

高温蒸発生成物同定のための質量分析手法の開発と硫化鉱物への応用

Development of a mass spectrometric method for identifying high-temperature evaporation products and its application to sulfide minerals

*稲田 栞里¹、石橋 篤希^{1,2}、坂井 南美²、羽馬 哲也¹

*Shiori Inada¹, Atsuki Ishibashi^{1,2}, Nami Sakai², Tetsuya Hama¹

1. 東京大学 大学院総合文化研究科、2. 理化学研究所 開拓研究本部

1. Department of Basic Science, The University of Tokyo, 2. RIKEN Pioneering Research Institute

Introduction

Evaporation of rocky planetary materials is a key process of elemental volatility fractionation found in Solar System samples. For example, various degrees of sulfur depletion in chondrules are interpreted as results of evaporation of sulfides such as FeS¹. Previous laboratory studies in cosmochemistry have investigated evaporation kinetics of minerals and melts modeling meteorite components by analyzing evaporation residues, which has enabled discussions of timescales of evaporation events in the early Solar System^{2,3}. However, chemical processes underlying measured kinetics have remained elusive largely due to the lack of knowledge about gaseous products of evaporation³⁻⁵. In addition, evaporation of rocky dust has recently attracted increasing attention in astronomy as a formation pathway of refractory molecules (e.g., SiS and CaS) detected around massive protostars^{6,7}. Identification of evaporation products is important also as a basis for interpreting such observations. The biggest challenge for this has been the experimental difficulty in realizing collision-free conditions to detect nascent products of high-temperature evaporation of materials of interest (typically at >1000 K). To overcome this problem, in this study we developed a new experimental apparatus utilizing mass spectrometry. This apparatus was applied to sulfides contained in primitive chondrites (CaS, MgS, and FeS) to discuss their microscopic evaporation processes and a potential link to astronomical observations.

Methods

The apparatus consists of an ultra-high vacuum chamber (10^{-6} - 10^{-5} Pa during the experiments, corresponding to mean free paths of 10^3 - 10^4 m), a tungsten plate for resistive heating, a quadrupole mass spectrometer (QMS) placed ~10 cm above the heater, and a radiation thermometer. This configuration sufficiently fulfills the collision-free condition (mean free path $\gg$ detection distance). Powdered sulfide samples were loaded on the heater and were evaporated at up to ~1700 K. The released gases were detected by QMS after electron impact ionization.

Results and Discussion

CaS (s) and MgS (s) were found to evaporate mainly as Ca or Mg, S, and S₂ with different S/S₂ ratios. CaS (g) was detected as a minor product from CaS (s), whereas MgS (g) was below the detection limit. FeS (s) evaporated incongruently unlike the other samples as S₂, S, and S₃. Although the observed evaporation behaviors are consistent with thermodynamics in certain respects (e.g., congruency/incongruency), the products do not necessarily follow thermodynamics. For example, the present results are inconsistent with $P_{\text{CaS}}^{\text{eq}}/P_{\text{Ca}}^{\text{eq}} < P_{\text{MgS}}^{\text{eq}}/P_{\text{Mg}}^{\text{eq}}$ (P_i^{eq} : equilibrium vapor pressure of species *i*) above CaS (s) and MgS (s) at the experimental temperatures. The ratios of the sulfur species from FeS (s) are also different from the

equilibrium pressure ratios. These results suggest that the evaporation processes are governed by molecular-level dynamics of crystal decomposition and surface reactions between the fragments before release to the gas phase, rather than the Gibbs energy minimization. This should be the reason why the evaporation kinetics cannot be interpreted only in terms of the simple kinetic model based on equilibrium calculations. The present results also help interpretation of observations of sulfur-bearing refractory molecules around protostars, providing hints about astronomical settings of evaporation recorded in Solar System materials. Identification of evaporation products realized by our new method will thus enable multifaceted understanding of evaporation of planetary materials and its roles in the Solar System material evolution.

References

¹Tachibana & Huss (2005) GCA 69, 3075.

²Tachibana & Tsuchiyama (1998) GCA 62, 2005.

³Richter et al. (2007) GCA 71, 5544.

⁴Inada et al. (2024) JCP 160, 154710.

⁵Inada et al. (2025) GCA 404, 172.

⁶Tanaka et al. (2020) ApJL 900, L2.

⁷Tasa-Chaveli et al. (2025) ApJL 993, L42.

キーワード：蒸発、硫化物、質量分析、宇宙化学、天文観測

Keywords: evaporation, sulfides, mass spectrometry, cosmochemistry, astronomical observation