



## COSIMA-Rosetta calibration for in situ characterization of 67P/Churyumov–Gerasimenko cometary inorganic compounds



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### ABSTRACT

Cometary Secondary Ion Mass Analyzer (COSIMA) is a time-of-flight secondary ion mass spectrometry (TOF-SIMS) instrument on board the Rosetta space mission. COSIMA has been designed to measure the composition of cometary dust particles. It has a mass resolution  $m/\Delta m$  of 1400 at mass 100 u, thus enabling the discrimination of inorganic mass peaks from organic ones in the mass spectra. We have evaluated the identification capabilities of the reference model of COSIMA for inorganic compounds using a suite of terrestrial minerals that are relevant for cometary science. Ground calibration demonstrated that the performances of the flight model were similar to that of the reference model. The list of minerals used in this study was chosen based on the mineralogy of meteorites, interplanetary dust particles and Stardust samples. It contains anhydrous and hydrous ferromagnesian silicates, refractory silicates and oxides (present in meteoritic Ca–Al-rich inclusions), carbonates, and Fe–Ni sulfides. From the analyses of these minerals, we have calculated relative sensitivity factors for a suite of major and minor elements in order to provide a basis for element quantification for the possible identification of major mineral classes present in the cometary particles.

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### 1. Introduction

Comets spend most of their lifetime far away from the Sun and are therefore only little affected by solar radiation. In addition, as they are small bodies, they are very likely not altered by internal differentiation. Therefore, comets are considered to be among the most primitive objects in the Solar System and might even still contain residual

material of the solar nebula. In other words, comets may have preserved refractory and/or volatile interstellar material left over from the Solar System formation and can provide key information on the origin of our Solar System.

While remote observations allow measurements of collective properties of cometary dust, mass spectrometers flown on spacecraft allow the compositional analysis of individual particles. The latter technique was first introduced on the Giotto and Vega 1/2 missions to comet 1P/Halley (Kissel et al., 1986a, 1986b). The measurements showed that in comet Halley's dust, a mineral component is mixed

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with organic matter in individual particles (Lawler and Brownlee, 1992).

Remote observations of comet C/1995 O1 (Hale–Bopp) and other bright comets, as well as laboratory analyses of cosmic dust of inferred cometary origin, showed that cometary dust is an unequilibrated, heterogeneous mixture of crystalline and glassy silicate minerals, organic refractory material, and other constituents such as iron sulfide and possibly minor amounts of iron oxides (Bradley, 2005; Crovisier et al., 1997; Dobrică et al., 2012; Hanner and Bradley, 2004, and references therein). The olivine and pyroxene minerals are mostly Mg-rich, while Fe is distributed in silicates, sulfides, and Fe–Ni metal. Remote infrared spectra of silicate emission features in comet Hale–Bopp have led to identification of the minerals forsterite and enstatite in both amorphous and crystalline form. This mineralogy is consistent with the composition of chondritic porous anhydrous interplanetary dust particles (CP-IDPs) (e.g., Brunetto et al., 2011) and of Ultra-Carbonaceous Antarctic MicroMeteorites (UCAMMs) (Dobrică et al., 2012). The high deuterium to hydrogen (D/H) ratios of the organic refractory material in these IDPs (Messenger, 2002) and in UCAMMs (Duprat et al., 2010), as well as the physical and chemical structure of glassy silicate grains, suggest a primitive origin of cometary dust. Although primitive cosmic dust contains a fraction of presolar dust (e.g., Zinner, 2014), the origin of deuterium anomalies in the organic matter is still a matter of debate. In situ measurements of particles from comet Halley have also shown that carbon is enriched in cometary particles relative to CI chondrites; some of the C is in an organic phase (Jessberger et al., 1988).

“Ground truth” was provided by the Stardust mission, which in 2006 successfully returned samples of dust collected in the coma of comet 81P/Wild 2 (Brownlee, 2014; Brownlee et al., 2006). The bulk of the Stardust samples appears to be a weakly constructed mixture of nanometer-sized grains, interspersed with much larger ( $> 1 \mu\text{m}$ ) crystalline and amorphous ferromagnesian silicates, Fe–Ni sulfides, Fe–Ni metal, and other phases (Zolensky et al., 2006). The very wide variety of olivine and low-Ca pyroxene compositions in comet Wild 2 requires a wide range of formation conditions, probably reflecting very different formation locations in the protoplanetary disk (e.g., Frank et al., 2014). The restricted compositional ranges of Fe–Ni sulfides, the wide range for silicates, and the absence of hydrous phases indicate that comet 81P/Wild 2 likely experienced little or no aqueous alteration. Less abundant Wild 2 materials include refractory grains such as calcium–aluminum-rich inclusions (CAIs), high-temperature phases (Brownlee, 2014, and references therein), whose presence appears to require radial transport in the early protoplanetary disk.

