), no unambiguous identification of the mineral was possible in the infrared spectra. The broad, strong spinel feature (Fig. 2, Table 1) usually falls into the range from 14.5 μm to 14.9 μm , where the band maximum seems to shift with the iron content (see below). The band maximum of spinel is difficult to determine due to melilite and sodalite bands in this wavelength range. A minor second spinel band at 13.0 μm to 13.3 μm occasionally occurs in the spectra of Vigarano 1 and 2 (Fig. 1c) (Gadsen et al. 1975; Chihara et al. 2000; Fabian et al. 2001).

Identification of CAI Minerals in Mixtures

In the spectral range between 8.0 μm and 12.0 μm , several features typical for minerals in CAI and of silicates typical in circumstellar disks can be found (e.g., olivine, pyroxene, silica and amorphous silicate) (e.g., Van Boekel et al. 2005; Honda et al. 2006). The clear identification of the mineral species in CAI is difficult because of overlapping features. In contrast the wavelength range from 12.0 μm to 16.0 μm is less populated by features (Fig. 2). This wavelength range helps to identify CAI minerals more

precisely (compare Posch et al. 2007): Melilite bands occur at ~ 12.3 μm , 14.0 μm and between 15.3 μm and 15.7 μm (e.g., Chihara et al. 2007). Spinel is best identified in the wavelength range between 12.0 μm and 16.0 μm , where a strong band occurs between 14.4 μm and 14.9 μm (Gadsen 1975; Karr 1975; Ferraro 1982; Chihara et al. 2000). Sodalite is identified by a sharp band at 13.6 μm and a weaker band at 14.9 μm (see Farmer 1976; Salisbury et al. 1992). Ca-rich pyroxenes show a moderate feature at 15.8 μm (Salisbury et al. 1992; Koike et al. 2000).

Spinel as a Temperature Proxy? Effects of Fe-Content in Spinel on Band Positions

The strong spinel band occurs between 14.4 μm and 15.0 μm and shifts to higher wavelengths with increasing iron content. Spinel with a very low iron content of <2 wt% FeO is found in Ormans INTERIOR and Vigarano 1 and 2. The band maximum in the spectra of these CAIs is located between 14.4 μm to 14.62 μm . The probable band maximum of iron-rich spinel found in Allende INTERIOR and RIM occurs at 14.88 μm (Fig. 3). Overlapping bands of other phases complicate the localization of the band maximum, but a similar trend was also observed by Posch et al. (2007) and Gadsen (1975).

The lack of data points between the iron-poor and iron-rich end members makes an unambiguous statistic analysis of the correlation between band position and iron content difficult. The linear correlation (R^2) varies between 0.48 and 0.86, depending on which band position is used for Allende RIM (two possible maxima at 14.62 and 14.88 μm).

The iron content of spinel depends on the degree of thermal metamorphism in at least CO chondrites, where iron diffuses from surrounding matrix material into spinel with increasing temperature. CAI in CO 3.0 chondrites only contain spinel with minor amounts of iron, whereas in CO 3.4 or higher they contain up to 50–60 mol% of the iron-rich spinel end-member hercynite (Russell et al. 1998).

Based on the limited data set available and keeping the aforementioned provisos in mind, this shift in band position could be used as indicator for heating processes within the source objects, e.g., when dust is produced by collisions of planetesimals in debris disks. But mixing with dust from other sources could make such calculations difficult.

Comparison with Astronomical Spectra

In this section, we compare the spectra from CAI with the infrared spectra from astronomical measurements of micron- and submicron-sized dust in young circumstellar disks and AGB stars (Figs. 4a–d).

It should be kept in mind that, if CAI-like materials occur in astronomical environments, it is probably a component in a mixture with other types of material. We compare mainly

Table 1. Band positions of significant bands in the CAI and matrix spectra. For each averaged group of measurements, the results of equivalent bands are arranged in the same column. For the different CAI, they may not necessarily represent the same mineral. Bold = characteristic bands. Bold and underlined = band only from 2 Allende INTERIOR spectra to avoid CO₂ bands. All band positions in μm .

