Prebiotic Organic Globules

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Abstract

Analogs of organic globules observed in carbonaceous chondrite meteorites and in interplanetary dust particles and of rod to spherical structures observed in terrestrial archean microstructures have been synthesized in our experiments conducted with proton irradiation on a mixture of simple inorganic constituants, CO, N_2 and H_2O. Our analyses of these laboratory organic globules show that the proton irradiation residue contains proteinous and non-proteinous amino acid precursors. On the basis of morphology, of hydrothermal and mineral environment, we suggest that the meteoritic organic globules and the archean carbon microstructures could be composed of amino acid precursors.

Organic matter in meteorites, cometary and interstellar dust particles has been observed inside micrometer and sub-micrometer spheres and nanotubules, called organic globules. It has been suggested that these globules could have delivered prebiotic organic matter on Earth. Their shapes and sizes are variable and their exact composition seems unknown. Most of the globules observed in the carbonate-free sections of the Tagish Lake meteorite are hollow with aggregates of two to five globules[1]. The isotopic analysis of the globules and of the surrounding meteorite matrix suggests that the globules aggregated before incorporation in the Tagish Lake parent body. Their diameter varies from 140 nm to

1700 nm. They match the sizes (40-2000 nm) and bulk compositions of the CHON particles discovered during Halley's comet encounters. Similar globules (10-1000 nm) have been observed in the crushed pieces and in the acid residues of The Orgueil, Tagish Lake and Murchison meteorites[2-4]. Their shapes vary from round to tubular and they are solid or hollow, singled or clustered.

Laboratory organic globules have been generated with benzene or anthracene introduced in a helium plasma[5,6]. The total gas pressure was 20 Torr and the plasma particles were He^+ ions and essentially protons. The deposits were brownish to yellowish and white. The globules diameters vary from 17 to 133 nm, 40% of them having a hollow core, for benzene and from 25 to 400 nm for anthracene. They all show spherical shapes in contrast to the variety of shapes observed in natural organic globules. They have been identified as laboratory analogs of the organic globules found in carbonaceous chondrites and in interplanetary dust particles.

Spherical, cylindrical and filamentous structures have been observed in the terrestrial australian 3.5 Ga Kitty's Gap chert, Warrawoona Group, Pilbara. They have been interpreted as fossils of microorganisms[7-9] and as hydrocarbon compounds obtained through Fischer-Tropsch reactions with volcanogenic CO[10]. Also the rod to vibroid-shaped terrestrial structures observed in the south-african 3.3 Ga old Josefsdal chert, Onverwacht Group of the Barberton greenstone belt, have been identified to microfossils[9] and the filamentous carbonaceous microstructures, observed in the south-african 3.2 Ga old siliciclastic Moodies Group deposits of Barberton, have been interpreted as organic walls of microfossils[11].

Here we show that the content of extraterrestrial organic globules may be peptide-like polymers containing proteinous and non proteinous amino acids and that these amino acid precursors can be formed from the simple molecules CO, N_2 and H_2O irradiated with protons. We also show that the filamentous and spherical structures that we observe in our experiments resemble the archean carbon microstructures morphologically. We further notice that these extraterrestrial and archean microstructures could have been synthesized in similar hydrothermal and mineral characteristics than in laboratory experiments.

Earlier experiments mixing amino acids in an artificial sea medium, at 105°C during 8 weeks[12] and at 250°C-350°C under 134 atm hydrostatic pressure for 6 hours[13] produced microspheres, 0.3 μm to 3 μm in diameter, called marigranules and marisomes resembling exactly those of our experiment. They could be synthesized only in the presence of polar amino acids and of a glass tube. They were not synthesized at 200°C, and their shapes, purely spherical to strectched spheres were dependant on the temperature. Some were empty. Analyses of the marigranules and marisomes IR spectra suggested the possibility that the amino group was linked to silicates.

In other experiments a gaseous mixture of CO, N_2 and H_2O irradiated with protons, helium ion beams, electron beams, gamma and X-rays, in a glass tube, produced amino acid precursors which led, after acid hydrolysis, to proteinous and nonproteinous amino acids[14-16]. It has been reported that a mixture of CO_2, N_2 and H_2O, irradiated with protons did not lead to the production of amino acids[14]. Asymmetric synthesis of amino acid precursors have also been performed after proton irradiation of a mixture of CO, NH_3 and H_2O followed by irradiation with right and left ultraviolet circularly polarized light[17].

Our experiment combined and continued these past ones, starting with a proton - irradiated mixture which led to a residue. We analysed this residue and we compared it to the extraterrestrial organic globules and to the archean carbon microstructures.

Proton irradiation has been performed, in a glass tube, during two hours at room temperature, on a mixture of gaseous constituents: carbon monoxyde, dinitrogen and water. After proton irradiation, an aliquot of the radiation products was gently dried at ambient temperature and pressure in clean bench to obtain involatile organic matter. Application of scanning electron microscopy, SEM, (Fig. 1) and of atomic force microscopy, AFM, (Fig. 2-3) were performed to observe the morphological characteristics of the yellow-colored residue synthesized during the irradiation. Micro- and sub-micrometer globule-spheres, tubules and fiber-filament soft tissues are observed. Their shapes and sizes resemble those of the meteoritic organic globules and of the terrestrial archean rod and spherical structures. Their molecular weights, determined with gel filtration chromatography, are distributed between several hundred and a maximum of 3000. A wide variety of amino acids were detected after acid-hydrolysis of the residue (Fig.4). The observed amino acids

include glycine, alanine, aspartic acid and non-proteinous amino acids such as α-alanine, β-alanine and γ-aminobutyric acid. The presence of non-proteinous amino acids indicates that the detected amino acids do not come from a contamination but are indigenous to the product. Among hydrolyzed amino acids, glycine was most abundant amino acid compound followed by D-, L-alanine and D-, L- α-aminobutyric acid in logarithmic decrease.

Consequently on the basis of morphology, we can propose a similarity between our laboratory organic spherical and filamentous structures composed of amino acid precursors and the organic extraterrestrial and archean globules and filaments.

