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Surface Energy Measurements of Silicates with Application to Nucleation and Condensation in Exoplanet Atmospheres WASP-17b and VHS 1256b

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Abstract

Surface energies are measured using oxide melt solution calorimetry of materials with different surface areas for several likely exoplanet condensates including forsterite (Mg_2SiO_4), and enstatite ($MgSiO_3$), SiO_2 and amorphous silicates. The exoplanet community currently relies on theoretical or estimated surface energy data for nucleation rate calculations for hot Jupiter cloud species, which are the basis for determining which species should dominate exoplanet atmospheres. This work inputs the newly measured surface energy data to calculate nucleation rates for each of the proposed cloud species in specific planetary atmospheres such as WASP 17-b and VHS 1256b.

Motivation

The exoplanet community currently relies on theoretical or estimated surface energy data for nucleation rate calculations for hot Jupiter cloud species, which are the basis for determining which species should dominate exoplanet atmospheres. This work inputs the newly measured surface energy data to calculate nucleation rates for each of the proposed cloud species given current measured surface energies and such forsterite (Mg_2SiO_4), zinc sulfide (ZnS), enstatite ($MgSiO_3$), with others planned.

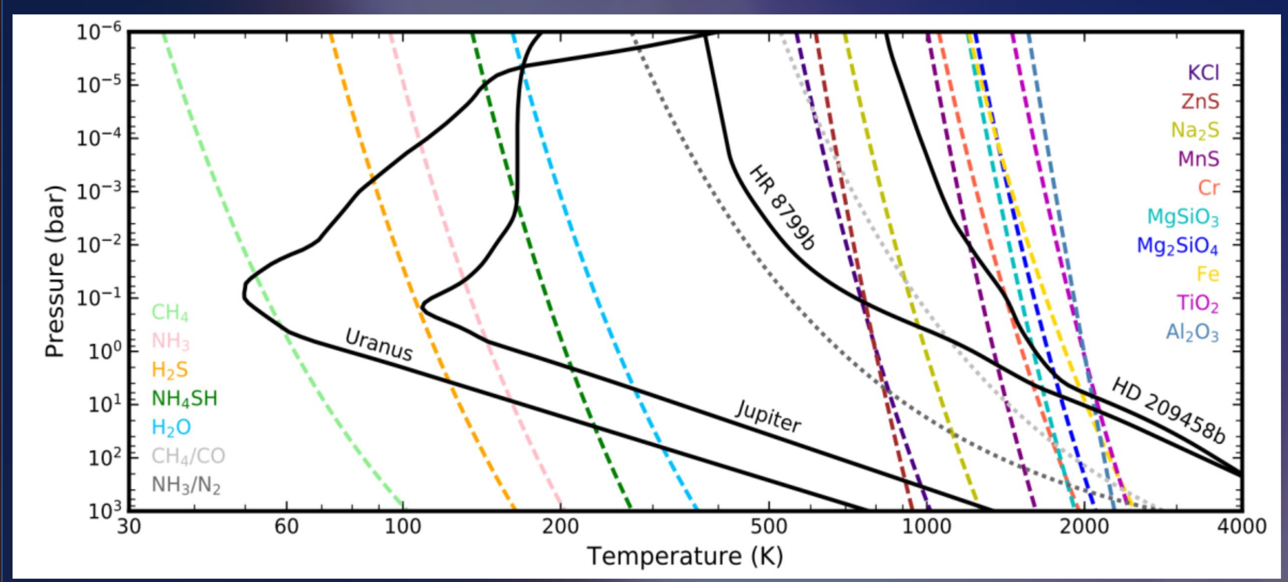


Figure 1. Dashed lines represent the condensation temperatures of several chemical species as a function of pressure. The black lines represent temperature-pressure profiles of Jupiter and Uranus and two exoplanets, HR 8799b (a young, directly imaged exoplanet) and HD 209458b (a hot Jupiter). Condensation of a given species occurs when a planet's temperature-pressure profile becomes lower than a species' condensation temperature profile. (Figure adapted from Gao et al. 2021a)

When modeling aerosol formation in hot Jupiter atmospheres, the surface energies that have been used for many condensates are close to an order of magnitude smaller than experimentally measured values using calorimetry and other methods (Table 1) (Boni & Derge 1956; Castro et al. 2006).
Historically, astrophysicists have relied on atomistic estimates of surface energies, but we argue here that it is time to start using experimentally determined values.