Matrix													
Allende	9.29	10.08	10.37	11.31	11.96			14.29			14.97		
Vigarano	9.29	10.08		11.26	11.96						14.88		
Ornans	9.19	9.92	10.37	11.31	11.96			13.59	14.45				
Allende													
RIM 1	9.29	9.73		10.97	11.31	12.08	12.56	13.59	14.62		14.88	15.34	15.63
RIM 2	9.29	10.16			11.26			13.59	14.62		14.88	15.34	
Average	9.28	10.16			11.26	12.08		13.59	14.62		14.88	15.34	
INTERIOR 1	9.29		10.25		11.26				14.12	14.39	14.97	15.43	15.82
INTERIOR 2	9.33		10.33					13.59	14.21		14.88		15.72
INTERIOR 4	9.33		10.29		11.31		13.30				14.88		15.72
INTERIOR (Close Rim)	9.33		10.33		11.31	12.26	13.30	13.81			14.97	15.43	15.82
Average	9.29		10.29		11.31				14.21		14.88		15.82
Ornans													
RIM	9.29		10.25		11.26	12.50							15.63
INTERIOR	9.29		10.29	10.92	11.21	12.50			14.54	14.79			
Vigarano													
CAI 1													
INTERIOR 1	9.36	9.84	10.25	10.97	11.16	12.32	13.30	14.05	14.45	14.79	14.97	15.34	15.72
INTERIOR 2	9.33	9.80	10.29	10.87	11.21	12.38		14.05	14.45	14.79	14.97	15.34	15.63
INTERIOR 3		9.84	10.25	10.92	11.21	12.38		13.97	14.54				
Average	9.33	9.84	10.29	10.87	11.21	12.38		14.05	14.45		14.97	15.34	
CAI 2													
INTERIOR		9.88	10.25	10.92		12.38	13.30	14.05		14.62			
RIM	9.47	9.69	10.25	10.87	11.11	12.32			14.45			15.34	15.63

band positions of the features, because relative intensities are difficult to compare in the scope of this study. Band positions are regarded as similar if the deviation between a strong, characteristic feature in our data and in the astronomical spectra are smaller than 0.25 μm . Usually the differences are smaller than 0.15 μm .

Astronomical spectra are measured with both ground-based and with space-based instruments. For the comparisons, we usually used spectra from ground-based observations, which cover the wavelength range between about 8.0 μm and 13.0 μm . They have a higher signal-to-noise ratio than the space-based Infrared Space Observatory (ISO) spectra (2.4 μm to 45.4 μm), which are used for comparisons in the wavelength range above 13.0 μm .

Circumstellar Disks

Several stars close to or within the main-sequence stage exhibit a brightness excess in the near infrared, mid-infrared and/or sub-millimeter range of their spectral energy distributions, which is caused by circumstellar dust. The lifetime of dust in these systems is shorter than the lifetime of the star itself, which indicates that the observed dust is not a remnant from the protoplanetary disk but is produced from collisions of planetesimals or the activity of cometary-like objects (see, for instance, Backman and Paresce 1993; Mann et al. 2006). The materials from which dust is derived possibly underwent alteration by fluids and/or thermal metamorphism on the potential parent bodies. Dust particles in these systems are often referred to as planetary debris. Currently there are more observations in the sub-millimeter than in the infrared for debris disks as a result of their fainter brightness and owing to the fact that for some of the best observed targets photospheric emission dominates the spectrum out to the 10 μm regime (Mann et al. 2006). Here, we compare spectra from dust around several stars with increasing age.

HD104237 (Fig. 4a)

Spectra of dust around the Herbig Ae star HD104237 (spectral type A8Ve, assumed age 5 Myr [Grady et al. 2004]) were measured using the TIMMI2 instrument at the 3.6 m telescope of the European Southern Observatory (ESO), La Silla, Chile (Van Boekel et al. 2005) and the Short Wavelength Spectrometer (SWS) of the Infrared Space Observatory (ISO) (Sloan et al. 2003). The spectrum of the ground-based measurements by Van Boekel et al. (2005) shows strong single bands at 9.4 μm and broad features between 10.0–10.2 μm and at 10.8 μm to 11.2 μm . Van Boekel et al. (2005) determined a mixture of 77% amorphous material with pyroxene composition, 6% forsterite and 12% enstatite. The SWS spectrum from ISO indicates further bands between 13.7 μm and 15.0 μm , and at 15.8 μm . The identification of the position of the band maxima is not unambiguous because of the low signal-to-noise ratio. The strong bands at 9.3 μm , 10.3 μm , and 11.3 μm of the