These structures are synthesized when carbon monoxyde is present. In the extraterrestrial and archean media, the source of CO could be hydrothermal. Indeed, CO has been obtained from CO_2 in a recent experiment simulating a hydrothermal flow system, conducted at 250°C-300°C and 250 bar, in a 100 mL cell[18]. In this experiment, a mixture of CO_2 dissolved in flowing seawater (NaCl: 0.5 mol/kg, pH5), of gaseous H_2 and of magnetite, produced dissolved CO and CH_4 together with C_1 -C_8 carboxylic acids and other unidentified organic species. Consequently, CO is avalaible in hydrothermal environments where olivine (a solid solution between forsterite Mg_2SiO_4 and fayalite Fe_2SiO_4) encounters serpentinization, producing H_2 and magnetite. The dinitrogen of the geological environment could react with CO and H_2O to form microspheres and tubules containing amino acids such as those synthesized in our experiments. The source of excitation could be gamma rays or proton irradiation from now extinct radionuclides such as ^{26}Al and ^{53}Mn. It is to be noticed that a residue of carbon particles together with methane and hydrocarbon gases have been obtained in laboratory experiments during serpentinization of olivine in a CO_2 bearing NaCl fluid at 300°C and 500 bar[19]. All particles were bilobed, pale yellow colored and 30 to 80 μm in size.

The laboratory production of hydrocarbons and of carbon monoxyde in hydrothermal experiments simulating the olivine serpentinization process together with the laboratory production of amino acid precursors in proton irradiation of a mixture of CO, N_2 and H_2O, confirm the suggestion that we wrote earlier[20] concerning the possible formation of amino acid precursors near hydrothermal sites where olivine encounters serpentinization

and considering extinct radionuclides as excitation source.

It is now accepted that meteoritic organic globules seem to have been synthesized inside parent bodies. They could have been submitted to the thermal energy of extinct radionuclides, in a mineral environment made of olivine or silicates and consequently they could have encounter temperature of ~250°C with hydrothermal activity transforming CO_2 into CO and producing hydrocarbons and amino acids as described above.

We may remark that the australian 3.5 Ga Kitty's Gap chert, has been submitted to hydrothermal activity during diagenetic silicification. Temperatures of 250-350°C have been reported[10]. The chert is composed of a crystal structure of quartz, made of SiO_4 tetrahedra and Kitty's Gap is located near a mafic and ultramafic environment[8] containing olivine. The geological environment is consequently favorable to the production of organic globules such as those that we observe in our experiments made in a glass tube. The micro fossil identification of Kitty's Gap has been based on a micro-environment which could have hosted life, on a morphological resemblance with procaryotes and on a difficult analysis of the carbon isotopic fractionation ($\delta^{13}C$ values between -22‰ -30‰) which could be either of biogenic or of abiogenic origin. Consequently, on the basis of morphology, of hydrothermal activity and of a quartz or silicate mineral environment, we suggest that the australian Kitty's Gap carbon microstructures could be composed of amino acid precursors. We further suggest that some microstructures observed in the south-african Barberton greenstone belt could also be composed of amino acid precursors abiotically synthesized in a hydrothermal environment of SiO_4 tetrahedra[21], of hydrothermal CO, of N_2 and of H_2O with extinct radionuclides as an excitation source.

Shapes and sizes of the meteoritic globules and of the archean microstructures vary from filamentous to purely spherical. It is known in chemical laboratories that the geometry of spherical compounds generated experimentally depend on characteristics such as the temperature, the proportion of the reactants, the speed of rotation of the medium. Consequently, the extraterrrestrial and terrestrial microstructures may have variable geometries depending on the dynamical and on the physico-chemical characteristics of the medium in which they were synthesized. We supplement our morphological comparison

considering temperature and mineral environment.

The origin of prebiotic molecules necessary for life to emerge could arise either from space or from terrestrial silicate hydrothermal sites. It is to be noticed that the described microspheres formed from an amino acid mixture have been produced only in a glass tube and not in a stainless steel tube[12,13]. The proton irradiation residue of a CO, N_2, H_2O mixture, leading to microstructures of amino acid precursors has also been performed in a glass tube. Hence, the presence of silicates or olivine might be of primordial necessity.

We demonstrated that organic globules and filaments containing amino acid precursors and showing the same morphological shapes and the same hydrothermal and mineral conditions of formation than those observed in meteorites and in early archean rocks, can be synthesized in the laboratory from a mixture of simple constituants CO, N_2 and H_2O under an excitation source, proton exitation, which existed at the time of the origin of life. Consequently the content of the extraterrestrial organic globules discovered in meteoritic, cometary and IDP's particles could consist not only of complexes of aromatic molecules as it has been proposed but also of amino acid precursors. And the content of the rod to spherical microstructures discovered in archean terrestrial cherts and siliciclastic deposits could also be assigned to amino acid precursors**.** We further suggest that the discovery of such organic globules inside the serpentinized peridotite rocks of the terrestrial upper mantle could lead to a choice of biomarkers for Life. The organic geochemistry of the peridotite rocks located near hydrothermal sites has been very little studied[22]**.** A search for bilobed organic globules and for aggregated micron and sub-micron spheres, filaments and tubules such as those observed in our experiments could be programmed.

Methods Summary

High-energy proton irradiation (3 MeV) has been performed at the Tokyo Institute of Technology using a Van de Graaff accelerator. A Pyrex glass tube was filled with inorganic gas components consisting of 350 Torr carbon monoxide (CO) and 350 Torr nitrogen (N_2) over liquid water (H_2O) which provided 20 Torr of water vapor at room temperature. The total energy delivered to the gas mixture, as determined by the product of

the number of particles delivered and the ionization energy loss of a single particle in the gas mixture was 4000 J.

Analytical analysis was performed with scanning electron microscopy (SEM, JSM-6700F, JEOL) and atomic force microscopy (AFM, Seico Instruments Inc., SII SPA 400 unit, Japan). The gel filtration chromatograph (GFC) was composed of a high performance liquid chromatography (HPLC) pump (TOSOH DP-8020) and a UV detector (TOSOH UV-8020). The columns used were TSKgel G2000 SWxL (7.8 mm i.d. x 300 mm) for gel filtration, and Inertsil ODS-3 (4.6 mm i.d. x 250 mm) for reversed-phase partition chromatography[17]. The mobile phase was a mixture of 25 mM acetonitrile (25 %) and 0.1 % trifluoroacetic acid (75 %). Molecular weights were calibrated using several molecular weights of polyethylene glycol (PEG) and human serum albumin[15]. An aliquot of the irradiation products was hydrolyzed with 6 M HCl at 110 □ for 24 hours. Amino acids in the hydrolyzed fraction were analyzed with an ion-exchanged HPLC system where a post-column derivatization with o-phthalaldehyde and N-acetyl-L-cystein was applied. The HPLC system used was composed of two high performance liquid chromatograph pumps (Shimadzu LC-6A), a cation exchange column (Shimpak ISC-07/S1504, 4 mm i.d.×150 mm), a post column derivatization system, and a Shimadzu RF-535 fluorometric detector [23].