Condensate Species	Surface energy from experimental data (erg cm^{-2})	Surface Energy used in Exoplanet Atmosphere Literature (erg cm^{-2})
Corundum Al_2O_3	2040 (anhydrous) [1]	690 (model) [5 via 6 via 7]
Rutile TiO_2 (CCN)	2060 ± 100 (anhydrous) [2]	425-508 (model) [5 via 8 via 9]
Forsterite Mg_2SiO_4	4410 ± 210 (anhydrous) [3]	436 (model) [5 via 6 via 7]
Enstatite $MgSiO_3$	TBD	N/A
ZnS zinc sulfide	1760 (anhydrous) [4]	860 (est.) [5 via 10]
MnS manganese sulfide	TBD	2326 (est.) [5 via 11]
Na_2S sodium sulfide	TBD	1033 (est.) [5 via 11]

Table 1. Surface energies of potential condensate particles in exoplanet atmospheres. Blue is the measured value from a paper that has been accepted in Geochimica et Cosmochimica Acta, [4] (Subramani et al. 2022), [1] (McHale et al. 1997), [2] (Castro et al. 2006), [3] (Chen & Navrotsky 2010), [5] (Gao et al. 2020), [6] (Kozasa et al. 1989), [7] (Boni & Derge 1956), [8] (Lee et al. 2018), [9] (Lee et al. 2015), [10] (Celikkaya & Akinc 1990), [11] (Zhang et al. 2003)

Surface energies for anhydrous crystalline and amorphous silicate nanoparticles

Material	Surface energy of crystalline species (J/m^2)	Surface energy of amorphous species (J/m^2)
$MgSiO_3$ (enstatite)	4.79 ± 0.45 †	1.8 ± 0.10 §
Mg_2SiO_4 (forsterite)	4.41 ± 0.21 #	1.657 **
Fe_2SiO_4 (fayalite)	2.47 ± 0.20 ‡	0.93 **
SiO_2 (silica)	1.00 ± 0.07 *	0.26 &

† (Householder et al. 2023)
§ (Householder et al. submitted)
# (Chen & Navrotsky 2010b)
‡ (Lilova et al. 2018)
& (Chiang et al. 1996)
* (Parks 1990)
**Am/Cry SE ratio of 0.3758 for enstatite was used to extrapolate the amorphous forsterite and fayalite surface energies.

Table 2. Surface energies of anhydrous crystalline and amorphous silicate condensates. Green is measured value for anhydrous crystalline enstatite. Blue is measured surface energy of amorphous enstatite.

Measuring Surface Energies

$$\text{Surface energy} = \frac{\Delta H_{ds}(\text{bulk}) - \Delta H_{ds}(\text{nano})(\text{kJ/mol})}{\text{surface area }(\text{m}^2/\text{mol})}$$

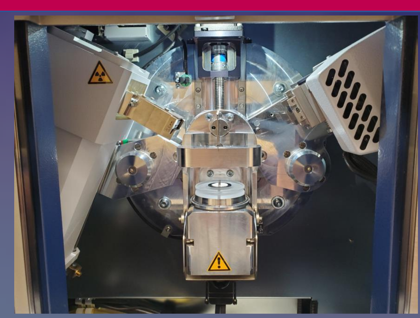
ΔH_{ds} = drop solution enthalpy

Nanoparticle Synthesis

Each chemical species has a different synthesis method. For ZnS, nano-sphalerite was synthesized using the hydrothermal method. Nano-enstatite was synthesized using the sol-gel method.

Nanoparticle Characterization

Thermogravimetry and Differential Scanning Calorimetry (TG – DSC): Setaram Labsys Evo



Powder X-Ray Diffraction (PXRD): Bruker D2 bench top diffractometer

Scanning Electron Microscopy, Scanning Transmission Electron Microscopy, Transmission Electron Microscopy

Brunnauer-Emmet-Teller (BET) Measurements: N_2 adsorption to measure the surface area of the nanoparticles - measured at 77 K using a 10-point BET technique on the analysis port of a Micromeritics ASAP 2020

FTIR Spectroscopy: Bruker Vertex 70 spectrometer

Oxide Melt Solution Calorimetry

High temperature oxide melt solution calorimetry is performed using a Tian-Calvet twin calorimeter AlexSYS at 1073 K in a sodium molybdate or lead borate solvent. The bulk and nano samples of the species are methodically dropped into the solvent to obtain the drop solution enthalpy, ΔH_{ds}. The nano sample are water-corrected for in the thermochemical cycles. The surface energy is then given by ΔH_{ds} (bulk)-ΔH_{ds}(nano water corrected)(kJ/mol) / surface area (m^2/mol).