pyroxene-rich spectra from group 1 occur at similar positions in the TIMMI2 spectrum of dust around HD104237. Bands at about 9.3 μm , 9.8 μm , 10.3 μm , and the broad twin feature around 11.0 μm in group 2 spectra can also be retrieved in the astronomical spectrum. The spectrum of Ormans INTERIOR shows similarities to the TIMMI2 spectrum, but a main feature of group 2 at 11.6 μm indicating melilite is not measured in the astronomical spectrum. The low signal-to-noise ratio in the ISO spectrum allows no clear identification of bands in the range above 13 μm and the two spectra show deviations in this wavelength range. Therefore a clear identification, if these features belong to spinel or melilite, is impossible.

HD179218 (Fig. 4b)

The spectra of the dust around the Herbig Ae/Be star HD179218 (spectral type B9e, assumed age 1.3 Myr) were measured using the TIMMI2 instrument at the 3.6 m telescope of ESO, La Silla, Chile (Van Boekel et al. 2005) and SWS of ISO (Sloan et al. 2003). In the ground-based astronomical spectrum bands occur at 8.7 μm , 9.3 μm , 9.8 μm , 10.6 μm , 11.2 μm , 11.6 μm , and 12.7 μm . These spectral features have been interpreted as a mixture containing about 25% enstatite and 59% amorphous material with pyroxene composition (Van Boekel et al. 2005). The 8.0 μm to 12.0 μm range is dominated by pyroxene features which show no clear similarity to CAI of both groups. But there are correspondences between features in the 12 μm to 16 μm region of the ISO spectrum and spinel features in the CAI spectra from Ormans. The low signal-to-noise ratio in the ISO spectrum makes it difficult to locate the maximum of the potential spinel band. The estimated maximum at about 14.6 μm would indicate low iron content in this mineral.

Hen3-600 (Fig. 4b)

The spectrum of dust around the T Tauri star Hen3-600 (spectral type M3, age assumed to <10 My [Jayawardhana et al. 1999]) was obtained with the COMICS instrument at the 8.2 Subaru telescope (Honda et al. 2003). The astronomical spectrum shows bands at 9.2 μm , 10.1 μm , 10.5 μm , 10.9 μm , 11.2 μm , and 12.5 μm , which were interpreted as a mixture of crystalline forsterite, enstatite, silica and amorphous material with olivine composition (Honda et al. 2003). Both groups of CAI show good similarities with the spectrum of dust around Hen3-600. Spectra of CAI of group 1 could also explain the relative intensities of the dust spectrum. The astronomical spectrum also exhibits evidence for the characteristic melilite twin feature at 10.9 μm to 11.2 μm that is found in spectra of group 2. The potential equivalent to the melilite peak at 11.6 μm in the dust spectrum at 11.76 μm is very weak and the feature corresponding to the melilite band at 12.5 μm has a low signal-to-noise ratio. Characteristic bands at about 9.8 μm in the dust spectrum fall into a range affected by ozone