We also verified enantiomer analysis after derivatization procedures of N-pivaloyl-(*S*)-2-butyl esters (NP/*S*2Bu) of the amino acid diastereoisomers[24]. The NP/*S*2Bu esters of the amino acid diastereoisomers were identified by a gas chromatograph/mass spectrometry (GC/MS; Agilent Technologies 6890N/5973MSD). The capillary column used for GC was an HP-5ms (30 m x 0.32 mm i.d., 0.52 μm film thickness; Agilent Technologies). The GC oven temperature was programmed as follows: initial temperature 40 °C for 4 min, ramped up at 10 °C min^{-1} to 90 °C, and ramped up at 5 °C min^{-1} to 220 °C, where it was maintained for 10 min. The MS was scanned over *m/z* of 50–550 with the electron-impact mode set at 70 eV.

In order to obtain the yield of amino acids, we used the G-value[25] (the number of formed molecules per 100 eV) of glycine in the hydrolyzed products, because (i) glycine is the most abundant amino acid and (ii) it was proved that glycine was formed in

proportion to total energy deposit including particle and photon irradiation[16].

References and Notes

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The authors thank K. Kawasaki (Tokyo Institute of Technology) for his experimental support, K. Kobayashi (Yokohama National University) and N. Ohkouchi (Japan Agency for Marine-Earth Science and Technology) for discussions. This research was partly supported by the Japan Society for the Promotion of Science (Y.T), and a Grant-in-Aid for Creative Scientific Research (19GS0211).

Figures captions

Figure 1a. Three-Dimensional Scanning Electron Microscopy, 3D-SEM, image of the aliquot (a) of the proton irradiation product obtained during abiotic synthesis of amino acid precursors from a gas mixture of CO-N_2-H_2O excited with 3 MeV proton irradiation.

Figure 1b. Three-Dimensional Atomic Force Microscopy, 3D-AFM, image of the same aliquot.

Figure 2a. 3D-SEM of the aliquot (b) of the proton irradiation product.

Figure 2b. 3D-AFM of the same aliquot.

Figure 3a. 3D-AFM image of the aliquot (a) of the proton irradiation product obtained during abiotic synthesis of amino acid precursors from a gas mixture of CO-N_2-H_2O excited with 3 MeV proton irradiation.

Figure 3b. 3D-AFM image of the aliquot (b).

Figure 4a. Relative abundance of amino acids abiotically synthesized (total as 100) from a gas mixture of CO-N_2-H_2O under 3 MeV proton irradiation. Abbreviations. Gly, glycine; D,L-ala, D,L-alanine; D,L-α-ABA, D,L-α-aminobutyric acid; D,L-asp, D,L-aspartic acid;

β-ala, β-alanine; D,L-ser, D,L-serine; others, including very minor amino acids.

Figure 4b. Relative abundance of amino acids on a logarithmic scale.

Supplementary Information

Supplementary Figure Schematic view of the Van de Graaff accelerator (Tokyo Institute of Technology) used for high energy (3 MeV) proton irradiation of inorganic gas mixtures (CO-N_2-H_2O).

Supplementary note

Ultra-pure grade carbon monoxide and dinitrogen gases were purchased from Nihon Sanso Co.. All glassware was heated in a high temperature oven (DR-22, Yamato Co., Tokyo, Japan) at 500°C to eliminate any possible contaminants prior to use. Deionized water was further purified with a Millipore Milli-Q LaboSystem^{TM} and a Millipore Simpli Lab-UV (Japan Millipore Ltd., Tokyo, Japan) to remove inorganic ions and organic contaminants.