Results

Zinc Sulfide

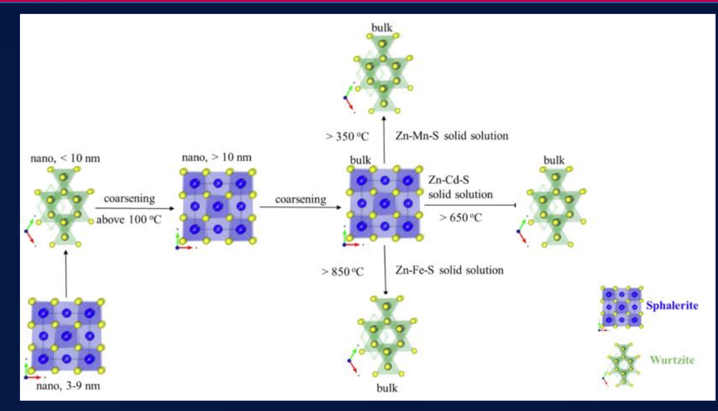
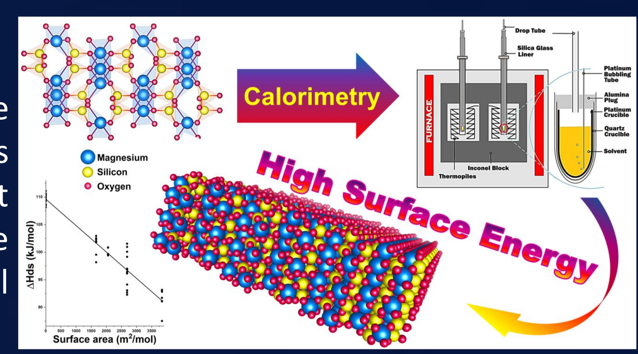


Figure 2. Formation of polymorphs from nanosized sphalerite and wurtzite in the presence of impurities

Until our measurements it was assumed that sphalerite was the dominant zinc sulfide polymorph in hot exoplanet atmospheres (Kopparapu et al., 2018; Gao and Benneke, 2018), but our work suggests that the formation process follows a path shown in Figure 2. ZnS precipitating rapidly from a gas phase in a planetary atmosphere (or elsewhere) is likely to form initially as a poorly crystalline or amorphous nanophase, and as the cloud condensation nucleus grows, that phase transforms to fine nanocrystalline wurtzite, followed by nano and bulk sphalerite due to coarsening, and then the condensate would transform to bulk wurtzite given a high enough temperature.

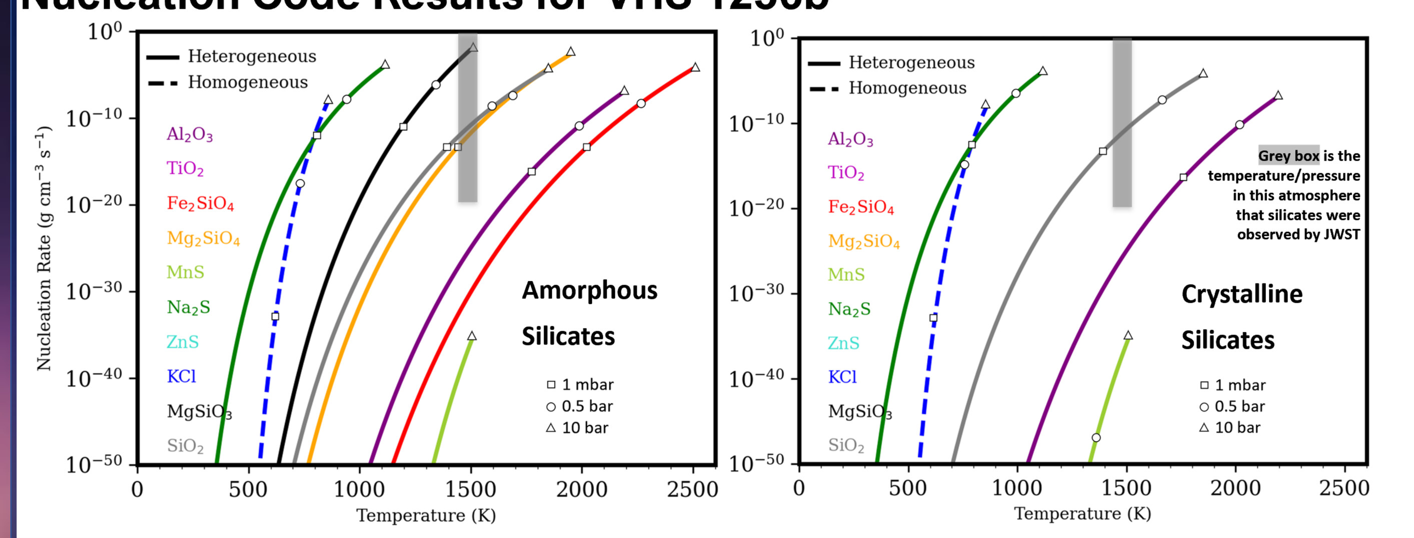
Enstatite

The newly measured surface energy of enstatite (Householder et al. 2023) The high surface energies of enstatite and forsterite likely inhibit direct condensation of crystalline nanoparticles of these two key silicates in a wide range of astrochemical environments.



