CHEMICAL COMPOSITION OF AMORPHOUS SILICATE DUST AROUND OXYGEN-RICH AGB STARS: CONDENSATION EXPERIMENTS USING THE INDUCTION THERMAL PLASMA SYSTEM.

H. Enomoto[1] and A. Takigawa[1], [1]Department of Earth and Planetary Science, The University of Tokyo, Japan (kirsikkapuu0202@g.ecc.u-tokyo.ac.jp).

Introduction: The majority of presolar grains are originated from outflows of asymptotic giant branch (AGB) stars [1]. Observations of O-rich AGB stars have shown prominent dust features at 10 and 18 μm originated from Si-O stretching and O-Si-O bending vibrations of circumstellar amorphous silicate, respectively. Amorphous silicate dust analogues with various Mg/Si ratios and Mg/Fe ratios synthesized in laboratories, however, show narrower peaks than observed dust features and cannot reproduce the relative strength of 10 and 18 μm. Synthetic optical functions derived from observed spectra of circumstellar/interstellar dust and laboratory dust analogues known as "astronomical silicate" or "O-rich/O-deficient circumstellar silicate" [2;3] have been widely used in the interpretation of observational data. While astronomical silicate well explains the observed spectra compared to the laboratory dust analogues, the nature of astronomical silicate, such as crystal structure and chemical composition, remains poorly constrained. It is even unclear if astronomical silicate should be a single material or a mixture of various dust grains. Fe-free silicate glass of the solar abundance (Mg, Al, Si, Ca, and Na) is proposed as a more realistic dust analogue [4] but still cannot replace the astronomical or circumstellar silicate optical functions because it less matches the observed dust spectra than the synthetic optical functions.

Since the structures of amorphous silicates depend on synthetic processes and conditions, particles formed by gaseous condensation should be investigated as more realistic materials mimicking circumstellar dust. In this study, we carried out condensation experiments in the system of Si-Mg-Fe-Na-Al-Ca-Ni-O using an induction thermal plasma (ITP) system to reveal the nature of circumstellar dust around AGB stars.

Method: The induction thermal plasma system (JEOL TP-40020NPS [5]) was used in the experiments. An input power and a chamber pressure were set at 6 kW and 70 kPa, respectively. Ar gas with a flow rate of 35 L/min was used as the main plasma-forming gas. The starting materials are mixtures of <10 μm sized oxides and metallic powder reagents of Na_2SiO_3, MgO, Al, $CaCO_3$, Fe, Ni, SiO_2, and Si (Kojundo Chemical Lab. Co., Ltd.). The starting material was injected and vaporized in a radial-shaped plasma flame (~10^4 K) with an Ar carrier gas at a flow rate of 2–3 L/min.

Nanoparticles condensed at a rapid cooling rate (~10^4 K/s) were collected after the experiments.

We performed three sets of experiments (CI-02, CI-03, CI-04; Table 1). The starting materials in CI-02 and CI-03 were prepared as the CI chondritic composition [6] in the Si-Mg-Fe-Na-Al-Ca-Ni-O and in Si-Mg-Na-Al-Ca-O system, respectively. The elemental fraction of CI-04 is enriched in Al compared with CI-03 (Table 2). The redox condition in CI-02 was adjusted to prevent condensation of neither iron oxide nor iron silicide [7, 8]. In the CI-02 and CI-03 experiments, 1 L/min O_2 gas was added to prevent the formation of metals and silicides.

The run products collected from the lower wall of the chamber were used for analysis. The crystal phases of the products were examined by powder X-ray diffraction (XRD; Rigaku SmartLab). A zero-fraction sample holder of Si single crystal was used. Condensed particles were embedded in KBr pellets and Fourier transform infrared (FT-IR) spectra were obtained with JASCO FT/IR-4200. Chemical compositions and textures of condensates were analyzed by FE-EPMA (JEOL JXA-8530F) and FE-STEM (JEOL JSM-2800).

Table 1: Chemical compositions of starting materials.

Run	Mg	Si	Fe	Al	Ca	Na	Ni
CI-02	1.03	1	0.85	0.08	0.06	0.06	0.05
CI-03	1.03	1	-	0.08	0.06	0.06	-
CI-04	1.03	1	-	0.75	0.06	0.06	-

Results: The XRD patterns of the condensates are shown in Figure 1. All run products showed amorphous halos at 20°–30°. The strong peaks of kamacite were observed for the product in CI-02. It is confirmed by STEM observations that ~1-20 nm sized Fe-Ni metallic grains were present within amorphous silicate grains. Some peaks of crystalline phases are derived from unvaporized residues of the starting materials; periclase in all runs, quartz in CI-02, and silicon in CI-03 and CI-04.