Fig. 1a

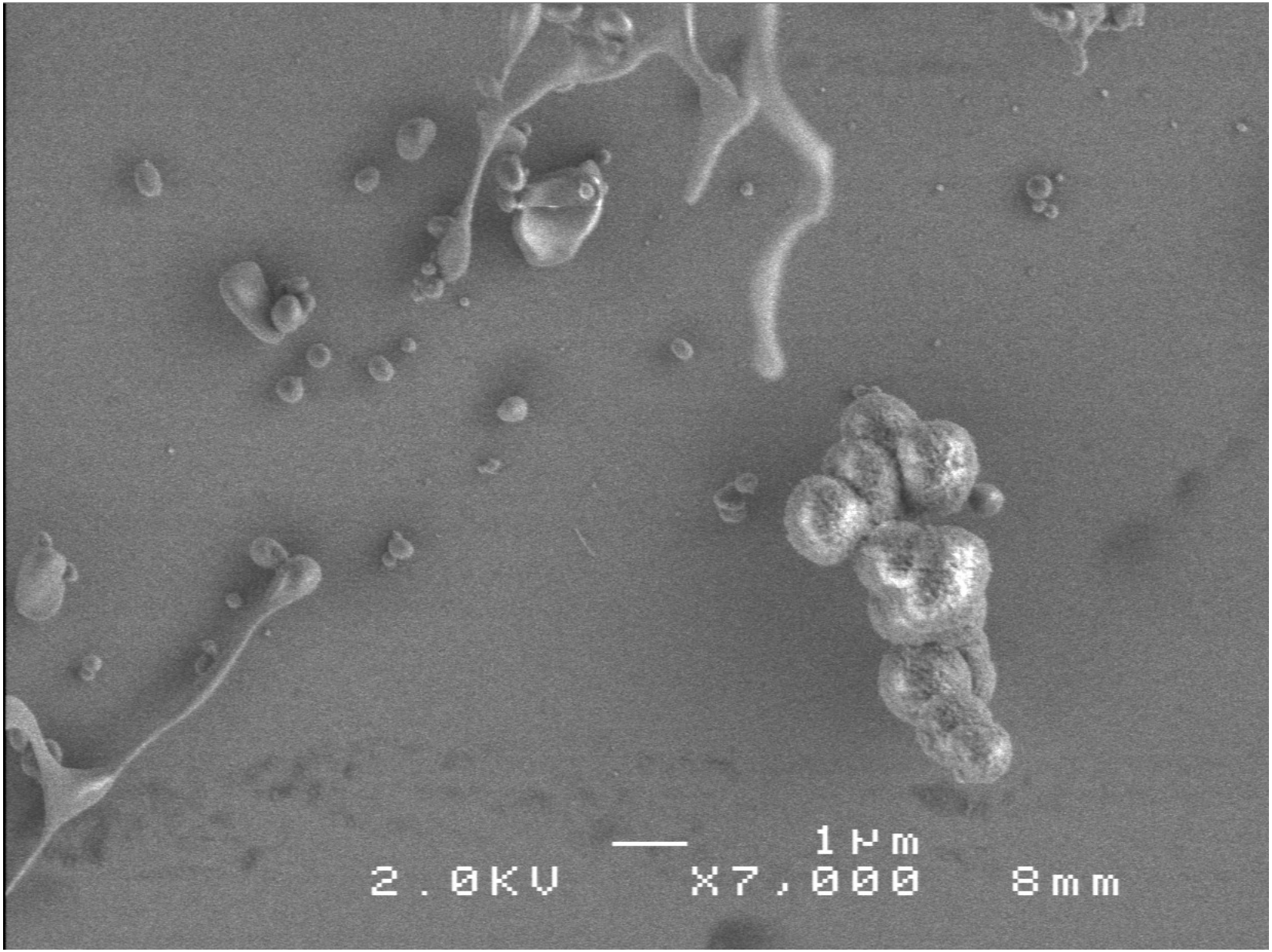
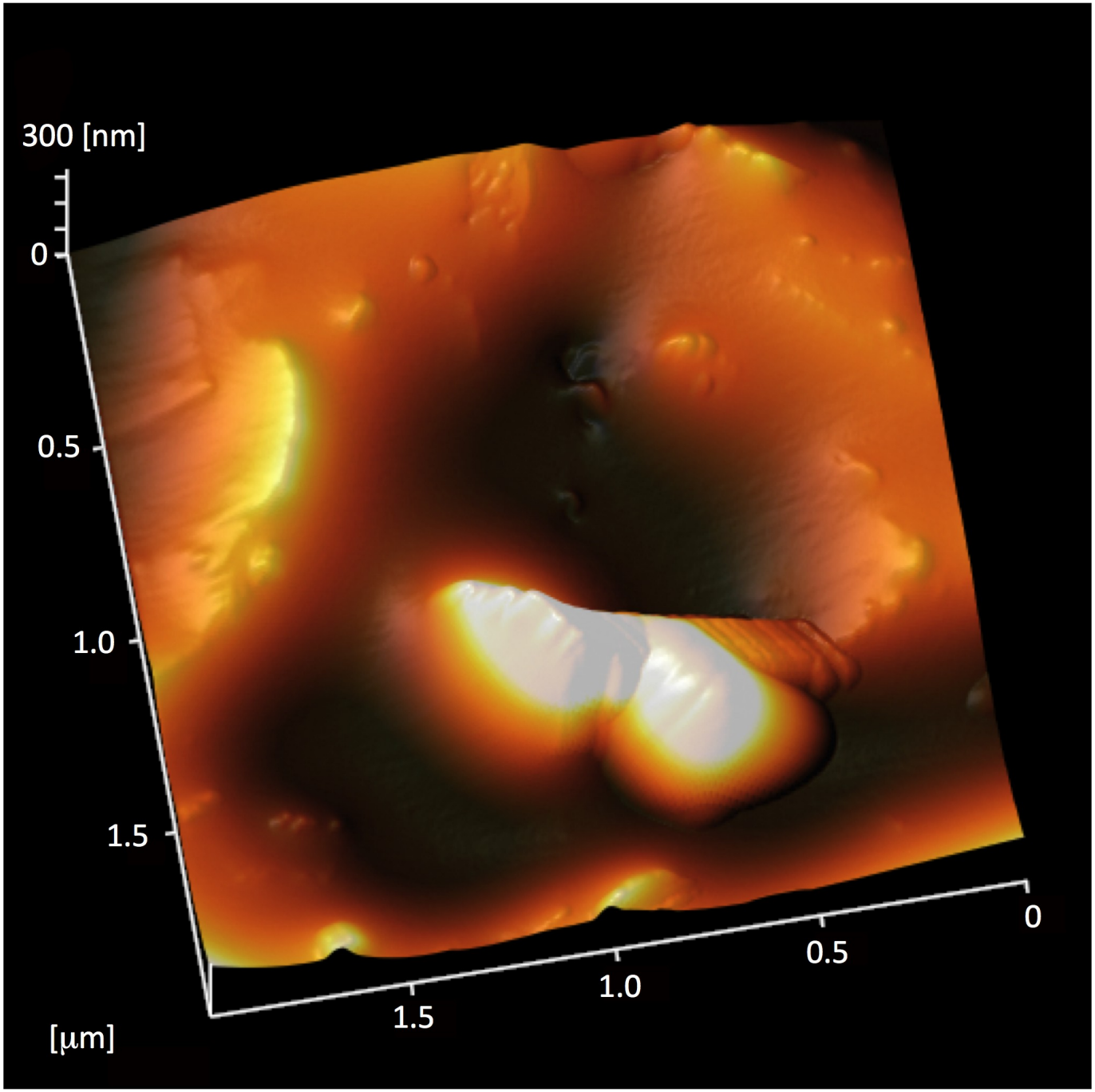