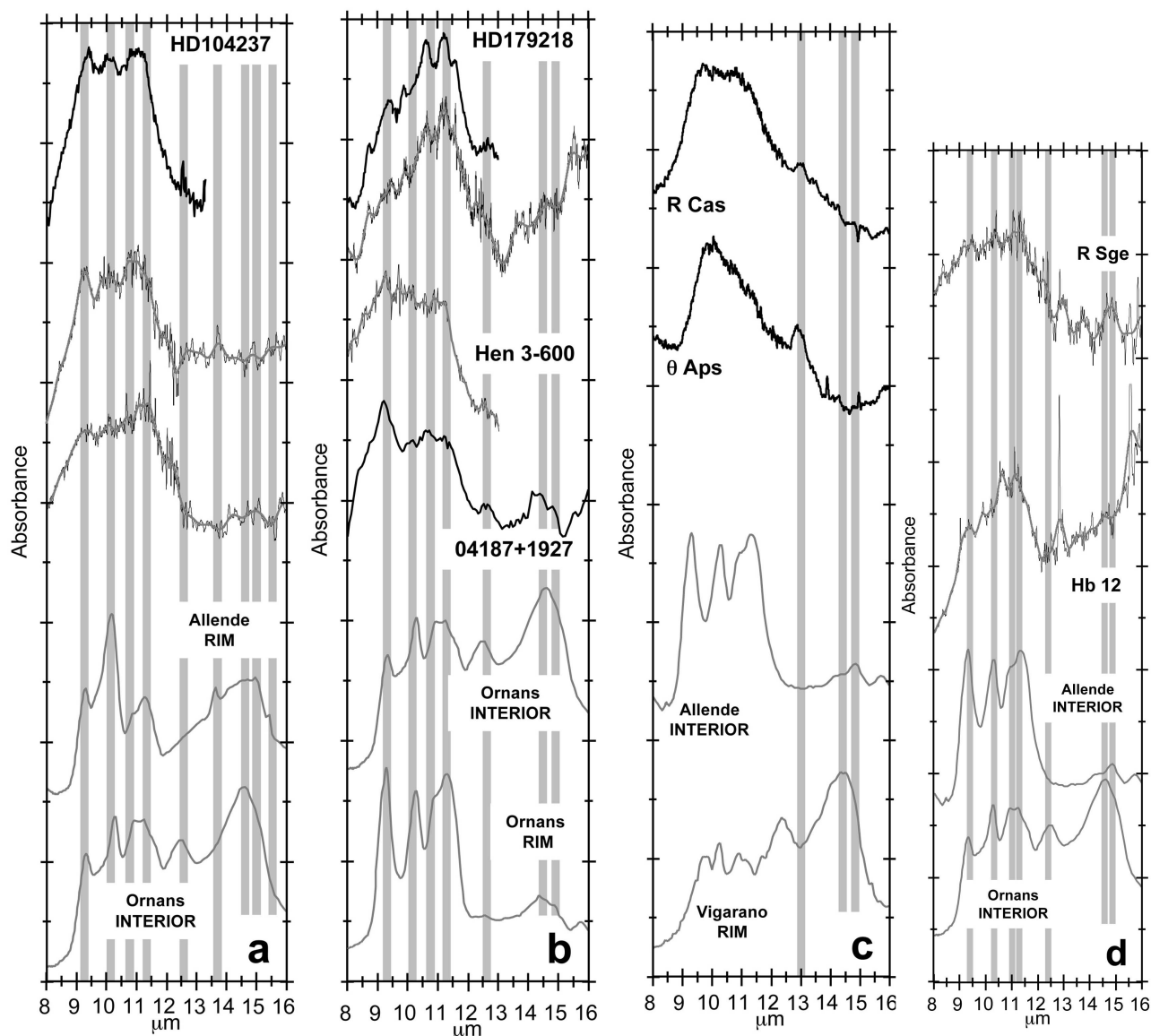


Fig. 4. Comparison of CAI powder mid-infrared spectra with astronomical spectra. a, b) Dust in circumstellar disks of Herbig AE stars HD104237, HD179218, and Tauri stars Hen3-600, 04187_1927 (Honda et al. 2003; Sloan et al. 2003; Van Boekel et al. 2005; Furlan et al. 2006). c) AGB stars R Cas and θ Aps. d) Post-AGB star R Sge and planetary nebulae Hb 12 (Fabian et al. 2001; Sloan et al. 2003). The spectra are presented in relative absorbance (a). The black spectra on top are astronomical spectra. Ground-based observations (ESO/TIMM12 and Subaru/COMICS) are presented from 8 μm to 13 μm (always on top), space-based data (ISO/SWS or SPITZER/IRS) from 8 μm to 16 μm (always below ground based spectra). To allow a better comparison, some astronomical spectra are overlain by a spectrum (grey) smoothed using FFT (Fourier filtering technique) over a range corresponding to 0.2 μm . For the comparisons in the discussion the original spectra were used. The laboratory data are in dark grey on the bottom (8 μm to 16 μm). Vertical broad light grey bands compare important features of the laboratory spectra with the astronomical spectra, the width of the bars is 0.25 μm .

absorption, so no clear identification of features in this wavelength range is possible. The spectrum from Ornans INTERIOR is most similar to the spectrum of Hen3-600.