FT-IR spectra of the products in CI-02 and CI-03 showed strong peaks at 9.8 and 18.3 μm and a weak peak at 14 μm (Fig. 2). There is no significant difference between the spectra of CI-02 and CI-03 regardless of the presence of kamacite. For the Al-rich sample (CI-04), the strongest peak is at 9.8 μm, similar to those of CI-02 and CI-03, but it has a shoulder at 11.3 μm. The broad peak at 14 μm of CI-04 is stronger than those of CI-02 and CI-03 and broad peaks at 17 and 22 μm appear instead of the 18 μm peak.
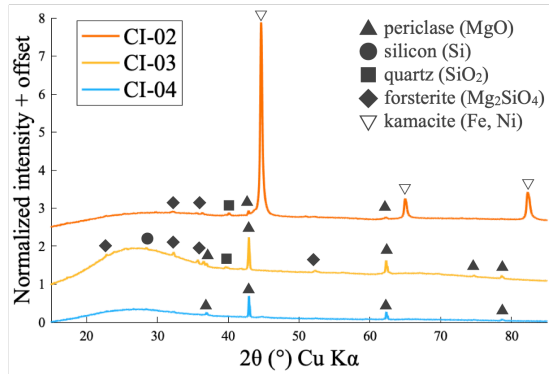
Figure 1. XRD patterns of the experimental products. Open and filled symbols indicate a condensed phase and unvaporized residues of the starting materials.
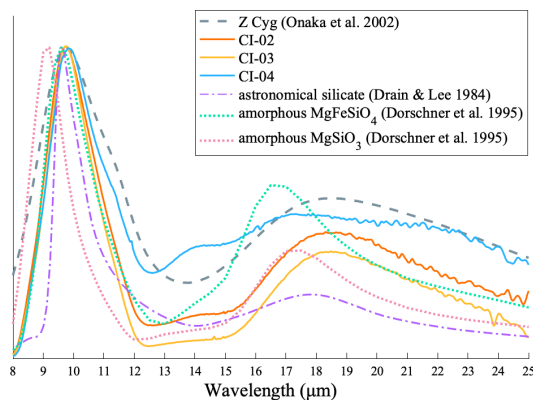

Figure 2. Comparison of dust emissivity of an O-rich AGB star Z Cyg (gray dash line; [3]) with absorbance spectra of the run products (solid lines). Those of silicate glass of $MgSiO_3$ and $MgFeSiO_4$ compositions [11] and astronomical silicate [2] are also shown.

Discussion: The peaks at 9.8 and 18.3 μm observed in all run products are derived from Si–O stretching and O–Si–O bending modes of amorphous silicates, respectively. Weak peaks at 14 μm are attributed to either Si–O or Al–O vibration. Shoulders at ~11.5 μm and 22 μm in the CI-04 products are due to Al–O vibration in AlO_4 tetrahedra and AlO_6 octahedra, respectively [9]. The peak at 22 μm could be from the unvaporized MgO as well. The ratio of non-bridging oxygens to tetrahedral cations (NBO/T) is 2 for CI-02 and CI-03 and 0.8 for CI-04, respectively. CI-04 contains more Al in the amorphous silicate relative to the CI composition and has a more polymerized structure resulting in the weak peaks/shoulders at ~11, 14, 17, and 22 μm.

Dust emissivity of a silicate-rich AGB star (Z Cyg) was derived from observations at multiple variable phases as a function of temperatures of the inner dust shell [10]. The peak positions at 9.8 and 18 μm in the best-fitted dust emissivity were explained by astronomical silicate [2, 10], but the 20–25 μm bump

was not reproduced because astronomical silicate has a convex downward slope at 18–25 μm.

The spectra of all products in the current experiments well reproduced the peak positions of 9.8 and 18 μm peaks in the circumstellar dust emissivity (Fig. 2). In addition, slopes at 18–25 μm are slightly convex upward unlike previous dust analogues such as Mg-Fe-Si-O glasses/amorphous silicates nor astronomical silicate [11] because of the presence of additional Al, Ca, and Na in the amorphous silicates.

The strengths of the 18 μm peak relative to the 10 μm peak in CI-02 and CI-03 are weaker than the observed dust emissivity (Fig. 2). On the other hand, the 11 μm shoulder and the relative strength of 10 and 18 μm peaks in CI-04 better match the observed dust emissivity than the other dust analogues, while the strength of the 14 μm peak and spectral shape at ~18 μm do not match the observation (Fig. 2).

The discrepancy between observed dust and the ITP condensates could be explained either by the inner dust shell temperature of Z Cyg or the chemical composition of amorphous silicates. If the inner dust shell temperature is set at ~200 K lower, the dust spectra of the ITP condensates of the CI composition (CI-02 and CI-03) explain both peak positions and relative strength of the observed 10 and 18 μm dust emission. If we attempt to explain the differences only by chemical compositions of amorphous silicates, the circumstellar silicate dust must be enriched in Al relative to the CI chondritic composition although not as much as CI-04. Amorphous presolar silicate grains, however, generally have low Al content except for a few Al-rich presolar silicate grains [e.g., 1, 12].

These results indicate that the circumstellar silicate dust must not be pure Mg-Fe-silicates but contain Al and possibly other cations such as Ca and Na, while the content of cations in amorphous silicates should be studied more systematically. Also, unbiased and systematic analyses of the chemical composition of amorphous presolar silicates are the key to linking circumstellar and presolar silicate mineralogically.

References: [1] Nguyen A. N. et al. (2016) *ApJ*, **818**, 51. [2] Draine B. T. and Lee H. M. (1984) *ApJ*, **285**, 89. [3] Ossenkopf V. et al. (1992) *A&A*, **261**, 567. [4] Speck A. K. et al. (2015) *ApJ*, **809**, 65. [5] Kim T. H. et al. (2021) *A&A*, **656**, A42. [6] Lodders K. et al. (2009) in Landolt-Börnstein (Berlin: Springer), 560. [7] Matsuno J. et al. (2021) *ApJ*, **911**, 47. [8] Enju S. et al. (2022) *A&A*, **661**, A121. [9] Tarte (1967) *AcSpA* **23**, 2127. [10] Onaka T. et al. (2002) *A&A*, **388**, 573. [11] Dorschner et al. (1995) *A&A*, **300**, 503. [12] Vollmer C. et al. (2009) *ApJ*, **700**, 774.