Fig. 1b



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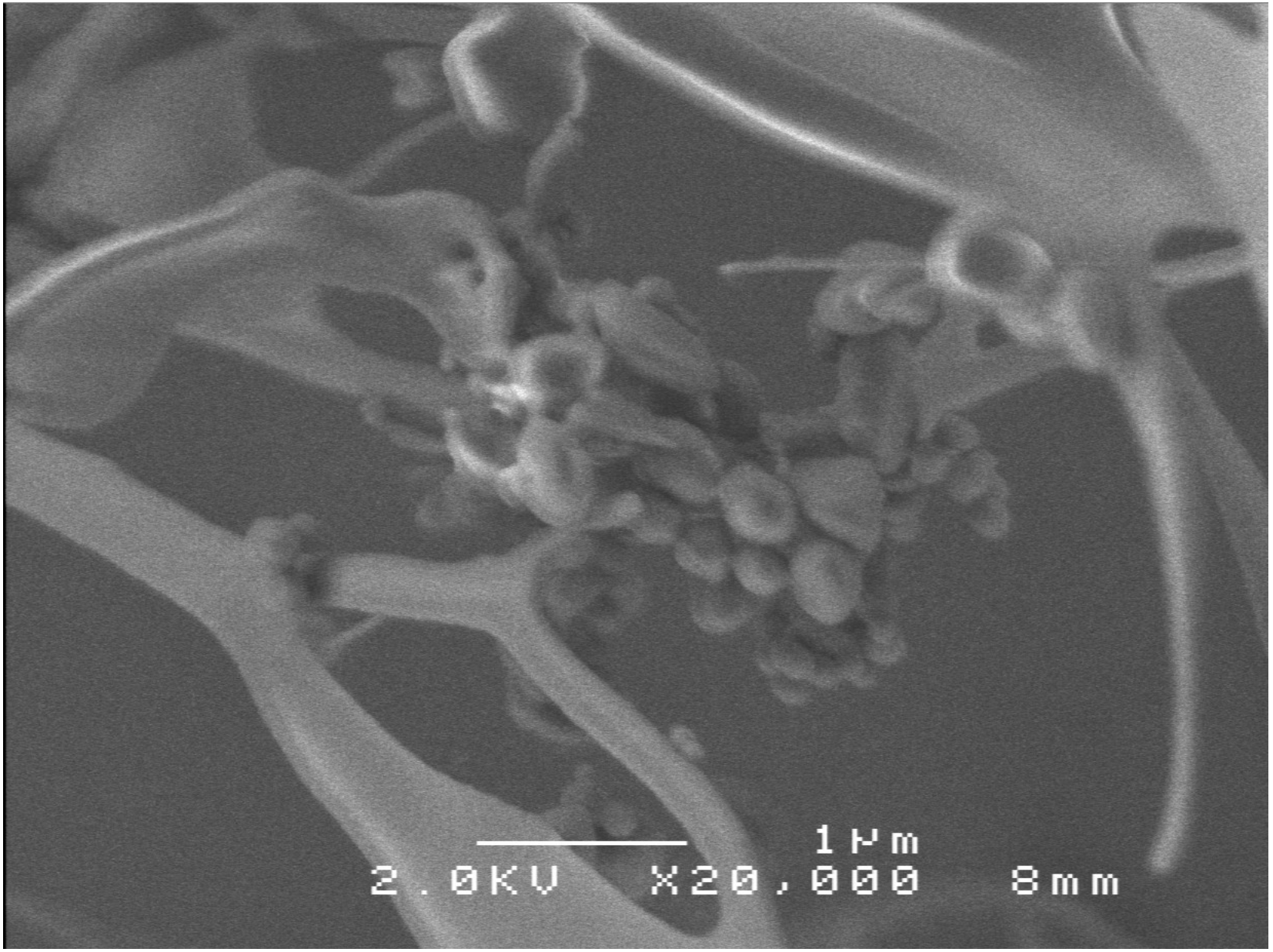
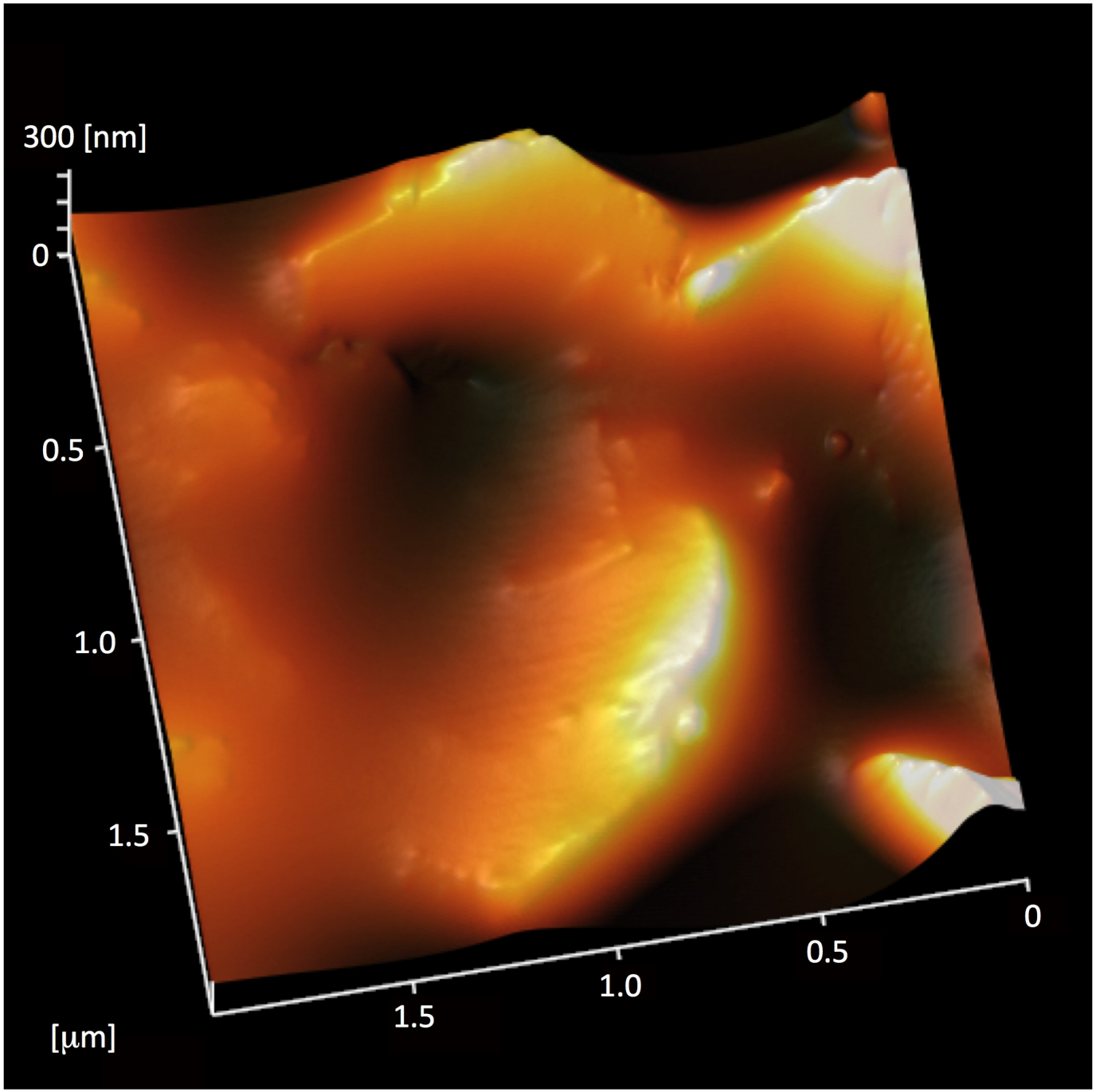