04187_1927 (Fig. 4b)

The spectrum of dust in the Tauri system 04187_1927 (M0 type, <3 Myr, Furlan et al. 2006) was obtained with the IRS spectrometer of the Spitzer Space Telescope. The astronomical spectrum has characteristic features at 9.21 μm ,

12.6 μm , 14.15 μm to 14.83 μm , and at 15.59 μm . Several smaller bands occur at 10.18 μm , 10.6–10.72 μm , 11.08 μm , 11.21 μm , and 11.39 μm .

All major features of the group 1 spectra of Allende INTERIOR and Ornans RIM can be found in the astronomical spectrum. Also the spectrum of Ornans INTERIOR representing group 2 is similar. With exception of the feature at 10.6 μm , all significant bands in the astronomical spectrum can be explained by a mixture of Ornans INTERIOR and RIM.

The clear bands in the 12.0 μm to 16.0 μm range indicate the occurrence of melilite and (Fe-rich) spinel (Figs. 2 and 3).

Oxygen-Rich AGB Stars (Fig. 4c)

Dust formation in oxygen-rich AGB stars possibly takes place in a condensation sequence similar to the beginning of the solar system (Lodders and Fegley 1999; Heras and Hony 2005). Although the environment and chemistry in which these condensation sequences take place is probably different from those for young planetary systems, CAI can possibly serve as analogue materials that formed in a similar process. Also, a recently found presolar grain (<1 μm) with a CAI-like mineral composition shows oxygen-isotope ratios typical for ejecta of red giants (Vollmer et al. 2007).

Spectra of the variable star of Mira Cet type R Cas and the semi-regular pulsating star θ Aps were measured with the SWS of ISO. Both spectra show a band at about 13.0 μm , which is characteristic for spectra of oxygen-rich AGB stars (Fabian et al. 2001; Sloan et al. 2003). The origin of the 13.0 μm feature has been attributed to non-stoichiometric spinel (e.g., Fabian et al. 2001), polytypes of Al_2O_3 (e.g., Onaka et al. 1989) or SiO_2 , and polymerized silicates (Speck et al. 2000).

Heras and Hony (2005) calculated mixtures of Al_2O_3 , melilite, olivine, spinel, and (Mg, Fe)O as best fits for oxygen-rich AGB stars. These compositions are similar to those of some CAI (Brearley and Jones 1998).

In contrast to the spectra of R Cas and θ Aps, no strong feature occurs in the mid-infrared region around 13.0 μm in the measured CAI spectra. Only very weak features occur at this wavelength in spectra of Allende INTERIOR and Vigarano 1 and 2. Our results have identified spinel bands in CAI spectra in the 14.4 μm to 15.0 μm region. The spinels in our study were close to the stoichiometric composition or in the case of Allende iron-rich, in contrast to the non-stoichiometric spinels from Fabian et al. (2001).

RV Tauri/Post-AGB Stars (Fig. 4d)

These objects mark the short-lived (about 10^4 years) phase after the stage of an AGB star. AGB stars have lost mass in form of a dusty envelope, which probably forms a circumstellar disk (De Ruyter et al. 2006). Molster et al. (2002) identified the crystalline silicates olivine and pyroxene in such objects. Although the spectrum of R Sge measured with SWS of ISO has a low signal to noise ratio (Fabian et al. 2001; Sloan et al. 2003), it exhibits some clear features in the range from 12.0 μm to 16.0 μm . The astronomical spectrum has features equivalent to those in the spectra of group 1, including potential spinel features between 14.5 μm and 14.9 μm . A feature at 13.7 μm in the astronomical spectrum is near the sodalite band at 13.6 μm in the spectra of group 1.

Identification of bands in the wavelength range from 8.0 μm to 12.0 μm is difficult, but there could be equivalents between the spectrum of Vigarano 1 as well as Ornans

INTERIOR and the spectrum of R Sge (at 9.3 μm , 10.3 μm , 10.9 μm to 11.3 μm , and at 12.4 μm). Very weak features in the astronomical spectrum match the bands at 9.8 μm and 11.6 μm in the spectrum of Vigarano 1. The characteristic melilite band at 12.4 μm could agree with the astronomical spectrum, but a clear identification is again difficult. The strong spinel bands of group 2 are indicated by a feature between 14.4 μm and 15.0 μm in the astronomical spectrum, with a maximum at about 14.8 μm in the smoothed spectrum. This indicates spinels with higher iron content and therefore a history of thermal processing. This is consistent with the evolved state of this object.