Silicate Nucleation Results

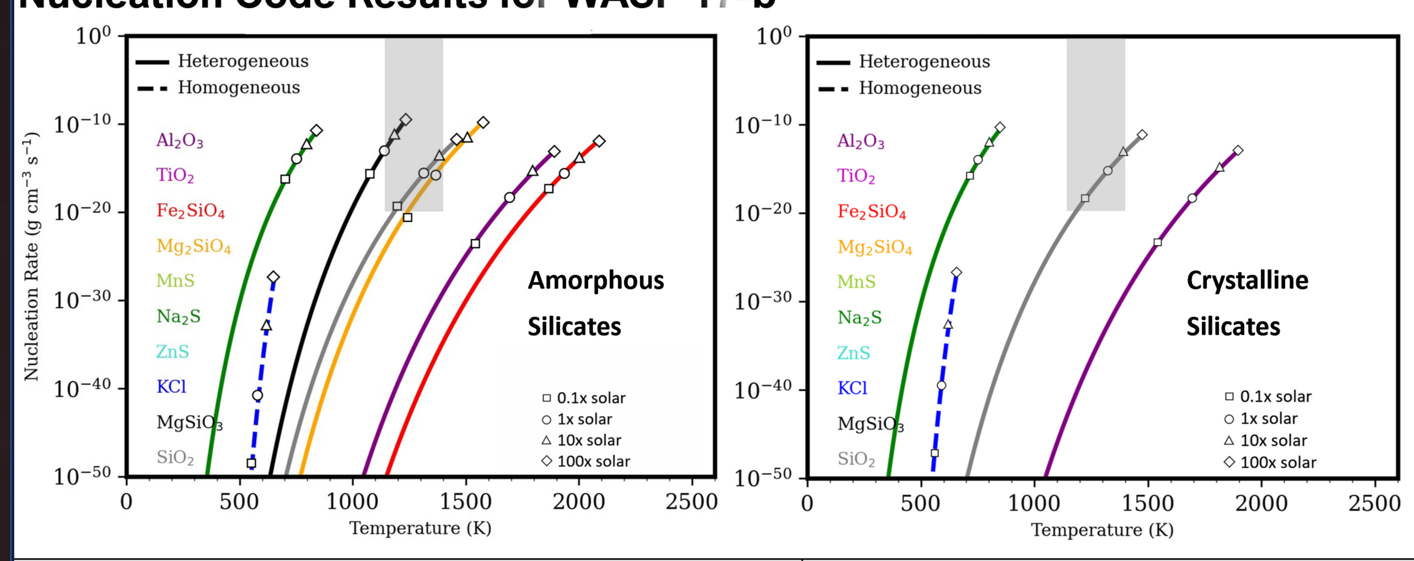
Nucleation Code Results for VHS 1256b



Results of the public nucleation code provided by Gao et al. (2018) for select cloud species of a hot giant exoplanet with 1x solar metallicity	Nucleation results when the *crystalline* silicate surface energies are used
Enstatite, quartz and forsterite dominate nucleation at the equilibrium temperature if they INITALLY nucleate as *amorphous*	**Because Mg-rich silicates were seen by Webb they must initially condense as amorphous**

Nucleation rates as a function of temperature for select cloud species for an atmosphere analogous to VHS 1256 b with varying atmospheric pressures of 1 mbar, 0.5 bar and 10 bar with 1x atmospheric solar metallicity. The grey rectangle encompasses the temperatures at which the JWST observed silicates in VHS 1256 b. (left) Nucleation rates using surface energies for select amorphous silicate cloud species. (right) Nucleation rates using surface energies for select crystalline silicate cloud species.

Nucleation Code Results for WASP 17-b



Amorphous species nucleation rates as a function of temperature for a hot exoplanet at atmospheric pressure of 0.1 mbar with varying solar metallicities	Nucleation results when the *crystalline* silicate surface energies are used
At 0.1 mbar there may not be enough material for condensation of Mg-rich silicates	**Crystalline silica is the dominant nucleating material in this atmosphere**

Nucleation rates as a function of temperature for select cloud species in a hot Jupiter atmosphere analogous to WASP-17b, with varying atmospheric solar metallicities of 0.1, 1.0, 10, and 100x solar and total atmospheric pressure of 0.1 mbar. The grey rectangle encompasses the temperatures at which the JWST observed SiO2 in WASP-17b. (left) Nucleation rates using surface energies for select amorphous silicate cloud species. (right) Nucleation rates using surface energies for select crystalline silicate cloud species.

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