Fig. 2b



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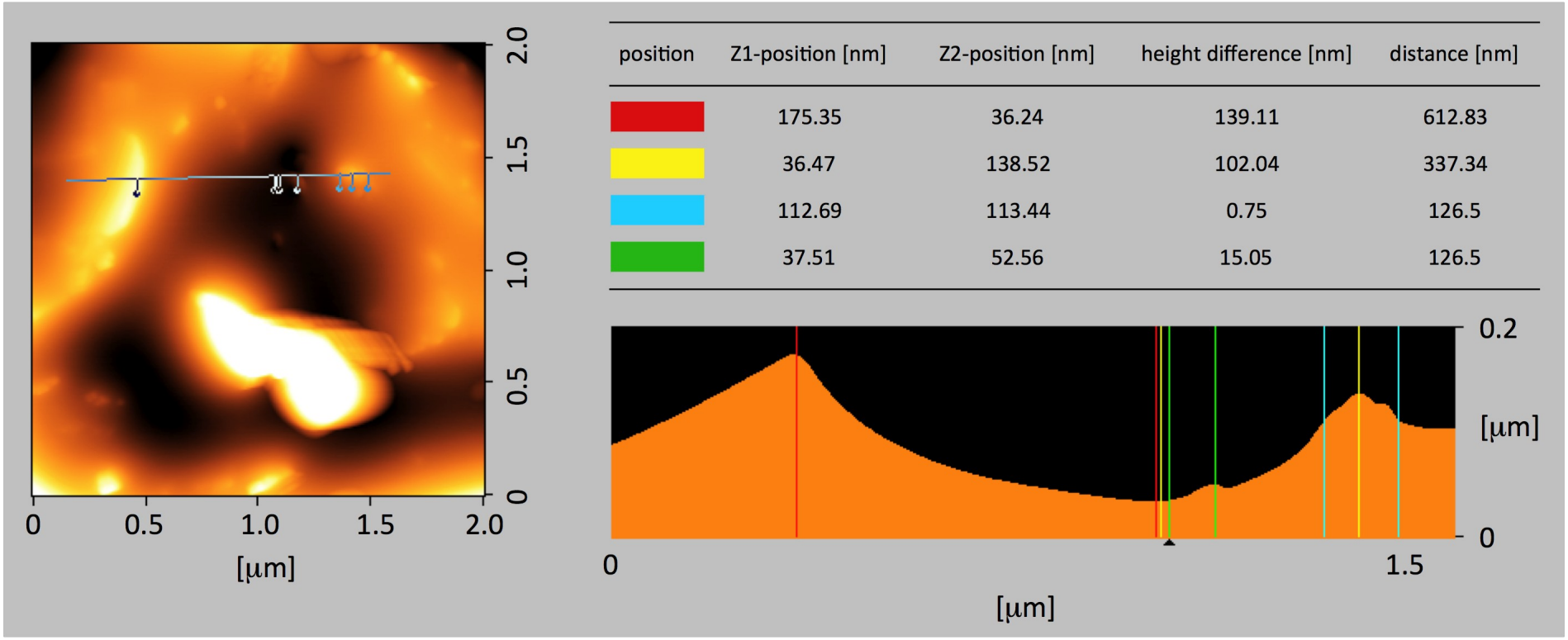
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Sup. Fig. 3b

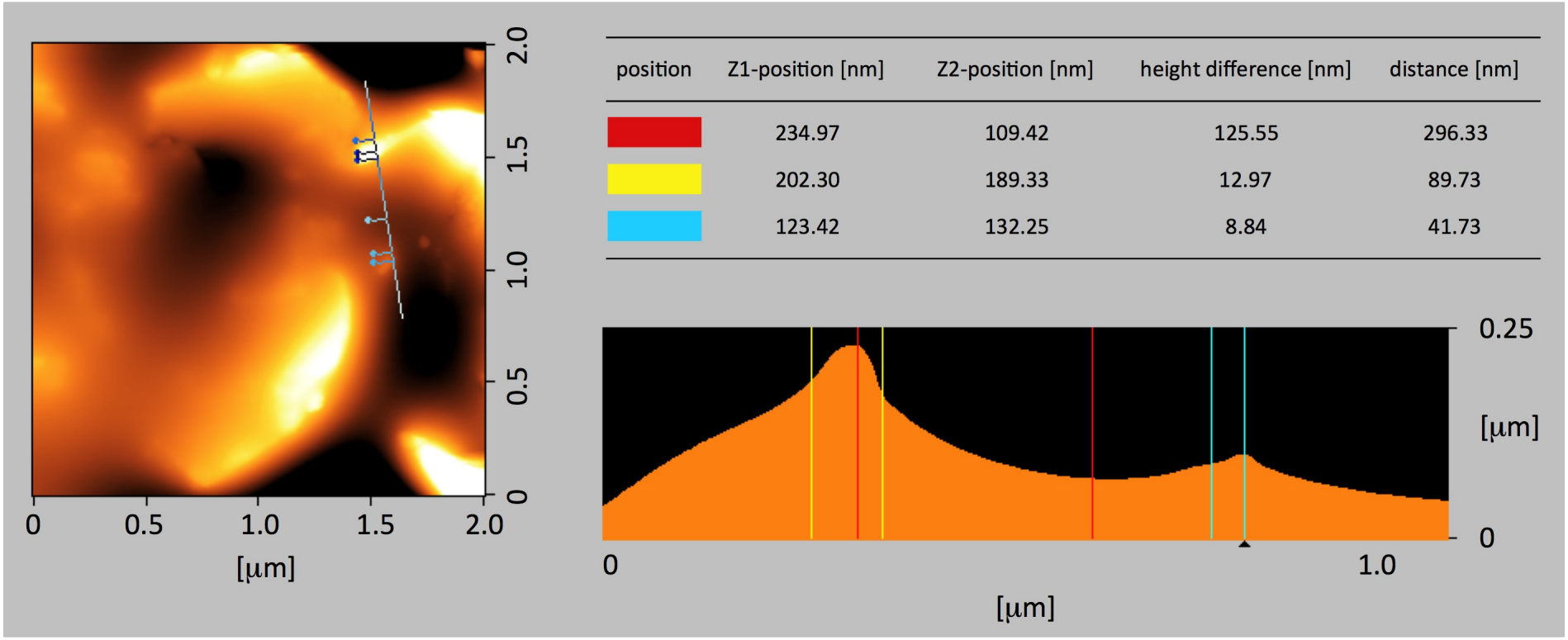
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Fig. 4a