Planetary Nebulae (Fig. 4d)

After the stage of a post-AGB star, some stars eject their surrounding material as planetary nebulae and remain as neutron stars or white dwarfs. Planetary nebula Hb 12 is characterized by a bipolar outflow (Hora et al. 2004) and was measured with SWS of ISO (Fabian et al. 2001; Sloan et al. 2003). Earlier mid-infrared studies deduced the occurrence of silicates in this spectrum (Aitken et al. 1979). The astronomical spectrum has low statistics especially above 11.0 μm . It also shows strong line emission features at 9.0 μm , 10.5 μm , around 11.0 μm , 12.8 μm , and 15.5 μm (Pottasch and Surendiranath 2005). Vigarano 1 and Ornans INTERIOR show similarities for their peaks at 9.3 μm , 10.3 μm , and 10.9 μm to 11.2 μm with the astronomical spectrum. There could be corresponding features in the spectra of Vigarano 1 and Ornans INTERIOR for the bands at 12.3 μm to 12.5 μm , and the spinel and melilite bands from 14.0 μm to 14.9 μm in the astronomical spectrum.

The high number of features in the spectrum of Hb 12 and their identification with both silicates and oxides, indicates that the dust is well mixed. The planetary nebula possibly exhibits a range of formation environments similar to the way that solids assumed to have formed the solar system.

SUMMARY AND CONCLUSIONS

Mid-infrared transmission and absorption spectra have been taken from powdered material separated from CAI in the CV chondrites Allende, Ornans and CO chondrite Vigarano.

The spectra allow distinction between pyroxene- and spinel-rich (group 1) and melilite- and spinel-rich (group 2) CAI. The wavelength range from 8.0 μm to 12.0 μm is usually crowded with features from mineral components typical of circumstellar environments, mainly the silicates olivine and pyroxene. The wavelength range from 12.0 μm to 16.0 μm is better suited to identify the highly refractory phases spinel and melilite in mixtures.

Band positions of spectra obtained from CAI in the laboratory have been compared with spectra acquired by astronomical techniques from stellar objects with a range of ages and hence evolutionary stage.

There are similarities in the spectra of CAI of group 1 and

spectra of dust in circumstellar disks of the Herbig Ae star HD104237, the T Tauri stars Hen3-600 and 04187_1927, as well as the post-AGB star R Sge. Bands occurring in the spectra of melilite- and spinel-rich CAI of group 2 could occur in the spectra of dust around HD104237, Hen3-600 and 04187_1927 (Ornans INTERIOR). The spectra of Ornans INTERIOR and Vigarano 1 show similarities with the spectrum of dust around the post-AGB star R Sge and of the planetary nebulae Hb 12. The dust around the Herbig Ae star HD179218 could be carrier of spinel as indicated by features in the 12.0 μm to 16.0 μm range. Comparison with astronomical spectra indicates that no spinel or refractory minerals similar to those found in CAI occur in the dust around oxygen-rich AGB stars.

The maximum position of the broad band between 14.4 μm and 14.9 μm seems to be related to the iron content of spinel. In chondrites this parameter is taken to be an indication of the extent of thermal metamorphism on parent bodies. An infrared band position between 14.4 μm and 14.9 μm in debris disks around stars could be used as temperature proxy for the extent of thermal processing experienced by the dust, but detailed studies of spinel samples with a wider range of defined compositions are needed for confirmation.

Although no quantitative estimations were made, it is safe to assume that the CAI component in most material mixtures in circumstellar environments at least around young stars is only a minor component. This is mirrored by the composition of primitive chondrites, where the highest abundance of CAI is 13 vol% in CO chondrites (e.g., Brearley and Jones 1998).

Although potential similarities to CAI spectra were found in circumstellar environments in all considered evolutionary states, the comparisons are based on the strong mineral bands in the mid-infrared range from 8.0 μm to 16.0 μm . Far-infrared studies would be necessary to confirm any similarities. Also further studies of CAI from other types of chondrites and with different composition is needed for a complete picture.

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