Spitzer Space Telescope observations of comet 9P/Tempel 1 during the Deep Impact encounter revealed emission signatures that were assigned to amorphous and crystalline silicates, amorphous carbon, carbonates, phyllosilicates, polycyclic aromatic hydrocarbons, water gas and ice, and sulfides (Lisse et al., 2006). Good agreement is seen between the Tempel 1 ejecta spectra, the material emitted from comet Hale–Bopp, and the circumstellar material around the young stellar object HD100546 (Malfait et al., 1998). The atomic abundance of the observed material is consistent with solar and CI chondritic abundances. The presence of the observed mixture of materials requires direct condensation from the gas and/or efficient methods of annealing amorphous silicates and mixing of high- and low-temperature phases over large distances in the early protosolar nebula.

In August 2014, the European Space Agency’s spacecraft Rosetta arrived at Jupiter-family comet 67P/Churyumov–Gerasimenko (hereafter 67P/C–G). The Rosetta spacecraft carries eleven scientific instruments to study the nucleus of the comet as well as the gas, plasma, and particle environment in the inner coma as a function of heliocentric distance. On November 12, 2014, the lander spacecraft Philae has performed the first ever landing on a comet nucleus and provided in situ analysis of its physical and compositional properties (Gibney, 2014; Glassmeier et al., 2007, and references therein; Hand, 2014).

One of the core instruments of the Rosetta payload is the COmetary Secondary Ion Mass Analyzer (COSIMA) that presently collects and analyzes the composition of dust particles in the coma of 67P/C–G (Kissel et al., 2009; Kissel et al., 2007). COSIMA is a high-resolution time-of-flight secondary ion mass spectrometry (TOF-SIMS) instrument (Vickerman and Briggs, 2013), which uses an indium primary ion beam to analyze the chemical composition of collected cometary particles. The size of the primary beam is about  $50 \mu\text{m}$  in diameter, and the mass resolution is  $m/\Delta m \sim 1400$  at 50% peak height (FWHM) at  $m/z = 100$  u. The bombardment of indium ions onto the sample produces secondary ions that are subsequently accelerated into a time-of-flight mass spectrometer, generating a secondary ion mass spectrum. By switching polarity of the mass spectrometer potentials, COSIMA is able to collect either positive or negative secondary ions, to allow a complete analysis of the samples, since atoms or molecules are ionized either as positive or negative ions according to their first ionization potential and their electron affinity, respectively. The goal of the COSIMA investigation is the in situ characterization of the elemental, molecular, mineralogical, and possibly isotopic composition of dust in the coma of comet 67P/C–G.

A twin of the COSIMA instrument flying on board Rosetta is located at the Max-Planck-Institut für Sonnensystemforschung (hereafter MPS) in Göttingen. This instrument serves as a reference instrument (Reference Model, RM) for the COSIMA flight instrument (named COSIMA XM). Pre-launch tests have shown that the performances of the RM and the XM are similar. Since the launch of Rosetta in 2004, the RM has been extensively used for laboratory calibration measurements. We have obtained a “library” of COSIMA mass spectra of well prepared and specially selected reference samples. Our reference samples are, among others, pure minerals expected to be present at the comet. These reference spectra will facilitate interpretation of the mass spectra expected from the comet with the COSIMA XM.

In this paper, we describe calibration measurements with the COSIMA RM that we performed with a set of mineral samples during recent years. A similar calibration campaign with samples of organic compounds is described in Le Roy et al. (2015).

## 2. Samples and methods

### 2.1. Sample selection and determination of compositions

For our COSIMA reference measurements, we selected minerals that have either been detected in comets or that were identified in other primitive Solar System materials, namely meteorites (in particular carbonaceous chondrites) or interplanetary dust particles (IDPs) and Antarctic micrometeorites. The selected mineral groups include anhydrous silicates (in particular olivines, pyroxenes, and feldspars of different compositions), hydrated silicates, oxides and hydroxides, carbonates, sulfides, pure elements, and alloys (Table 1). For the abundant minerals in comets, in particular anhydrous silicates, more than one sample was measured from the same mineral class (e.g., olivine). The samples were either purchased from a commercial provider (MPS samples – Krantz Mineral Shop in Bonn, Germany) or obtained from collections of the natural history museums in Los Angeles, London, Paris, and Vienna. A few samples were also provided through personal collaborations. The compositions of the mineral samples were either obtained from the literature, or were measured by electron microprobe at University Paris VI, CAMPARIS. Major and minor elements were measured at 15 keV, 10 nA. Oxygen, carbon, and hydrogen were not measured but calculated by stoichiometry (for oxygen) or by difference (for carbon and hydrogen). The corresponding formula were calculated and compared to the theoretical values (Tables 1 and 2).

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