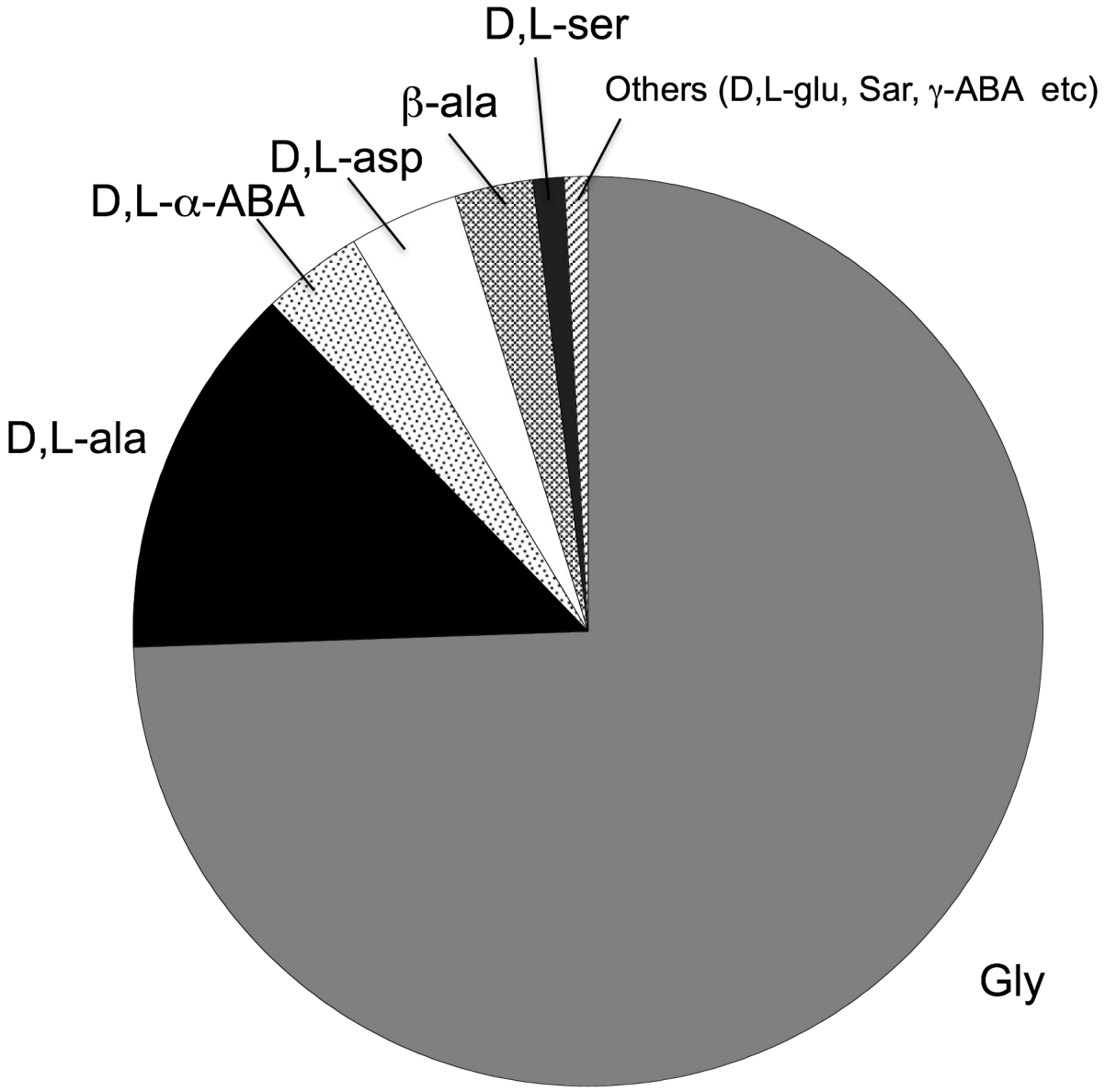
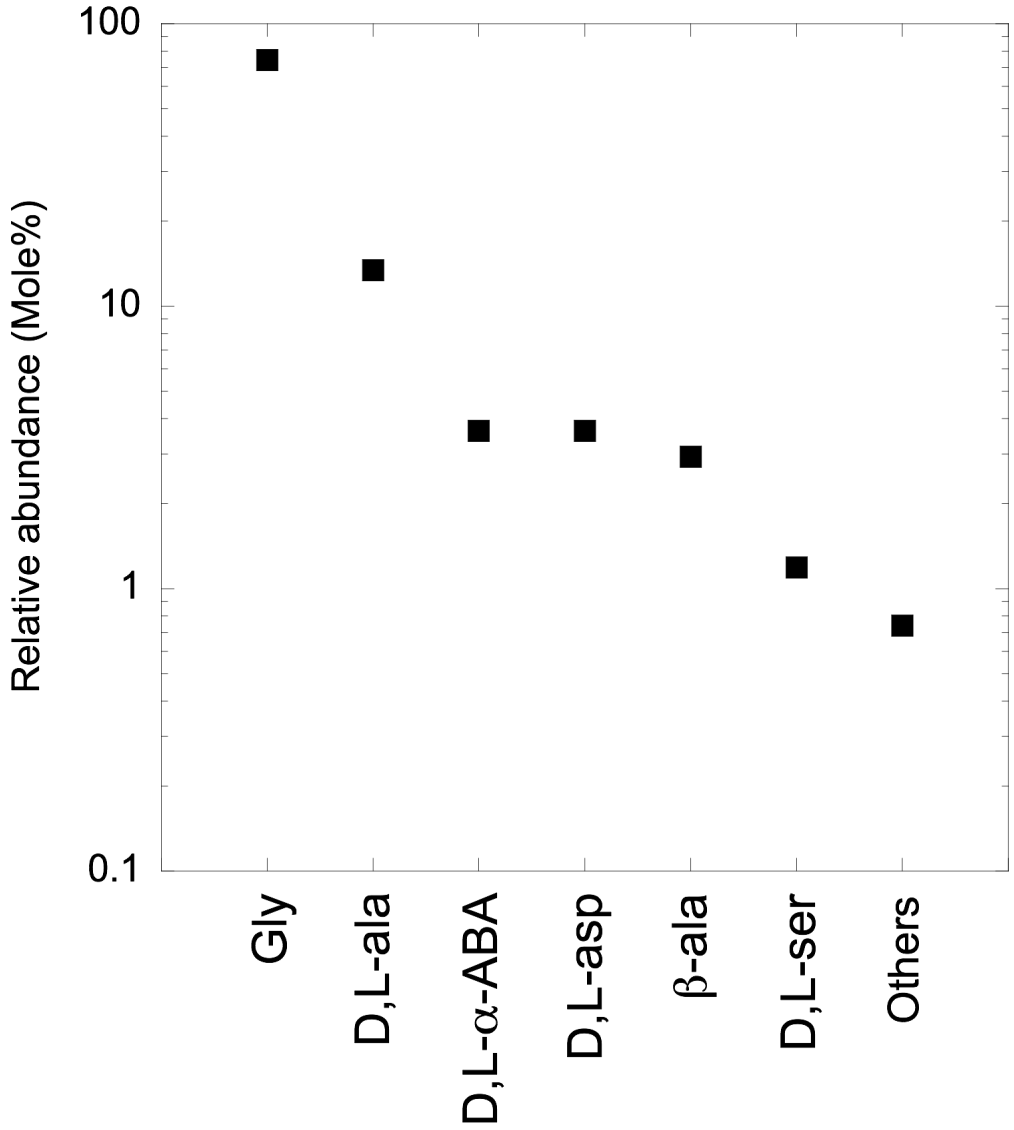


Fig. 4b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Relative abundance (Mole%)
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D,L-ala
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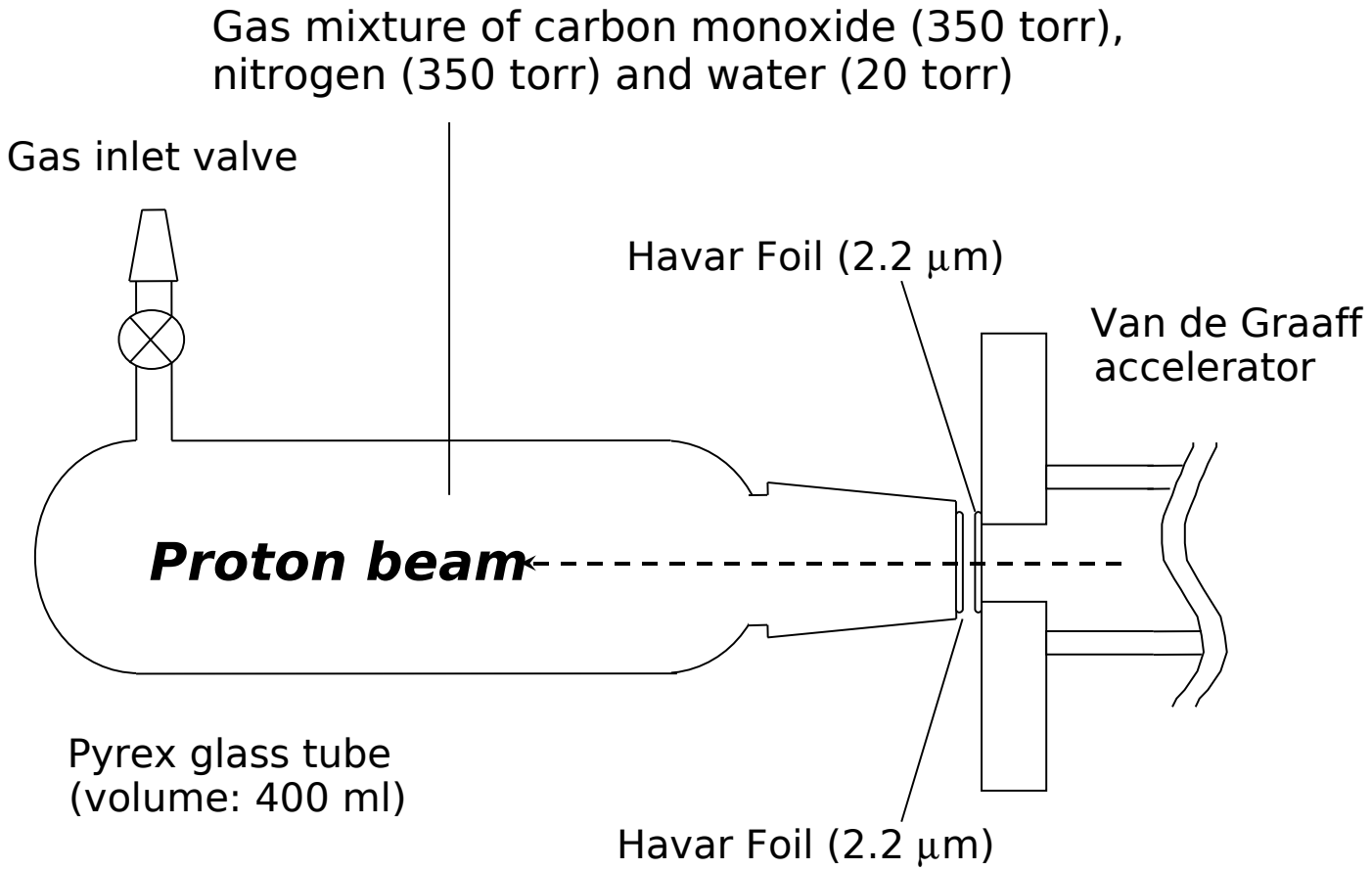
D,L-asp
β-ala
D,L-ser
Others

Sup. Fig.


Gas mixture of carbon monoxide (350 torr),
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Gas inlet valve
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Van de Graaff
accelerator
Proton beam
Pyrex glass tube
(volume: 400 ml)
Havar Foil (2.2 μm)